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Analytical Chemistry

BASED ON THE TEXT OF

F. P. TREADWELL

Late Professor of Analytical Chemistry at the Polytechnic Institute of Zurich

TRANSLATED, ENLARGED AND REVISED

BY

WILLIAM T. HALL

Associate Professor of Analytical Chemistry, Massachusetts Institute of Technology

VOLUME II

QUANTITATIVE ANALYSIS

SIXTH EDITION

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PREFACE TO THE SIXTH ENGLISH EDITION

F. P. Treadwell was born in New Hampshire in 1857. He completed his education in Germany, receiving the Ph.D. degree at Heidelberg. In 1878 he became assistant to Bunsen but left him in 1883 to work under Victor Meyer. In 1894 he was made Professor of Analytical Chemistry at Zurich where he remained until his death in 1918.

Twenty years have elapsed since the second volume of the English edition of this book appeared. Numerous changes have been made from time to time but now for the first time the text has undergone a complete revision. Hardly a page has remained unaltered.

In the main the methods are the same as those described in the tenth edition of the German text but at least twenty per cent of the book is unlike the German text. The aim has been to make the methods conform to the best American practice. Particularly with regard to standards of mass and volume has this been true. As far as possible the work at the German testing bureaus has been replaced by results published by the Bureau of Standards at Washington. This attempt to follow the Bureau of Standards has even led to the adoption of the *milliliter* instead of *cubic centimeter*. This change has been adopted by the principal instrument makers of the United States although not sanctioned by the editors of our Chemical Journals. Most burets, pipets and measuring cylinders are now marked in milliliters and it seems irrational to tell a student that *ml.* means *cubic centimeter*. It is of course more practical to define the liter as the volume occupied by one kilogram of water under certain conditions than it is to attempt to measure the volume in cubic centimeters. It is estimated, however, that the liter represents 1000.027 cubic centimeters or one drop of water more than the theoretical value. Since this is about as close as the volume can be read in an ordinary measuring flask it is easy to see why most chemists prefer to use *c.c.* instead of *ml.* since all the other nations of the world are doing it.

Before the publishers agreed to publish an English edition of this book in 1902, the opinion of several well-known chemists was asked. One of the strongest letters in praise of the Treadwell book was written at that time by Dr. W. F. Hillebrand, who knew Treadwell personally. At Dr. Hillebrand's suggestion, again, Dr. G. E. F. Lundell has now

carefully read the entire text of the fifth edition and has offered more than one hundred suggestions based, for the most part, on his experience as an analyst at the Bureau of Standards. Dr. Lundell has also furnished directions for a number of new methods and for some old ones that have been altered at the Bureau.

Besides this painstaking work of Dr. Lundell, the entire proof has been read by S. G. Simpson, C. E. Carlson and A. F. Kaupe, all graduates of the Massachusetts Institute of Technology.

Owing to an unexpected demand for the book during the last few months, it has been necessary to rush the book through the press in about one-half the time that had been planned. Probably some typographical errors have escaped correction. The editor will be grateful to have such errors pointed out and any suggestions with regard to possible improvements will be welcomed.

WILLIAM T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
February, 1924

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QUANTITATIVE ANALYSIS

INTRODUCTION

The purpose of a quantitative analysis is to determine the relative quantities of the constituents present in a compound or in a mixture. The methods to be employed depend upon the nature of the substances to be determined, so that as a rule *a qualitative analysis should precede the quantitative one.* In quantitative analysis we distinguish two essentially different methods of procedure:

I. GRAVIMETRIC ANALYSIS (Analysis by Weight).
II. VOLUMETRIC ANALYSIS (Analysis by Volume).

In the case of *gravimetric analysis* the constituent to be determined is separated from a solution in the form of an insoluble compound of known chemical composition; from the weight of this compound the weight of the desired constituent is computed.

Suppose, for example, a sample of barium chloride is to be analyzed. The amount of barium present can be determined by dissolving a weighed amount of the chloride in water, precipitating the barium from the solution by the addition of sulfuric acid and weighing the insoluble barium sulfate formed.

If from a grams of barium chloride, p grams of barium sulfate are obtained, the percentage of barium present may be calculated as follows:

$$\frac{p \times \text{Ba} \times 100}{\text{BaSO}_4 \times a} = \text{per cent of barium.}$$

In this and in all similar expressions the atomic and molecular symbols represent atomic and molecular weights.

In *volumetric analysis* the constituents are not weighed, but are determined by measuring the volumes of solutions of known concentrations which react with them.

Thus a sample of caustic soda containing sodium chloride as impurity can be analyzed volumetrically and the percentage purity estimated. A portion of the substance weighing a g. is dissolved in water, some methyl orange is added and hydrochloric acid of known strength is

run into the solution from a buret until the alkali is just neutralized, this point being reached when the yellow color of the solution changes to pink. If t ml. of hydrochloric acid were necessary, of which 1 ml. will neutralize f g. of pure sodium hydroxide, then

$$\frac{t \times f \times 100}{a} = \text{per cent of sodium hydroxide.}$$

Gravimetric Methods of chemical analysis consist of (*a*) *Direct Methods* and (*b*) *Indirect Methods.* In a direct method the substance to be determined is usually precipitated from the solution in the form of one of its characteristic, insoluble compounds and the precipitate is weighed. The above-mentioned determination of barium in barium chloride is an example of a direct analysis.

There are several kinds of indirect analyses. The moisture content is often determined by weighing a sample before and after drying. If the evaporated water is collected and weighed, the moisture is determined directly. If, on the other hand, it is assumed that the change in weight of the substance is due only to loss of water, then the water is determined indirectly.

A common type of indirect analysis is based upon the fact that when two or more substances are subjected to the same chemical treatment they experience relatively different changes in weight.

A mixture of pure chlorides of sodium and potassium may be analyzed indirectly by merely determining the chlorine content. If a sample of the mixture weighing a g. yields p g. of silver chloride, then the quantities of sodium and potassium chloride in the mixture can be computed as follows:

Let x represent the weight of sodium chloride and $a-x$ the weight of potassium chloride. Then

$$\frac{\text{AgCl}}{\text{NaCl}}x + \frac{\text{AgCl}}{\text{KCl}}(a - x) = p$$

or,

$$2.452\,x + 1.922\,(a - x) = p$$

and,

$$x = 1.888\,p - 3.628\,a$$

Although this method appears simple and attractive, it should be used with caution. The experimental errors in determining the weights p and a are multiplied respectively by the coefficients 1.888 and 3.628.

It has been proposed to analyze a mixture of sodium and potassium chlorides by treatment with sulfuric acid and weighing the sulfates. In this case, if a denotes the weight of the original chlorides, x the weight

of sodium chloride and p the weight of the sulfates, a computation similar to the above gives

$$x = 21.55\ p - 25.181\ a.$$

Here the analytical errors are multiplied by large factors and the results are unreliable. An error of 0.3 mg. in the weight of the sulfates becomes an error of 7.5 mg. in the computed weight of sodium chloride.

OPERATIONS

The principal operations of quantitative analysis are those of weighing, filtration, and the washing, drying, and ignition of precipitates.

Weighing

The balance, as used for purposes of quantitative chemical analysis, is shown in Fig. 1.

It consists of a horizontal lever with two arms of equal length, and in order to be serviceable it must be *accurate* and *sensitive*.

It fulfills the first condition if

(1) The arms of the lever are of equal length;

(2) The point of support (the fulcrum) lies above the center of gravity;

(3) The fulcrum (a knife-edge) and the knife-edges from which the pans are suspended lie in the same plane and are parallel to one another.

The beam of the balance is provided with a long pointer which swings over a fixed scale near the base of the balance case. A small adjustable nut on the pointer, sometimes above and sometimes below the beam, serves to raise or lower the center of gravity of the moving parts and thus change the sensitiveness. At one end of the beam, and in some balances at both ends, is found another adjustable nut which serves to make the effective weights of the arms equal.

At the middle of the beam, on the under side, is a knife-edge which is usually made of polished agate. When the balance is in use, this knife-edge rests upon a plate of polished agate so that the beam can swing with very little friction. At the ends of the beam are other knife-edges from which the balance pans are suspended. When not in use, the beam should be raised so that the knife-edges are not in contact with their bearings. This is effected by means of a frame operated by a milled head at the front of the balance case. By turning the milled head clockwise, the beam is raised. With an equal load in each pan,

and the beam resting on the knife-edge, the pointer should swing an equal number of divisions both sides of the zero of the scale when the beam is in motion and should finally come to rest at the zero mark. If a small weight is added to either pan the beam and the pointer will swing through an angle and take up a new position of equilibrium. This new position will be the result of the moments of three effective forces, — the weight of the beam and the weights in each pan.

The angle α which the pointer at its new resting place makes with its original position, is determined by the size of the excess weight, p, the length of the balance arm, l, the weight of the beam, q, and the dis-

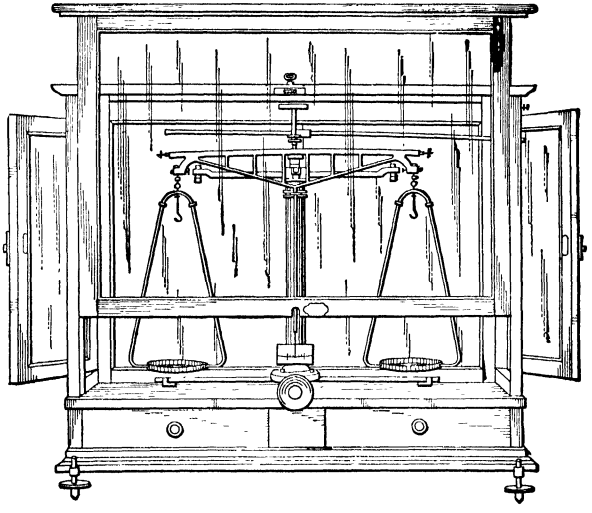


FIG. 1.

tance, d, between the center of gravity and the point of support of the beam. Expressed mathematically,

$$\tan \alpha = \frac{p \cdot l}{q \cdot d}$$

The *sensitiveness*, or *sensibility*, is measured by the angle α when p has a definite weight, usually one mg. Since the tangent of a small angle is practically the same as the angle and the tangents of the angles that the pointer makes are directly proportional to the number of divisions between the two points of rest on the scales, it is customary to regard the sensitiveness or sensibility as *the number of scale divisions that the zero point is displaced by an excess weight of one mg.*

It follows, then, that the sensitiveness of a balance is directly proportional to the length of the balance arms and inversely proportional

to the weight of the beam and to the distance of the center of gravity below the point of support. It is clear also that the observed deflection is proportional to the length of the pointer.

The conditions for maximum sensitiveness are more or less conflicting. Thus long arms are incompatible with minimum weight. The length of arms is also limited by the fact that the longer the arms are, the greater the time required for one complete swing of the pointer. The weight of the beam also affects the time of swing in the same manner. On the other hand it is important that the beam should be rigid.

Long arm balances, although sensitive, possess the disadvantage of a long time of swing which renders weighing a tedious process. For moderate loads, short arm balances with light beams of aluminium alloy are sensitive and fast.

It is possible to decrease the time of swing by lowering the center of gravity but this makes the balance less sensitive. For ordinary work it is well to adjust the sensitiveness so that one-tenth of a mg. will displace the zero point one scale division with light loads. The center of gravity must always be below the knife-edge or the balance will be in neutral or unstable equilibrium.

Precautions in the Use of a Balance

1. The balance should rest upon a firm support which is practically free from mechanical vibration. Direct sunlight should not fall upon the balance as it will cause irregularities and errors in weighing.

2. When not in use the balance beam should always be raised off the knife-edges as otherwise these are likely to be injured by jarring.

3. The beam should always be lowered slowly and carefully.

4. The beam should never rest upon the knife-edge while weights or substances are being added to or removed from the pans.

5. The beam may be set swinging by dropping the rider upon the beam or removing it for a moment. It may also be set in motion by fanning one pan gently with a motion of the hand but in no case should motion be started by touching the pan or by suddenly lowering the beam upon its knife-edge.

6. All weighings should be made methodically, trying the weights one after another in their proper order.

7. Before making a weight, the adjustment should always be tested. The balance is properly adjusted (*a*) when it is level, (*b*) when the pointer rests at the zero mark with the beam raised, (*c*) the pointer should swing equal distances on either side of the zero when the beam is set in motion with no load in the pans. If the balance has pan arrests

which work independently of the mechanism that lowers the beam, these arrests should be adjusted so that the pointer is at the zero mark when the beam is on its knife-edge and the pan arrests are in place.

8. Final adjustment with the rider and all observations regarding the swing of the pointer should be made with the balance case closed to prevent errors arising from air currents. On leaving the balance, the case should always be closed.

9. The weight of a substance should be recorded *first*, by adding up the weights missing from the box (in which every weight should always have its own place) and *second* by adding up the weights that are on the pan. After the final weight has been made, it is convenient to make this second addition when the weights are being returned to the box. By always checking the weights as a matter of habit, serious errors are often avoided.

10. Substances to be analyzed should never be placed directly upon the balance pan but on a watch-glass or in a tube. The object should not be warmer or colder than the air in the balance case. Air currents from a hot body make it weigh too light and condensation of moisture on a cold body makes it appear too heavy.

11. Care should be taken not to overload the balance.

A separate set of weights should be provided with each balance. In analyzing a given material, the chemist is required to determine the weight ratios of the various constituents. He reports the percentage of iron present rather than the weight. It is important, therefore, that the weights in any set should stand in the proper relation to one another and relatively unimportant whether the 10 g. corresponds exactly to the 10 g. weight in some other set. In analyzing ores for precious metals, it is customary to weigh out a large sample on a " pulp balance " which need not be sensitive to one mg. The analysis is finished by weighing a very small fragment of metal on a " button balance " sensitive to 1/100 of a milligram. Ordinarily, however, all of the weighings used in any chemical analysis should be made with the same balance and the same set of weights. If a weight is lost or misplaced, a new weight should always be tested to see if it bears the proper relation to the other pieces in the set.

Sets of weights used in chemical analysis usually contain a 50 g. weight and sometimes a 100 g. weight. Sometimes the smallest weight is 1 mg. but a set need not contain any weight smaller than 10 mg. The numbers on the weights indicate g. when the value is 1 g. or over and mg. if the weight is a fraction of a gram.

Weights smaller than 10 mg. are usually obtained by the use of a " rider " or small piece of aluminium wire which may be shifted to

various positions on the beam of the balance. The manner in which the beam is divided varies with balances of different makes. When the rider is placed directly over the knife-edge that supports the right pan, it indicates its true weight and when it is placed at a fraction of the distance between middle and outer knife-edges, it indicates that fraction of its true weight. Riders as a rule weigh 5, 6, 10 or 12 mg. Balances which are made so that the rider can be placed directly over the pan suspension usually take a 10 mg. rider or a 5 mg. rider. Balances which are made with the top of the beam rounded off at the ends usually take a 12 or 6 mg. rider. The large divisions on the beam graduations are always one mg. apart when the proper rider is used. The smaller subdivisions are either tenths or fifths of a milligram.

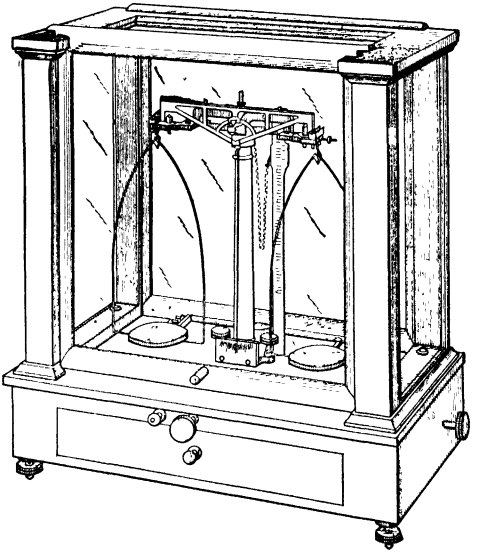


FIG. 2.

The *chainomatic balance* (Fig. 2) does not require a separate rider. One end of a small gold chain is fastened to the balance beam and the other end to a hook which can be moved up and down a vertical scale. This hook is operated by a milled head outside the balance case on the right. Movement of the hook changes the weight of chain that is supported by the beam so that the positions on the scale correspond to milligrams. This may be adjusted while the balance is in motion.

Methods of Weighing

Ordinary Method of Direct Weighing. Place the object to be weighed on the left pan. If the container is glass and has been recently wiped dry, allow it to stand a few minutes in the balance case before attempting to weigh it. Using the weight forceps, place a weight on the right pan that is judged to be a little heavier than the object to be weighed. Slowly lower the beam a little and notice which way the pointer swings. If the pointer swings to the right, the object is heavier and if to the

left the weight is too heavy. Raise the beam and exchange the weight for the next heavier one if it was found to be too light. Repeat the trials until a weight is found that is too heavy, always remembering to have the beam raised whenever anything is added to or removed from the pan. Remove this weight and replace it with the next lightest one and continue trying the smaller weights in order, until the range covered by the rider is reached. Close the balance case and adjust the rider until the pointer swings equal distances to the left and right of the middle division.

Record the weight from the empty places in the box and check this result by counting the weights on the pan. Confirm by counting as the weights are replaced in the box. By making these three readings, mistakes are avoided. In counting always start with the largest weight and take the others in order.

Length of Swings. In making weighings the general tendency is to make the pointer swing through too wide an arc. The balance acts as a pendulum and, except for retardation, must swing an equal distance on each side of the point of rest. The retardation of long swings is such that their middle points do not coincide with the point of rest. The retardation, however, is practically proportional to the length of swing and becomes inappreciable in a single moderately short swing, or in several shorter ones, so that the middle point can be determined by direct observation. In a short swing the pointer is moving slowly and it is easy to read the end points of the swing. There is less danger of parallax error in reading short swings and less probable error because two short swings can be observed which are practically identical. For these reasons H. L. Wells* advocates the use of swings from 0.5 to 2 scale divisions in total length.

Instead of trying to get two exactly equal swings it is better to adjust the rider until the swings are nearly the same and then estimate from the known sensibility of the balance how much the rider should be moved to make them equal. Place the rider just a little beyond this point and test the swings again. With a little practice it is possible to estimate the weight within 0.1 mg. without waiting to get a swing of equal distances both sides of the center of the scale. If the balance is adjusted so that the sensitiveness amounts to at least 5 divisions for 1 mg., then a swing that varies less than $\frac{1}{4}$ division on the two sides of the center shows that the weight to the nearest 0.1 mg. has been found. It is easily possible to make the entire adjustment of the rider within 30 seconds. With substances that take up or

* *J. Am. Chem. Soc.* **42**, 411 (1920).

give up water on standing, a rapid weight is more accurate than one that is made slowly. For all ordinary analytical work, this method of weighing is to be preferred to the more tedious processes that will next be described.

For very precise work, weighings are often made by the

Method of Swings. First of all determine the zero-reading of the balance by setting the beam in motion (without any load in either pan), observing and recording the turning-points, or extreme positions, of the pointer on the scale of an uneven number of swings (say five) and taking the mean of the readings. The first two swings are inaccurate on account of the jar in shutting the balance-door, etc., so that they are disregarded. In order to give the same algebraic sign to all the observed readings it is best to number the divisions on the scale from left to right from 0 to 20 so that the zero-point in case both balance-arms were of equal length would be numbered 10. It is to be noted that when the zero-reading (*i.e.*, the point of the scale at which the pointer rests when the balance is in equilibrium with nothing in either scale-pan) coincides with the zero of the scale, it may change during the course of the day, so that disregard of this fact may lead to a considerable error. The cause of the displacement of the zero-reading is that the first condition for the accuracy of a balance is not fulfilled. On account of unequal warming the arms become of unequal length.

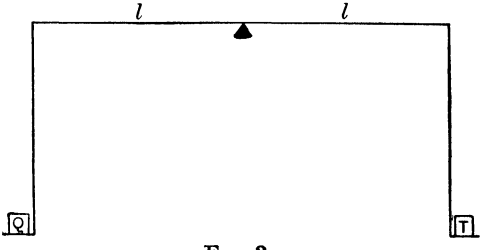


FIG. 3.

The next thing to be determined is the sensitiveness of the balance for the object to be weighed. For this purpose place the object in the left balance-pan and weights in the right pan until equilibrium is established as nearly as possible and determine the rest point of the pointer on the scale in the same way that the zero reading was made above. Add or remove additional weight of 1 mg. by means of the rider and determine the rest point again.

The difference (d) between this and the previous point of rest gives the sensitiveness of the balance. Assuming the zero-reading to lie at 10.22, the first rest, obtained with a load of 19.723 g., to be at 9.80, and the rest point with a load of 1 mg. less (*i.e.*, with a load of 19.722 g.) to lie at 12.32, then the sensitiveness of the balance will amount to $12.32 - 9.80 = 2.52$ scale divisions.

As the zero-reading of the balance was at 10.22 and the rest point with a load of 19.723 g. was 9.80, it follows that the object was lighter than the weights in the right-hand pan, and in fact the excess of weights in the pan was sufficient to move the point of rest 10.22 − 9.80 = 0.42 of a division on the scale. This amount can be calculated from the determination of the sensitiveness of the balance as follows:

Since 2.52 of the scale divisions correspond to 1 mg., then 0.42 of a scale division corresponds to $\frac{0.42}{2.52} = 0.17$ mg., or about 0.2 mg.

The true weight of the body in air is consequently 19.723 − 0.0002 = 19.7228* g.

In making a weighing one should always accustom himself to note the observations methodically, as follows:

Assume that a platinum crucible is to be weighed.

Zero-Reading		I. Rest Point with Load of 12 052 g		II. Rest Point with Load of 12 053 g.	
Left	Right	Left	Right	Left	Right
4.2	17 6	5 8	18 7	3 5	15.8
4.6	17 1	6 2	18.3	3 8	15 4
5.1	.....	6 6	....	4.2	
Sum = 13.9	34 7	18 6	37 0	11 5	31.2
Mean = 4.63	17 35	6 2	18 5	3 83	15.60
... .	4 63	. .	6 2	.... ..	3 83
Sum of both means = 21 98		. . . ..	24 7	. .. ...	19 43
Mean = 10 99		.. ..	12 35	.... .	9.71

Sensitiveness = 12 35 − 9 71 = 2.64 scale divisions.
12 35 − 10.99 = 1.36 scale divisions.
1.36 : 2.64 = 0.5 mg.
Weight of crucible = 12.052 + 0.0005 = 12.0525 g.

The sensitiveness of a balance varies slightly with the load. It is simplest to determine once for all the sensitiveness for 50 g., 20 g., 10 g., 5 g., and 2 g., place a card in the balance with the results obtained and use the numbers as required.

* As most analytical balances will scarcely detect with certainty less than $\frac{1}{10}$ mg., the weight is expressed only to the fourth decimal. If the fifth decimal place in a calculation amounts to five or more, the number in the fourth decimal place is increased one.

In this way the sensitiveness of a balance

with a load of	was found to equal
50 g.	2.23 scale divisions
20 "	2.28 " "
10 "	2.64 " "
5 "	2.66 " "
2 "	2.66 " "

The determination of the zero-reading, however, must be made with every weighing. If a number of weighings are to be made one after another it suffices to determine the zero-point at the beginning and at the end and to use the mean of the two determinations. In case of very heavy loads, however, the zero-reading should be determined before and after each weighing and the mean value used.

Both of the preceding methods of weighing are subject to a constant error if the lengths of the balance arms are not exactly the same. Such an error can be corrected by either of the two following methods of *indirect weighing*. The balance beam may be regarded as a lever with the fulcrum in the middle. In a lever, equilibrium results when the statical moments are equal.

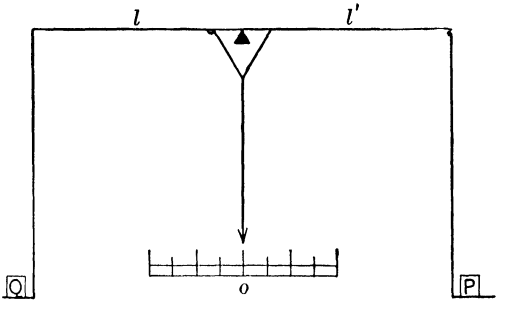


FIG. 4.

By *statical moment* is understood the product of the force multiplied by the length of the lever-arm, and the length of the lever-arm is the perpendicular distance from the axis of revolution (the fulcrum) to the line of action of the force.

Double Weighing or Transposition Weighing

Place the object, whose weight Q (Fig. 4) is to be found, in the left balance pan and establish equilibrium by putting weights amounting to P g. in the right pan. Then

$$(1)\quad Ql = Pl_1$$

when l is the length of the left arm and l_1 the length of the right arm of the balance.

Next place the object in the right pan and establish equilibrium by weights in the left pan. In this case the weights will not as a rule

amount to P g., but to P_1 g. Since, however, equilibrium has been reached, we have

$$(2)\quad Ql_1 = P_1 l.$$

If equation 1 is multiplied by equation 2, we obtain

$$\begin{aligned} Q^2 l l_1 &= P_1 P l l_1 \\ Q^2 &= P_1 P \\ Q &= \sqrt{P_1 P}. \end{aligned}$$

The true weight is obtained, therefore, by taking the geometric mean of the two values. For practical purposes, however, it is sufficiently accurate to take the arithmetical mean, in which case the true weight of the object would be:

$$Q = \frac{P + P_1}{2}.$$

Borda's Method of Substitution. Method of Taring

Place the object Q in the left pan and counterbalance or tare it by means of shot, sand or weights. Then remove Q and establish equilibrium again by placing weights in its place. We have, then, as a result of the first weighing,

$$Ql = Tl_1$$

and from the second weighing,

$$Pl = Tl_1$$

from which it follows:

$$\begin{aligned} Ql &= Pl \\ Q &= P. \end{aligned}$$

This method is used chiefly in weighing large objects.

Ratio of Lengths of Balance Arms. In a perfect balance of the type used in the chemical laboratory, the two arms of the beam are equal. Most balances are not perfect and there is usually a slight difference in the lengths of the arms. If r is the length of the right arm and l that of the left arm then the true weight, w_0, of an object is the apparent weight w_a, as obtained by weighing it in the usual manner, multiplied by the arm ratio.

$$w_0 = w_a \frac{l}{r}.$$

If the true weight has been determined for an object of suitable size (such as that of about half the load which the balance is designed to

bear) then the arm ratio $\frac{l}{r}$ can be determined from the above equation and used as a correction factor. The ratio should be expressed to the fifth decimal.

Reduction of Weighings to Vacuo

When a substance is immersed in water it experiences a buoyant or floating effect. Its apparent weight is diminished by the weight of water that it displaces. In exactly the same way, an object weighed in air against brass weights is buoyed up by the air that it displaces but the weights are also subject to the same effect. If brass is weighed in the air against brass weights, the buoyancy will be the same on both sides of the balance and the weight will be the same in a vacuum as in the air. If a material of lower density is weighed against brass, the weight in a vacuum will be greater than the apparent weight in air and conversely if a denser material such as gold is weighed with brass weights, the weight in a vacuum will be smaller than the weight in air.

The degree of precision to be attained in the buoyancy correction depends upon the precision with which the volumes and the density of air can be determined. In the case of the weights, several materials are used in the construction of every set. The larger weights may be gold, gold plated or brass and the smaller weights may be of platinum, German silver, or aluminium. Moreover, many brass weights have interior cavities with enclosed air. The density of the air varies with the temperature, moisture and carbon dioxide content, barometric pressure and the value of gravity. Since, however, in chemical work relatively small volumes of materials are used for the weighings, it is not necessary to consider slight variations in these factors.

Ordinarily, the weight of 1 ml. of air at room temperature is assumed to be 1.2 mg. and the density of brass weights is assumed to be 8.0.*

If ∂ denotes the density of the object weighed, Δ the density of the weights, ρ the weight of 1 ml. of air, p_0 the weight in vacuo and p the weight in air, the weight in vacuo can be found by the following formula

$$p_0 = p + \left(\frac{p_0}{\partial} - \frac{p_0}{\Delta}\right)\rho$$

* For determining the true weights of large masses of materials, as is necessary in some physical experiments, it is necessary to know the density of air with greater precision. Density tables taken from W. Felgentraeger's *Theorie Konstruction und Gebrauch der feineren Hebelwage*, and Circular No. 3, of the U. S. Bureau of Standards will be found on page 15.

Since the density of air and of the weights is accurate only to two significant figures in the usual computation, not more than three significant figures should be used in the value of p_0 and p in the parenthesis. In this formula, therefore, p_0 may be replaced by p and we have

$$p_0 = p + \left(\frac{p}{\delta} - \frac{p}{\Delta}\right)\rho$$

In using this formula, it is customary to express the density of air, ρ, in milligrams and if the values of p (in grams) inside the parenthesis are taken to only two significant figures, the correction can be easily found with the aid of the slide rule.

Instead of making the computation, the following table of Kohlrausch may be used:

REDUCTION OF A WEIGHING MADE WITH BRASS WEIGHTS TO VACUO. METHOD OF F. KOHLRAUSCH

δ	k	δ	k	δ	k
0.7	+1.56	2.0	+0.45	8	−0.00
0.8	1.35	2.5	0.33	9	0.017
0.9	1.18	3 0	0.25	10	0.030
1.0	1.05	3.5	0.19	11	0 041
1.1	0.94	4.0	0.15	12	0.050
1.2	0.85	4.5	0.12	13	0 058
1.3	0.77	5.0	0 09	14	0.064
1.4	0.71	5.5	0.07	15	0.070
1.5	0.65	6.0	0 05	16	0.075
1.6	0.60	6.5	0 03	17	0.079
1.7	0.56	7.0	0 02	18	0.083
1.8	0.52	7.5	0 01	19	0.087
1.9	0.48	8.0	0.00	20	0.090
2.0	0.45			21	0.093

$k = 1.20\left(\frac{1}{\delta} - \frac{1}{8.0}\right)$ mg. If a substance of specific gravity δ weighs g grams in the air, then $g \cdot k$ mg. are to be added to the weight in air in order to obtain the weight in vacuo.

The following table* gives the density of air in milligrams per cubic centimeter for air of 50 per cent humidity and for a place where "g" equals 981.3 centimeters per second. The temperatures should be that of the balance case and that of the barometer should not vary by more than 5°.

* W. Felgentraeger, *Theorie Konstruktion und Gebrauch der feineren Hebelwage.* Cf. Circular No. 3, U. S. Bureau of Standards.

DENSITY OF DRY AIR (MILLIGRAMS PER MILLILITER)

T / b	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°
690	1 103	099	094	090	086	082	077	073	069	065	061	057	052
1	104	100	096	092	087	083	079	075	071	066	062	058	054
2	106	102	097	093	089	085	081	076	072	068	064	060	055
3	108	103	099	095	091	086	082	078	074	070	065	061	057
4	109	105	101	096	092	088	084	080	075	071	067	063	059
5	111	106	102	098	094	089	085	081	077	073	068	064	060
6	112	108	104	099	095	091	087	083	078	074	070	066	062
7	114	110	105	101	097	093	088	084	080	076	072	067	063
8	116	111	107	103	098	094	090	086	082	077	073	069	065
9	117	113	109	104	100	096	092	087	083	079	075	070	066
700	1 119	115	110	106	102	097	093	089	085	080	076	072	068
1	120	116	112	107	103	099	095	090	086	082	078	074	069
2	122	118	113	109	105	100	096	092	088	084	079	075	071
3	124	119	115	111	106	102	098	094	089	085	081	077	072
4	125	121	117	112	108	104	099	095	091	087	082	078	074
5	127	122	118	114	110	105	101	097	092	088	084	080	076
6	128	124	120	115	111	107	103	098	094	090	085	081	077
7	130	126	121	117	113	108	104	100	096	091	087	083	078
8	132	127	123	118	114	110	106	101	097	093	089	084	080
9	133	129	125	120	116	112	107	103	099	094	090	086	082
710	1 135	130	126	122	117	113	109	105	100	096	092	087	083
1	136	132	128	123	119	115	110	106	102	097	093	089	085
2	138	134	129	125	121	116	112	108	103	099	095	090	086
3	140	135	131	127	122	118	114	109	105	101	096	092	088
4	141	137	132	128	124	119	115	111	106	102	098	094	089
5	143	138	134	130	125	121	117	112	108	104	099	095	091
6	144	140	136	131	127	123	118	114	110	105	101	097	092
7	146	142	137	133	128	124	120	115	111	107	102	098	094
8	148	143	139	134	130	126	121	117	113	108	104	100	095
9	149	144	140	136	132	127	123	119	114	110	106	101	097
720	1 151	146	142	138	133	129	124	120	116	111	107	103	099
1	152	148	144	139	135	130	126	122	117	113	109	104	100
2	154	150	145	141	136	132	128	123	119	114	110	106	102
3	156	151	147	142	138	134	129	125	120	116	112	107	103
4	157	153	148	144	140	135	131	126	122	118	113	109	105
5	159	154	150	145	141	137	132	128	124	119	115	111	106
6	160	156	151	147	143	138	134	130	125	121	116	112	108
7	162	158	153	149	144	140	136	131	127	122	118	114	109
8	164	159	155	150	146	141	137	133	128	124	120	115	111
9	165	161	156	152	147	143	139	134	130	125	121	117	112
730	1 167	162	158	153	149	145	140	136	131	127	123	118	114
1	169	164	160	155	151	146	142	137	133	129	124	120	115
2	170	166	161	157	152	148	143	139	135	130	126	121	117
3	172	167	163	158	154	149	145	140	136	132	127	123	119
4	173	169	164	160	155	151	147	142	138	133	129	124	120
5	175	170	166	161	157	153	148	144	139	135	130	126	122
6	177	172	168	163	159	154	150	145	141	136	132	128	123
7	178	174	169	165	160	156	151	147	142	138	133	129	125
8	180	175	171	166	162	157	153	148	144	139	135	131	126
9	181	177	172	168	163	159	154	150	145	141	136	132	128
740	1 183	178	174	169	165	160	156	151	147	142	138	134	129
1	185	180	176	171	166	162	157	153	148	144	140	135	131
2	186	182	177	173	168	164	159	155	150	146	141	137	132
3	188	183	179	174	170	165	161	156	152	147	143	138	134
4	189	185	180	176	171	167	162	158	153	149	144	140	136
5	191	186	182	177	173	168	164	159	155	150	146	141	137
6	193	188	183	179	174	170	165	161	156	152	147	143	139
7	194	190	185	180	176	171	167	162	158	153	149	144	140
8	196	191	187	182	177	173	168	164	159	155	150	146	142
9	197	193	188	184	179	175	170	166	161	157	152	148	143
750	1 199	194	190	185	181	176	172	167	163	158	154	149	145
1	201	196	191	187	182	178	173	169	164	160	155	151	146
2	202	198	193	188	184	179	175	170	166	161	157	152	148
3	204	199	195	190	185	181	176	172	167	163	158	154	149
4	205	201	196	192	187	182	178	173	169	164	160	155	151
5	207	202	198	193	189	184	179	175	170	166	161	157	152
6	209	204	199	195	190	186	181	177	172	167	163	158	154
7	210	206	201	196	192	187	183	178	174	169	164	160	155
8	212	207	203	198	193	189	184	180	175	171	166	161	157
9	213	209	204	200	195	190	186	181	177	172	168	163	158

DENSITY OF DRY AIR (MILLIGRAMS PER MILLILITER).—*Continued*

b \ T	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°
760	1 215	210	206	201	196	192	187	183	178	174	169	165	160
1	217	212	207	203	198	193	189	184	180	175	171	166	162
2	218	214	209	204	200	195	190	186	181	177	172	168	163
3	220	215	211	206	201	197	192	187	183	178	174	169	165
4	221	217	212	208	203	198	194	189	184	180	175	171	166
5	223	218	214	209	204	200	195	191	186	181	177	172	168
6	225	220	215	211	206	201	197	192	188	183	178	174	169
7	226	222	217	212	208	203	198	194	189	184	180	175	171
8	228	223	219	214	209	204	200	195	191	186	181	177	172
9	230	225	220	215	211	206	201	197	192	188	183	178	174
770	1.231	226	222	217	212	208	203	198	194	189	185	180	175
1	233	228	223	219	214	209	205	200	195	191	186	182	177
2	234	230	225	220	215	211	206	201	197	192	188	183	178
3	236	231	227	222	217	212	208	203	198	193	189	185	180
4	238	233	228	223	219	214	209	205	200	195	191	186	182
5	239	234	230	225	220	216	211	206	202	197	192	188	183
6	241	236	231	227	222	217	212	208	203	198	194	189	185
7	242	238	233	228	223	219	214	209	205	200	195	191	186
8	244	239	234	230	225	220	216	211	206	202	197	192	188
9	246	241	236	231	227	222	217	213	208	203	199	194	189
780	247	242	238	233	228	223	219	214	209	205	200	195	191

Calibration of a Set of Weights

A set of weights as furnished by the maker cannot as a rule be relied upon closer than to one mg. for weighings of about one g. For exact work in absolute weighing it is necessary to determine not only the relative errors of the weights among themselves but also the absolute error of the set by comparing one of the largest pieces with a standard weight.

Weights are tested by the U. S. Bureau of Standards upon application and the payment of a suitable fee.*

As already stated, it is not necessary that the various pieces in a set of weights should have the exact value stamped upon them. The analytical chemist is satisfied if the pieces stand in the proper relation to one another, or if the error of each piece is known.

Two methods of testing and calibrating a set of weights will be outlined. The first method is that of Kohlrausch and depends upon the assumption that the sum of the 50, 20, 10, 10′, 5, 2, 1, 1′ and 1″ pieces is exactly 100 g. It is best to weigh by the *method of swings* and correction for unequal balance arms should be made by *double weighing*, weighing by substitution, or by use of the *balance arm ratio*. When two or more weights of the same denomination are present in the set, they should be marked so that they may be distinguished from one another.

Procedure. Starting with the largest weight find its value in terms of the smaller ones, and continue in the same way with all the other weights of 1 g. and over

$$50\text{ g.} = 20 + 10 + 10' + 5 + 2 + 1 + 1' + 1'' + A\text{ mg.}$$

$$20\text{ g.} = 10 + 10' + B\text{ mg.}$$

$$10' = 10 + C\text{ mg.}$$

$$5 + 2 + 1 + 1' + 1'' = 10 + D\text{ mg.}$$

* In 1918 the fee was $2.00 for testing a single piece but a reduction was made for testing two or more pieces. Circular No. 3, U. S. Bureau of Standards.

With the aid of these equations, express the weights in terms of the 10 g. piece.

$$\begin{aligned} 5+2+1+1'+1'' &= \mathbf{10}\text{ g.} + D\text{ mg.} \\ 10 &= \mathbf{10} \\ 10' &= \mathbf{10} + C \\ 20 &= \mathbf{10}+\mathbf{10}+C+B \\ 50 &= \mathbf{10}+\mathbf{10}+\mathbf{10}+\mathbf{10}+\mathbf{10}+A+B+2C+D \end{aligned}$$

If it is assumed that the sum of the left hand members of these last expressions is equal to exactly 100 g., then the sum of the right hand members must also equal 100 g. We have $10 \times \mathbf{10} + A + 2B + 4C + 2D = 100$ g. and the 10 g. weight itself:

$$\mathbf{10} = 10 - \frac{A + 2B + 4C + 2D}{10}.$$

If we let $S = \frac{A + 2B + 4C + 2D}{10}$, then we obtain

$$\begin{aligned} \mathbf{10} &= 10\text{ g.} - S \\ 10' &= 10\text{ g.} - S + C \\ 5+2+1+1'+1'' &= 10\text{ g.} - S + D \\ 20 &= 20\text{ g.} - 2S + B + C \\ 50 &= 50\text{ g.} - 5S + A + B + 2C + D \\ &= 50\text{ g.} + \tfrac{1}{2}A \end{aligned}$$

The sum $\frac{1}{2}A + B + 2C + D - 5S$ should equal 0, which serves as a test for the accuracy of the observations.

Now compare the 5 g. weight with the $2 + 1 + 1' + 1''$ in exactly the same way,

$$\begin{aligned} 5 &= 2+1+1'+1'' + a \\ 2 &= 1+1' + b \\ 1' &= 1 + c \\ 1'' &= 1 + d \end{aligned}$$

According to the preceding work

$$5 + 2 + 1 + 1' + 1'' = 10.000 - S + D$$

consequently

$$10 \times 1 + a + 2b + 4c + 2d = 10.000 - S + D$$

and

$$\mathbf{1} = 1.000 - \frac{a + 2b + 4c + 2d + S - D}{10}.$$

If we let $s = \dfrac{a + 2b + 4c + 2d + S - D}{10}$, we obtain

$$
\begin{aligned}
1 &= 1.000 - s \\
1' &= 1.000 - s + c \\
1'' &= 1.000 - s + d \\
2 &= 2.000 - 2s + b + c \\
5 &= 5.000 - 5s + a + b + 2c + d.
\end{aligned}
$$

In the same way test the smaller weights until finally the following correction table is obtained

TABLE FOR CORRECTION OF WEIGHTS

$50 = 50$ g. $+ \frac{1}{2} A$ $20 = 20$ g. $- 2S + B + C$ $10 = 10$ g. $- S$ $10' = 10$ g. $- S + C$	$5 + 2 + 1 + 1' + 1'' = \overbrace{10}$ $= 10$ g. $- S + D$	$0.5 + 0.2 + 0.1 + 0.1' + \Delta^* = \overbrace{1}$ $= 1$ g. $- S + \alpha$	$\overbrace{0\ 1}$ $\Delta = 0.1$ g. $- s' + \sigma$
$\left.\begin{matrix}5\\2\\1\\1'\\1''\end{matrix}\right\} = 10$ g. $- S + D$	$5 = 5$ g. $- 5s + a + b + 2c + d$ $2 = 2$ g. $- 2s + b + c$ $1 = 1$ g. $- s$ $1' = 1$ g. $- s + c$ $1'' = 1$ g $- s + d$	$0.5 = 1$ g. $- 5s' + \beta + \gamma + 2\delta + \sigma$ $0.2 = 0.2$ g. $- 2s' + \gamma + \delta$ $0.1 = 0\ 1$ g. $- s'$ $0\ 1' = 0\ 1$ g. $- s' + \delta$ $\Delta = 0.1$ g.$' - s' + \sigma$	$0\ 05 = 0.5$ g. $- 5s'' + l + m + 2n + o$ $0.02 = 0.02$ g. $- 2s'' + m + n$ $0\ 01 = 0.01$ g. $- s''$ $0.01' = 0.01$ g. $- s'' + n$ Rider $= 0\ 01$ g. $- s'' + o$
Sum = 100 g.	10 g. $- S + D$	1 g. $- s + \alpha$	$0\ 1$ g. $- s' + \sigma$

* $\Delta = 0\ 05 + 0\ 02 + 0\ 01 + 0\ 01' +$ Rider on the 10 mg. division.

When weights are tested at the U. S. Bureau of Standards, the desired accuracy is shown by the following table:

Denomination	Precision of Corrections	Tolerance	Denomination	Precision of Corrections	Tolerance
kg	g	mg	mg	mg	mg
20	0.1	100	500	0.01	0.05
10	0.01	50	200	0.01	0 05
5	0.01	30	100	0.01	0.05
2	0.01	10	50	0 01	0.03
	mg		20	0.01	0.03
1	5 or 1	5	10	0.01	0.02
g			5	0.01	0.02
500	1	3	2	0.01	0.01
200	1	1	1	0.01	0 01
100	0.5 or 0.1	0.5	0.5	0.01	0.01
50	0.1	0.3	0.2	0.01	0 01
20	0.1	0.2	0.1	0 01	0 01
10	0.05	0.15			
5	0.05	0.15			
2	0.05	0 10			
1	0.05 or 0.01	0.10			

A method of weight calibration suggested by T. W. Richards* eliminates any error due to inequality in the length of the balance arms by using the substitution method. The weights to be standardized are weighed always on the left balance pan. It is recommended to begin the comparison with the smallest weight, get the value of every other weight in terms of the smallest weight and finally assume that some special weight is correct. It is necessary that all the fractional weights in the set to be calibrated should add up to one g. according to their face values. If the set contains only one 10 mg. weight, it is convenient to use in the calibration an extra 10 mg. weight from another set. In order to keep the rider in a convenient position on the scale, it is convenient to keep a permanent load of 0.5 mg. in the left balance pan. As tare for the weighings another set of weights, which need not be all accurate, is desirable.

Procedure. — Mark the different weights of the same denomination so that they are recognizable and always keep them in the same order in the box. Place one of the 10 mg. weights on the left scale pan and counterbalance it with any suitable tare, taking care that the rider is not too near either end of the scale. Using the method of swings, determine the rest point of the pointer and the sensitiveness of the balance. Replace the first 10 mg. weight with another of like value and determine the amount by which the rider must be moved to attain the same rest point, recording the difference to 0.01 mg. If the weights are practically the same, as they should be, this is best done not by actually moving the rider but from the displacement of the rest point as described under weighing by the *Method of Swings.*

If the second weight is found heavier than the first it is given a positive correction in this comparison. To make sure that the balance has remained in a constant condition during this trial, test the original weight again.

Next place the two 10 mg. pieces on the left pan and counterbalance them with a suitable tare. Replace the two small pieces with a 20 mg. weight and find its value in terms of the two smaller ones. Proceed in the same way with every weight in the box.

Assume for the purpose of calculation that the first 10 mg. weight is correct† and establish the value of all the other weights on this assumption. The values thus computed are consistent among themselves but are usually quite different from the face values of the individual weights. This is because the assumed standard is too small. It is better to assume that one of the larger weights is correct and, in fact, this may be

* *J. Am. Chem. Soc.* **22,** 144 (1900).

† Hopkins, Zinn and Rogers, *J. Am. Chem. Soc.*, **45,** 2528 (1920), recommend checking the observations against standard 50, 5, 1, 0.1 and 0.001 mg. wts. This makes its simpler for a beginner and easier to divide the work into several periods and also to some extent does away with compensating errors.

compared with a weight that has been standardized by the Bureau of Standards at Washington, although this is wholly unnecessary for most purposes. From the assumed, or corrected value of one of the larger weights, compute what the corresponding calibration correction should have been for each of the smaller weights. Thus if the calibration correction for the 10 g. weight was found to be + 0.01768 g. and it is now assumed to be correct, the 1 g. weight stands in its proper relation to the 10 g. weight if its calibration correction was found to be +0.00177 g. If its calibration correction was found to be less, then the weight is too light and a negative correction should be applied in using the weight.

The following table shows all the data and the results obtained in a sample standardization. In the first column the weights are named by their face values. In the second column the calibration values are given as obtained with one of the smallest weights as standard of comparison. These values are copied from a note-book in which each detail of each weighing was recorded. The third column gives the ideal value of each weight when the 10 g. piece is taken as the permanent standard and the fourth column gives the correction that must be applied to each weight.

CALIBRATION OF WEIGHTS

Face Value in Grams	Calibration Value	Ideal Calibration Value	Correction in Milligrams
0.01	Standard	0.01002	− 0.02
0.01′	0.01006	0.01002	+ 0.04
0.01″	0.01005	0.01002	+ 0.03
0.02	0.02005	0.02004	+ 0.01
0.05	0.05009	0.05009	0.00
0.1	0.10019	0.10018	+ 0.01
0.1′	0.10020	0.10018	+ 0.02
0.2	0.20035	0.20035	0.00
0.5	0.50088	0.50088	0.00
1	1.00183	1.00177	+ 0.06
2	2.00383	2.00354	+ 0.29
2′	2.00308	2.00354	+ 0.14
5	5.00884	5.00884	0.00
10	10.01768	10.01768	Standard
10′	10.01740	10.01768	− 0.28
20	20.03520	20.03536	− 0.16
50	50.08790	50.08840	− 0.50

Prepare a card from the individual corrections to show the corrections which should be applied to the usual combinations from 0.01 to 1.00 g. and from 1 g. upwards and keep this card in the balance case. In an ordinary gravimetric analysis, record the weights as follows:

	Observed Weight	Corrected Milligram	Corrected Weight
Weight crucible + substance	19.3105	$\left\{\begin{matrix}+0.39\\-0.01\end{matrix}\right\}$	19.3109
Weight crucible alone	16.9916	$\left\{\begin{matrix}+\ .06\\+\ .06\end{matrix}\right\}$	16.9917
Weight of substance			2.3192

The upper correction is that of the weights of one g. and over, while the lower is that of the fractional weights.

Weighing Samples of Factor Weights. In a busy laboratory it is often desirable to weigh out samples in such a way that the results of the analyses are known with as little computation as possible. Thus if the iron content of a sample weighing 0.6994 g. is determined by weighing ferric oxide, Fe_2O_3, the per cent of iron, Fe, is exactly 100 times the weight of the oxide. If 1 ml. of standard hydrochloric acid will neutralize 0.028 g. of pure sodium carbonate, then the percentage purity of a sample of sodium carbonate, containing no other substance of basic nature, will be just twice the number of cubic centimeters of acid used in the analysis of samples weighing 1.4 g. In every technical laboratory, therefore, the chemist has to learn to weigh out rapidly samples of specified weights. If the sample is a dry powder, unaffected by contact with the air, it can be weighed out on a watch glass. It is convenient to have a pair of counterpoised watch glasses for this purpose, *i.e.*, a pair of watch glasses which weigh so nearly alike that they can be balanced with the aid of the rider.

Place on the left balance pan the watch glass which is to hold the substance and on the right pan place the tare of the watch glass and additional weights amounting to the desired quantity. With the aid of a small spatula, or a palette-knife, transfer some of the powder to the watch glass in the left pan, until the pointer swings to the right with the beam lowered slightly so that the pointer can swing but a little way. Raise the beam, remove a little of the powder and, with the beam again lowered a little, add more powder by tapping the spatula. By repeating this process once or twice and finally testing with the balance beam altogether lowered, it is possible to get any desired weight within one or two tenths of a milligram. In chemical work it is a waste of time to try to make the original weight much more accurate than the rest of the analysis. Thus in determining the carbon content of a sample of steel with approximately 1 per cent of carbon present, the results of duplicate analyses with equal weight samples would be considered satisfactory if they indicated 1.00 and 1.01 per cent of carbon. In other words, errors arising from lack of homogeneity and

inaccuracies in the method of analysis may easily amount to 1/100 of the total carbon content. An error of 0.01 g. in the weight of a gram sample of the steel would be no greater than the allowable error of the analysis. In weighing out the sample, therefore, if the weight is accurate to the nearest centigram the error is less than that of the remainder of the work. On the other hand in determining the chlorine content of a sample of salt weighing about 0.25 g. it is important to get the weight to the nearest tenth of a milligram because the chlorine determination can be accomplished with an accuracy of one part in one thousand with samples of this size.

Reliability of a Result.* In order that the result of any measurement may be of scientific or technical value, it is desirable to have some numerical estimate or measure of its validity. By the *accuracy* of a result, should be understood the degree of concordance between it and the true value of the quantity measured. The true value is not usually known so that it is not always possible to obtain a numerical measure of the absolute accuracy of a measurement or analysis. By the *precision* or *precision measure* of a result is understood the best numerical measure of its reliability after all known sources of error have been eliminated or allowed for.

When any quantity is measured to the full precision of which the instrument or method is capable, it will usually be found that the results of repeated measurements do not agree exactly. Thus in the analysis of pure salt, the chlorine content will not always be found to be exactly 60.66 per cent although we may have reason to believe that this is the correct value.

All that we can hope to obtain from experimental data is the most probable value of the quantity or quantities in question. The branch of mathematics which treats of the general problem of the adjustment of errors of observation so that their effect upon the final result is reduced to a minimum is called Least Squares. According to the theory, the most probable values of a series of related observations are those for which the sum of the squares of the errors is a minimum. Here is not the place to go into the details of the mathematical proofs of the Method of Least Squares but it is important that every chemist should keep constantly in mind certain deductions that have been made from such studies.

In a series of observations, all of which possess an equal degree of probability, the most probable value of the quantity is the arithmetical mean.

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* The following discussion is based upon H. M. Goodwin's *Elements of the Precision of Measurements.*

Since the true value of the quantity is not known in most cases, the error of each determination and of the mean can not be determined. It is possible, however, to state how far each observation differs from the mean value and from these differences the *probable deviation* of the mean can be estimated. The average deviation of the mean, usually designated as *a.d.* is determined by dividing the sum of the deviations from the mean by the number of determinations made. The *a.d.* may be regarded as a numerical measure of the amount by which a new observation is likely to differ from the mean value, *m*.

Since the mean has a higher degree of probability than any single observation, it should have a smaller deviation from the truth. It can be shown that an arithmetical mean computed from n equally reliable observations is $\sqrt{n}$ times as reliable as any one observation. The deviation of the mean is usually denoted as *A.D.* According to the statement just made,

$$A.D. = \frac{a.d.}{\sqrt{n}}$$

A little study of this expression shows that it does not pay to increase the number of observations beyond a certain limit as the time and labor involved soon become excessive.

It is probable that more than half the time spent on chemical and physical computations is wasted owing to the retention of more figures than the precision of the data warrants. The habit should be acquired of rejecting at each stage of the work all figures which have no influence on the final result. In the following Rules for Computation the term *digit* denotes any one of the ten numerals including the zero, and the term *significant figure* is any digit which denotes or signifies the amount of the quantity in the place in which it stands. Thus a zero may or may not be a significant figure. When it is used merely to locate the decimal point as in the values 1,000 and 0.001, the zero is not a significant figure for the position of the decimal point is determined solely by the unit in which the quantity is expressed. There are two significant figures in the value 2.5 mg. even when it is written 0.0025 g. The number of decimal places in a result has in itself no significance in indicating the precision of a measurement. The statement that the results of an analysis agree within 1.2 milligrams gives no idea of the precision unless the entire value is known. A fractional or percentage precision measure, on the other hand, gives a definite idea of the precision of the measurement as it involves both the value of the quantity and its average deviation.

Rules for Computations

Rule I. In rejecting superfluous figures, increase by 1 the last figure retained if the following figure (that has been rejected) was 5 or over.

Rule II. In all deviation and precision measures retain two, and only two, significant figures.

Rule III. Retain as many figures in a mean result, and in data, as correspond to the second place of significant figures in the deviation or precision measure. According to this rule, two places of unreliable figures are retained in data so that accumulated errors due to rejections in the course of computation will not affect the first place of uncertain figures. Or, looked at from another point of view, the last figure may be regarded as quite unreliable but the next to the last significant figure should not vary by more than *one* or at the most *two* units from the mean.

Rule IV. The sum or difference of two or more quantities cannot be more precise than the quantity having the largest deviation. In adding or subtracting quantities, find the *a.d.* of each and retain in each quantity as many places as correspond to the second place of significant figures in the quantity with the largest deviation.

Rule V. In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, determine the percentage precision of the least reliable factor. If this is about ten per cent or better, use three significant figures in each factor of the computation and in the final result. If one per cent or better, use four significant figures in each factor of the computation and in the final result. If 0.1 per cent or better, retain five significant figures.

For computations involving a precision not greater than about 0.25 per cent use a 10 inch slide rule.

Rule VI. In carrying out the operations of multiplication and division by logarithms, retain as many places in the mantissa of the logarithm of each factor as are properly retained in the factors themselves under Rule V.

In ordinary chemical work the percentage precision of the result is often less than 0.1 per cent. Thus, in the determination of the chlorine content of a sample of pure salt weighing about 0.2 g., check values of 60.60 and 60.72 per cent chlorine would usually be considered satisfactory. This corresponds to a *percentage precision* of 0.12 parts in 61.0 or 0.2 per cent. According to the above rules only *four* figures should in this case be retained in all factors entering into the com-

putation and four place logarithms should be used. In the computation, the molecular weight of silver chloride should be taken as 143.3 instead of 143.34. If, on the other hand, a series of determinations all gave values ranging between 60.63 and 60.69 per cent chlorine, one would be justified in keeping *five* significant figures and using five place logarithms. This would not necessarily mean that the original weight of the salt and the final weight of the precipitate would have to be carried out to five significant figures because an error of 0.0002 g. in about 0.2 g. of salt would only correspond to 0.1 per cent of the entire weight. One would be justified, however, in recording the weights to five decimal places, using the Method of Swings.

For most chemical work, four significant figures are sufficient. In some cases, as in the determination of sulfur in steel, or in the conversion of small volumes of a solution (less than 1 ml.) into an equivalent volume of some other solution, only two significant figures should be used.

Filtration and Washing of Precipitates

How large should the filter be and how many times should the precipitate be washed?

With regard to the latter question it is evident that the precipitate should be washed until the soluble matter is completely removed. It is clear, however, that this point will never be reached because a part of the solution always remains on the filter, but it is not difficult to make the amount of the dissolved substance remaining so small as to be negligible. When the amount of dissolved substance remaining on the filter is so small that it could not be detected by the balance, the precipitate can be considered to be completely washed.

The aim should be not only to remove the soluble matter, but to accomplish this with as little wash water as possible.

No precipitate is absolutely insoluble, so that it is clear that every unnecessary excess of wash water causes harm by removing a fraction of the precipitate, and the greater the excess of the wash water the greater the amount of the precipitate dissolved.

The amount of wash water to be used depends largely upon the nature of the precipitate itself. Amorphous, gelatinous precipitates always require more washing than crystalline, granular ones.* As a rule, it may be said that the process of washing must be continued until the substance which is being washed out can be no longer detected in the

* The reason why some precipitates require more washing than others is due to the fact that the degree of adsorption varies. (Cf. Ostwald, *Die wissenschaftl. Grundl. der analyt. Chem.*)

last filtrate. In case the filtrate must be used for another determination, it is obvious that the filtrate should not be tested too soon.

Let us assume the filter to hold 10 ml., the solution to drain to the last drop from the paper, the amount of the solution held back by the precipitate and filter to be 1 ml. and to contain 0.1 g. of the solid substance which is to be removed by washing.

The filter is filled to the upper edge with wash water and allowed to drain to the last drop n times, until not more than 5/100 mg. of the substance to be removed by washing remains.

According to our assumption, 9 ml. drain off and 1 ml. remains behind; we have consequently:

Removed by the		There remains after the	
1st washing,	$0.1 \cdot 9/10$ g.	1st washing	$0.1 \cdot 1/10$ g.
2d "	$0.1 \cdot 9/10 \cdot 1/10$ g.	2d "	$0.1 \cdot 1/10 \cdot 1/10$ g.
3d "	$0.1 \cdot 9/10 \cdot (1/10)^2$ g.	3d "	$0.1 \cdot 1/10 \cdot (1/10)^2$ g.
.		.	
.		.	
.		.	
nth "	$0.1 \cdot 9/10 \cdot (1/10)^{n-1}$ g.	nth "	$0.1 \cdot 1/10 \cdot (1/10)^{n-1}$ g.

After washing n times, therefore, the amount removed by washing is the sum of the decreasing geometric series of which the first term is $0.1 \cdot 9/10$ and the constant factor is 1/10.

In case $n = 4$, the sum of the series is

$$\Sigma = \frac{0.1 \cdot \frac{9}{10}\left[\left(\frac{1}{10}\right)^4 - 1\right]}{\frac{1}{10} - 1} = 0.09999 \text{ g.}$$

After washing the precipitate four times, therefore, 0.09999 g. of the impurity has been removed. According to the assumption that there was originally 0.1 g. of this substance, there remains in the precipitate only 0.00001 g., or in other words a negligible amount.

Consequently, the filtrate should be tested qualitatively for the substance to be removed only after the precipitate has been washed four times.

Often the washing will be found to have been complete after the fourth washing, but as a rule this will not be the case, and in many cases it will be found necessary to repeat the operation for from ten to twenty times. In the processes which are described it will usually be stated how far to carry the washing.

Now with regard to the second point, how should a precipitate be washed with the least possible amount of wash water? According to

the above consideration it is necessary to wash every precipitate at least four times, in which case the filter should be entirely filled each time, and it is evident that the size of the filter-paper will influence the amount of wash water used.

The filter, therefore, should be made as small as possible, irrespective as to whether there is little or much liquid to filter. *The size of the filter used should be regulated entirely by the amount of the precipitate and not at all by the amount of the liquid to be filtered.* The mistake should not be made, however, of using too small a filter. The precipitate should never reach the upper edge of the paper; about 5 mm. should remain free, and even in this case the filter should not be so completely filled as in Fig. 5, *a*. It is better to have the filter filled about as much as is shown in Fig. 5, *b*, in order that sufficient room is left for the wash water.

The use of too large filters is one of the inexcusable analytical errors.

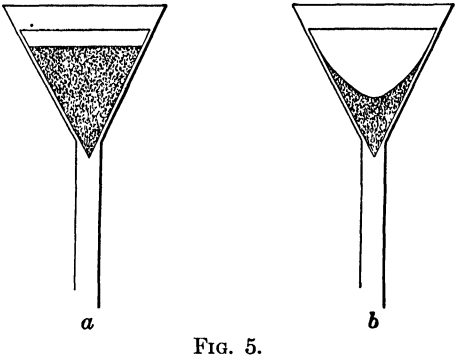


FIG. 5.

Adsorption by Precipitates. Whenever substances are in intimate contact with one another there is always a tendency for a slight change in concentration (quantity present in a unit volume) at the place of contact. This phenomena is called *adsorption* and the term differs from the closely related word *absorption* by meaning especially the change that takes place at the exposed *surfaces*. The 1901 edition of The Century Dictionary defined adsorption as "condensation of gases on the surfaces of solids" but the term is no longer restricted in this way and there may be adsorption of vapor by a liquid, of liquid by solid, and of solid by liquid. Of special interest to the analytical chemist is the adsorption from solution by a solid. In cases of adsorption there is usually more or less fixation at the surface but sometimes there is a tendency for the adsorbed material to penetrate into the adsorbent.

Since adsorption is primarily a surface phenomenon, it is not strange to find that the extent of the adsorption is determined largely by the amount of exposed surface. Subdivision always increases the surface of a solid. Thus Wolfgang Ostwald* has computed that a cube with

* *Theoretical and Applied Colloid Chemistry.*

edges one centimeter long and exposing only six square centimeters of surface will have six square meters of surface if broken into 10^{12} smaller cubes each with an edge of 1 μ (0.001 mm.). According to the same author a colloidal solution which will pass through a paper filter contains particles of suspended material ranging from 0.1 μ to 1 $\mu\mu$ (0.001 μ).

When the adsorbing surface is relatively small, as with the sides of a glass vessel or with a small filter paper, errors caused by adsorption are usually not serious and it is comparatively easy to wash free from the adsorbed material. In the case of crystalline precipitates with large grains the errors are not usually as serious as in the case of *gels* such as ferric or aluminium hydroxide. Adsorption is always more or less selective in nature and precipitates tend to adsorb some substances in solution to a much greater extent than they do others. In fact sometimes there is what is called *negative adsorption* although this case is of less importance than the more common *positive adsorption* which may cause serious errors in chemical analysis. It has been shown that aluminium hydroxide will decolorize dilute solutions of alizarine and certain other dyestuffs but has practically no adsorbing action on emerald green or chrysoidine. Freshly-precipitated, hydrated aluminium hydroxide and metastannic acid are capable of adsorbing large quantities of arsenic acid from solution and it is practically impossible to remove an appreciable quantity of the adsorbed material by washing. In all cases that have been studied quantitatively, the adsorption is expressed fairly well by the equation

$$\left(\frac{x}{m}\right)^n = kc$$

in which x is the amount adsorbed, m represents the units of adsorbing agent, c is the concentration of the solution, k is a constant and n is greater than 1 but is not necessarily an integer. As a general rule, the adsorption by a precipitate is less if the solution is dilute and if the precipitate is not allowed to remain long in contact with the solution.

In handling colloidal substances adsorption is not the only thing that the chemist has to fear. Most colloids are to some extent reversible and tend to return to the *sol* state when washed with pure water. The sol condition represents a finer state of subdivision than that of the *gel*. To prevent colloidal substances from passing through the filter, it is sometimes desirable to wait for some time before filtering, sometimes desirable to work with fairly concentrated solutions, to wash with the solution of an electrolyte instead of with pure water and to keep the mother liquid hot.

Since one of the most characteristic properties of colloids is the size of the individual particles, it is possible to obtain under some conditions almost any substance in the colloidal state. Many changes that have been attributed to chemical action in the past are known to be due merely to adsorption effects and to changes in the state of subdivision of the substance. It is impossible to always predict how a colloid will behave under conditions which have not been tested with the particular substance in question. Apparently, there are very few general rules that can be applied.

Paper Filters. Strength, uniform texture, proper porosity and a low ash are the desirable qualities in filter paper for quantitative work. A paper of 7 cm. diameter should have an ash of less than 0.05 mg. To get this low ash, the paper is washed with hydrochloric and hydrofluoric acids. This washing makes the paper softer and more porous but weakens it so that it is more easily torn.

The purpose of filtration is to separate a solid from the liquid in which it is suspended. The pores of the paper must be smaller than the particles of solid which are to be retained by the filter. Precipitates vary with respect to the size of the smallest particles. Some, like crystalline barium sulfate or gelatinous metastannic acid, are very finely divided and require a fine-grained paper. Such filter paper is a slow filtering medium. Consequently chemists are accustomed to use different grades of filter paper, some which make rapid filters and others which make slow filters but are required for precipitates that are likely to pass through the pores of a rapid filter paper.

Funnels are supposed to have an angle of exactly 60° and the simplest way to fold a circular cut paper is to crease it across a diameter and then, without opening the paper, make a second fold at right angles to the first one. To test the funnel, and this should be always done before starting to filter, open the filter so that it makes a cone to fit the funnel, wet the paper and see if it fits tightly against the side walls of the funnel. It is important that it should fit tightly along the upper edge which must always be below the rim of the funnel as otherwise the filter cannot be washed satisfactorily. Pour water into the funnel and, if the filter fits, the stem should fill with liquid. If the stem is too wide, this will not always happen. A little grease in the stem of the funnel will also interfere. If the filter does not fit when folded into a 60° cone, change the second fold sufficiently to make it fit.

It is convenient to mark the funnel so that it can always be told how much the second fold should be changed to make the filter paper fit the funnel. It is also well to mark the funnel so that it can be recognized as a rapid or as a slow funnel, for funnels vary greatly in this respect

The above method of folding a filter paper is the easiest and quickest but often considerable time is saved in the filtration by folding the paper so that liquid passes through it more rapidly. The following method of folding a filter accomplishes this end but it is harder to make the filter fit tightly to the funnel and there is more danger of having a little precipitate get by the filter.

(1) Fold the paper evenly across a diameter of the circle as in the above method.

(2) Open up the fold and make another at right angles to it creasing the paper on the same side as at first. This is done by merely bringing the two points on the circumference of the circle that were met by the first fold over against one another and flattening out the paper again.

(3) Turn the paper over and fold again exactly $22\frac{1}{2}°$ away from one of the first two folds. To get this position, bisect one of the quadrants formed by the previous two folds, by merely bringing two creases together and flattening out the paper so that a little crease is made on the circumference and make another bisection in the same way. At this last mark fold across the paper with the crease on the opposite side to that made by the original folds.

(4) Open up the paper and make another fold at right angles to the third fold. Change half of this last fold to make the paper fit the funnel.

For large funnels a *plaited or fluted filter* is often desirable. These can be purchased already folded but the quality of the paper is not always suitable for quantitative work. Swedish filter paper is satisfactory for most purposes when the filter itself is not to be ignited. This can be purchased in sheets and one quarter sheet is sufficient for a large funnel. Since all filter paper retains some of the solution poured through it so firmly that it is very difficult to remove the last traces of solute by washing, it is never wise to choose a large funnel simply because considerable liquid has to be filtered. To make a plaited filter,

(1) Fold the filter once along a diameter as in the first method. Do not open this fold.

(2) Make a second fold along the radius as in the first method.

(3) Open this second fold and make two other folds at right angles to each other, dividing the doubled filter into quarters. This is accomplished by taking half of the straight edge of the once folded filter and folding it over to make it coincide with the second fold. In all these folds, take care to make them accurately but do not crease the paper hard at the center.

(4) With the paper again folded only once, make a fold dividing one of the outside segments into halves and make a fold at right angles to this by bringing over the other half of the straight edge.

(5) Make two more folds starting with the other outside segment.

By these seven folds the original circle is divided into 16 parts of equal size and if the paper is opened, half of the creases will be found all on the same side in one half of the paper and all on the other side in the other half of the paper.

(6) With the paper again doubled as it was after the first fold, start at the outside, fold over into the first crease and then bring back the outer edge so that it is in line with the outer edge of the first crease. This makes a subdivision of the outside segment and brings the crease on the opposite side of the doubled paper.

Without opening this last fold, go into the next crease and again come back continuing until the middle fold is reached.

Start in the same way at the other side of the doubled paper and plait toward the center as from the other side.

In this way the paper will be divided into 32 equal segments. If the filter is made from a quarter sheet of Swedish paper, it is not necessary to cut out a circle at the start. When the plaiting is finished it is easy to tear off the ends of the folded paper so that it will fit into the funnel, without protruding above the edge, and leave a nearly circular edge.

Plaited filters are used chiefly when it is desired to filter off a large and bulky precipitate and it is not necessary to wash the precipitate thoroughly. Plaited filters made from Swedish paper filter rapidly but are likely to break at the point of the cone.

It is rarely advisable to use suction with a paper filter. The suction is likely to draw small particles of the precipitate into the pores of the paper and then filtration is usually as slow, or slower, than it would have been without the suction. If suction is used with a paper filter, it should rest in a filtering cone made of platinum, palau or a hardened parchment filter.

Wash Bottles

For transferring a precipitate to a filter and for washing it, a *wash bottle* is indispensable. Fig. 6 shows a sketch of the type most commonly used. It consists of a flat-bottomed, 750 ml. flask fitted with a rubber stopper and glass tubing bent so that the mouthpiece and outlet tubing are in line. It is best to make the outlet tube in two pieces so that the jet can be manipulated by moving two fingers of the same hand that holds the bottle. The nozzle may be made by drawing out tubing until a capillary is formed and then cutting off to make a stream of the proper size. A stouter tip may be made by simply fusing the end of the original tubing until it has contracted to the proper diameter.

The bend of the long piece of tubing inside the flask is made so that this reaches into the deepest part of liquid when the wash bottle is inclined slightly as in washing precipitates. A bend of the opposite kind is useful for washing precipitates out from beakers, when the bottle is inclined in the opposite direction.

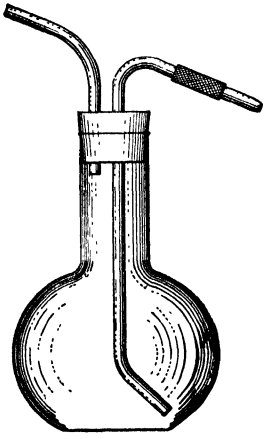


FIG. 6.

In washing the filter, the stream should always be directed against the upper edge of the paper; this is the hardest part of the paper to wash.

For washing with organic solvents that dissolve rubber, a bottle with a ground glass stopper is desirable but it is unnecessary for most work in inorganic chemistry.

Policemen

Sometimes a little precipitate adheres to the side of a vessel. To remove it, a piece of rubber over the end of a glass stirring rod is used. This so-called *policeman* may be made by sticking together the end of a piece of rubber tubing that fits the rod tightly, or it may be purchased from a chemical supply house. The policeman should not as a rule be used for stirring a solution and should not be allowed to remain in solutions.

The Drying and Igniting of Precipitates

Before a precipitate can be weighed it must be absolutely dry. Those precipitates which do not undergo a change of weight on ignition are treated as follows:

(*a*) THE PRECIPITATE IS IGNITED DRY

This method, in which the precipitate is separated from the filter, the filter burnt by itself, the ash added to the main part of the precipitate and the mixture then ignited to constant weight, is used in those cases when the ignited substance will be reduced by the burning paper, *e.g.*, in the case of precipitates of silver chloride, lead sulfate, bismuth oxide, etc.

To perform this operation it is first desirable to dry the filter and precipitate at 100°. Wet a common filter, stretch it over the top of the funnel, and then gently tear off the superfluous paper. The cover thus formed continues to adhere after drying. Place the funnel and filter in a drying-closet and dry at 100–105°. When perfectly dry, place a weighed crucible upon a piece of glazed paper of about 20 sq.

cm. (Fig. 8, left) and carefully shake the dry precipitate into the crucible, removing it from the paper as completely as possible by gentle rubbing with a platinum spatula. Brush any small particles of the precipitate which may have fallen upon the glazed paper into the crucible with the aid of a feather (Fig. 8). Small particles of the precipitate will still always adhere to the paper and these must be weighed. In order to accomplish this, set fire to the filter and weigh the ash by itself or mixed with the main part of the precipitate.*

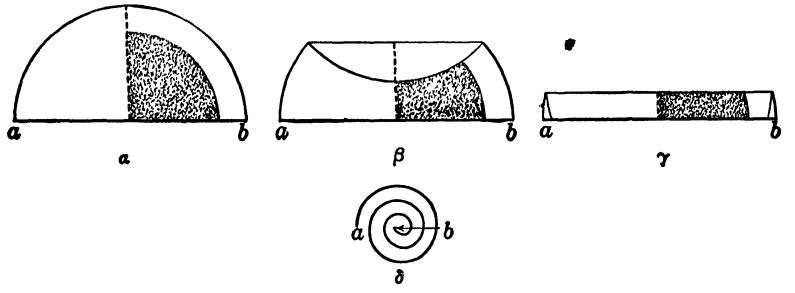


FIG. 7.

The combustion of the filter, to which small particles of the precipitate still adhere, is best accomplished by the method proposed by Bunsen as follows: Fold the filter together so that the precipitate occupies the position indicated in the shaded part of Fig. 7, α, and then fold again as indicated by β and γ of Fig. 7 to a narrow strip. Roll up the paper as indicated by δ, beginning at b, so that the portion

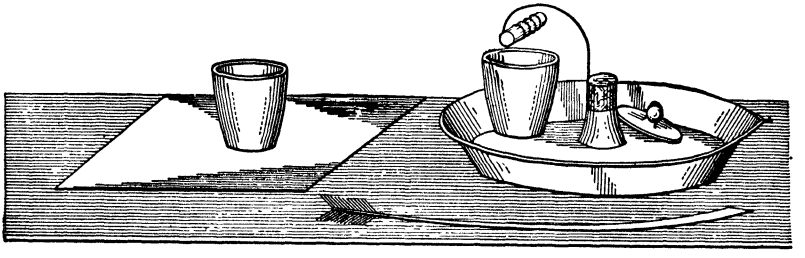


FIG. 8.

of the filter which is free from the precipitate is on the outside. Place the roll in the loop of a platinum wire with a previously ignited heavy platinum wire, supported (as indicated in Fig. 8) by means of a cork

* By using filter-paper which has been carefully washed with hydrochloric and hydrofluoric acids, it is permissible to neglect the weight of the ash from the filter itself. With an unknown paper it is necessary to determine the weight of the ash by a separate experiment and then correct the weight of the precipitate obtained.

in the opening of a porcelain plate and set fire to the filter by means of the gas-flame. Take away the flame and allow the paper to burn quietly. If carbonized particles still remain, apply the gas-flame repeatedly until it is no longer possible to make the particles glow any more. (Too strong ignition should be avoided.) Add the ash to the contents of the crucible by gentle shaking and the final use of the feather. Heat the crucible at first with a small flame, and gradually raise the temperature until the prescribed temperature of ignition for the given precipitate is reached. Finally remove the flame, allow the crucible to cool somewhat, and while still *warm*, but *not glowing*, place it in a desiccator (Fig. 9).

After cooling (at least three quarters of an hour for porcelain crucibles and 20 minutes for platinum ones) weigh the crucible and its contents.

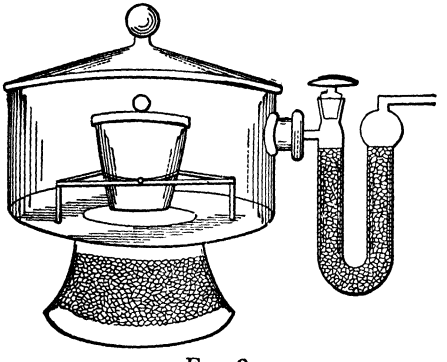


FIG. 9.

Many precipitates (silver chloride, lead sulfate, etc.) are partially reduced to metal by the above treatment. As, however, these metals are difficultly volatile, there will be no loss of the metal, only of the anion (chlorine in the case of silver chloride and SO_3 in the case of lead sulfate). This loss may be readily replaced. Moisten the metal in the crucible with a few drops of nitric acid to dissolve it, add a few drops of hydrochloric acid (in the case of a silver chloride precipitate), or of sulfuric acid (in the case of lead sulfate), and after evaporating off the excess of the acid, weigh the crucible. The only danger in this method is that in burning the filter the ash is heated too hot, so that some of the reduced metal melts and alloys with the platinum wire. If, however, the filter-paper is rolled up as was directed, there is always some paper free from precipitate between the precipitate and the platinum wire, yielding an ash which, although its weight is inappreciable, is still sufficient to protect the wire and prevent the reduced metal from coming in contact with it, provided it is not heated strongly enough to melt the metal.

Many precipitates (K_2PtCl_6, etc.) are changed so much by this treatment that it would be impossible to obtain correct results. In such cases the filter cannot be burnt, but it is previously dried at a definite temperature and weighed; afterwards the precipitate and filter are again dried at the same temperature and weighed again.

In order to dry the filter, place it in a drying-closet* (Fig. 10, *a*) upon a watch-glass and near an open weighing beaker, bring the tem-

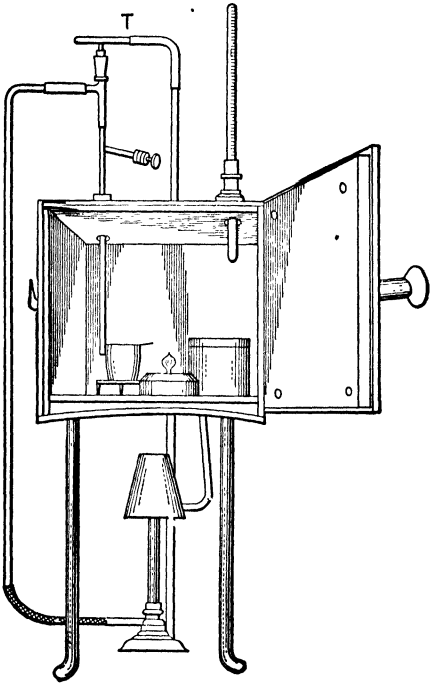


FIG. 10*a*.

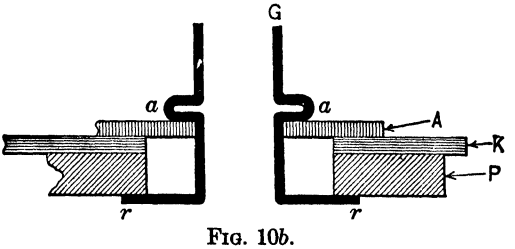


FIG. 10*b*.

perature to the desired point and keep it there, with the help of the thermo-regulator *T*, for ½ to 1 hour. By means of tongs quickly place

* The drying-closet shown in Fig. 10 is fitted with six removable porcelain plates which prevent any oxide falling from the metallic closet walls upon the substance to be dried, rendering it impure. The upper plate has two holes bored in it through which thermometer and thermo-regulator are placed. This upper plate is fastened to the top of the closet as follows: A glass rod, provided with a broad rim *rr* and an enlargement at *aa*, is pushed up through the opening *P* of the porcelain plate

the filter in the weighing beaker, and allow the latter to remain in a desiccator filled with calcium chloride (Fig. 9), for exactly one hour. Cover the beaker, remove it from the desiccator, allow it to stand in the air near the balance for 20 minutes and then weigh. Repeat this heating and weighing in exactly the same way until two consecutive weighings do not differ by more than 0.0002–3 g.

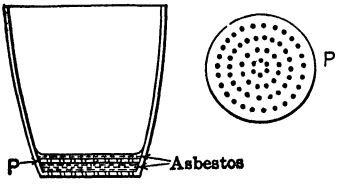
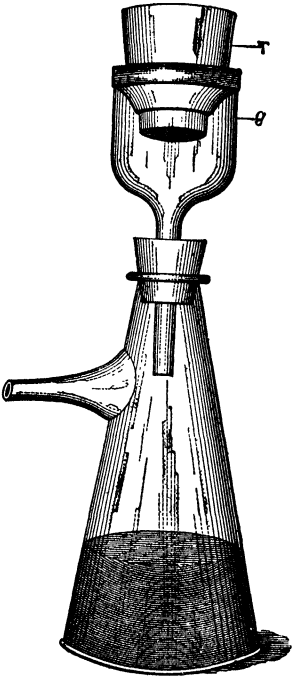


FIG. 11.

Collect the precipitate upon this weighed filter and after drying the filter in the funnel at 100° C. remove the filter and its contents from the funnel and dry in exactly the same way as before.

The same result is much more simply and accurately accomplished by the use of the *Gooch Crucible.*

This is, as shown in Fig. 11, a crucible with a perforated bottom. The crucible is provided with an asbestos filter, weighed after drying at the prescribed temperature, then the precipitate is filtered off into the crucible, which is again dried and weighed. The use of these crucibles permits such accurate and rapid work that it is worth while to describe the method of using them more in detail.


FIG. 12.

Preparation of Asbestos Filters

Cut some long-fibred, soft asbestos, of the non-hydrated variety, into pieces ½ cm. long, and digest with concentrated hydrochloric acid upon the water bath for an hour. A good sample of asbestos will then be separated into very small fibres. Collect

(Fig. 10) and *K* of the upper closet wall, and this is fastened by placing an asbestos ring *A* between *aa* and *K*.

The bottom plate rests upon a heavy iron wire so that it does not come directly in contact with the bottom of the closet. As the plates can be easily taken out, it is possible to clean them without difficulty. The only part of the apparatus that wears out is the bottom, so that it is best to have the closet so that it may be renewed from time to time without taking the apparatus to pieces.

Several forms of electric ovens are also in use. These require little attention and can be regulated to almost any desired temperature.

the mass in a funnel with a platinum cone, or upon a filter-plate, and wash with water. After drying, the asbestos may be ignited, but for most purposes this is not only unnecessary but disadvantageous.

For the preparation of a Gooch filter, shake some of the material with water in a flask, so that a thin suspension is formed. Stretch a piece of thin rubber tubing* (Fig. 12) over a funnel and place the crucible *T* in the opening. The funnel should be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel. Pour enough asbestos into the crucible to produce a layer of 1 to 2 mm. thickness, place a small filter-plate (Fig. 11, *P*) upon this layer and pour a little more of the asbestos suspension into the crucible. Wash the felt with water until no asbestos fibres run through, and, in order to see them, pour the liquid into a small beaker. Usually such a filter is prepared and used with a gentle suction,† but in many cases it filters more rapidly than paper without it.

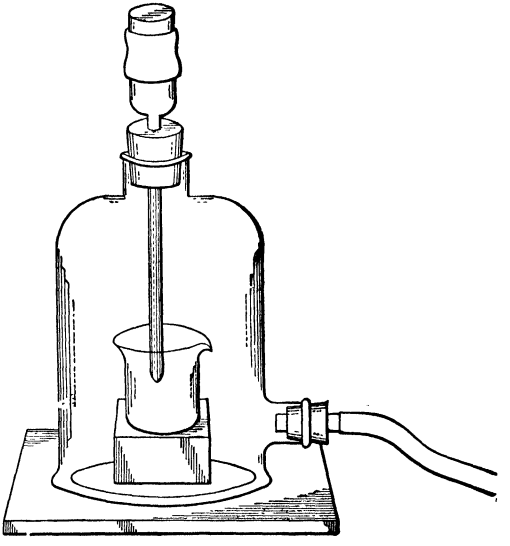


FIG. 13.

When suction is used it is sometimes desirable to filter into a beaker which is placed inside a bell jar arranged so that it can be evacuated (Fig. 13).

Dry the crucible at the proper temperature and afterwards weigh. Repeat the drying and weighing until a constant weight is obtained. It is advisable then to run about 500 ml. more of water through the crucible (in order to be

* In place of rubber tubing, Bailey's Gooch crucible holder or Walter's Gooch crucible holder may be used to advantage.

† Too great a suction should not be employed during the filtration, for in that case the precipitate or even the asbestos itself will be so compressed that the filtration will be prolonged and the washing made more difficult. By having the crucible suspended free by the rubber, the possibility of employing too much suction is avoided, for, as soon as this has reached a certain tension the air is forced between the rubber and the sides of the crucible, so that we have the effect of a safety-valve to a certain extent.

sure that no asbestos fibres run through) and again dry and weigh. If the weight is constant, the crucible is ready for the filtration.

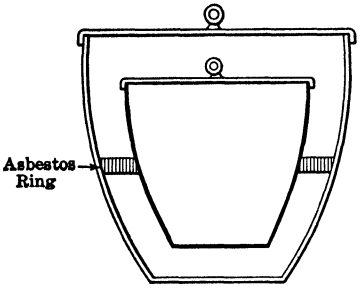


FIG. 14.

The same crucible can be used for a large number of determinations. When the amount of the precipitate in the crucible becomes too large, the upper part can be carefully removed and the crucible again used.

If it is desired to heat a precipitate contained in a Gooch crucible to a high temperature, place it (as shown in Fig. 14) within a larger porcelain crucible and heat at first gently and finally to the desired temperature, using a blast lamp or Méker burner if necessary.

For many purposes it is preferable to use instead of the Gooch crucible a glass tube with an asbestos filter. This is particularly desirable when it is necessary to heat the precipitate in a gas-stream.

The so-called Munroe crucible,* in which the filtering medium consists of a porous felt of spongy platinum, is a modification of the Gooch crucible which permits rapid and accurate work. The felt is prepared by igniting a carefully-dried layer of ammonium chloroplatinate, which has been poured over the bottom of a platinum Gooch crucible in the form of an alcoholic sludge while the crucible is held against several layers of filter paper. The felt can be shaped to the crucible during the ignition and subsequently burnished lightly with a glass rod of suitable form. In case imperfections develop, the felt should be saturated again with chloroplatinic acid, the crucible slowly lowered

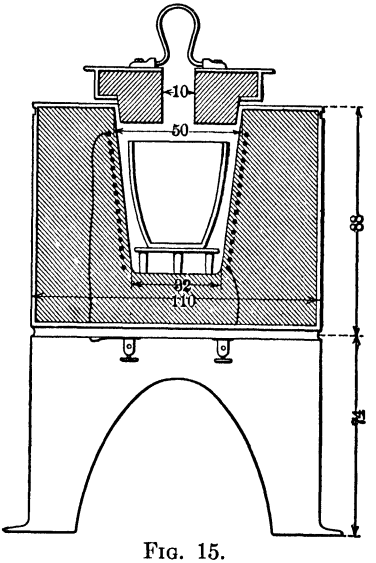


FIG. 15.

* C. E. Munroe, *J. Anal. Chem.*, **2**, 241; *Chem News*, **58**, 101. See also W. O. Snelling, *J. Am. Chem. Soc.*, **31**, 456, and O. D. Swett, *ibid*, **31**, 928. The last reference gives a table of suitable solvents for removing ignited precipitates from the Munroe crucible.

into a moderately concentrated solution of ammonium chloride, washed with alcohol, dried and ignited.

The use of an electric furnace, Fig. 15, is very convenient for igniting the crucible and its contents, especially in the case of those precipitates which are likely to undergo change on coming in contact with a reducing flame.

(*b*) THE PRECIPITATE IS IGNITED WET

Those precipitates which do not suffer any permanent change by the action of the products of combustion of the filter may be ignited wet. Allow the precipitate to drain as much as possible and while still moist place the filter and precipitate in a crucible, with the paper folded so that the precipitate is not exposed and so that the moisture will be expelled through a layer of paper and not directly into the air. Place the crucible in an inclined position upon a triangle (Fig. 16),* with the cover inclined against the upper edge of the crucible and resting on the triangle. Direct the flame of the burner against the cover, which quickly dries the filter, then scorches, carbonizes, and finally burns it. Then move the flame to the back of the crucible and slowly increase the temperature until finally the crucible is subjected to the whole heat of the burner, after which it can be heated over the blast-lamp if necessary.

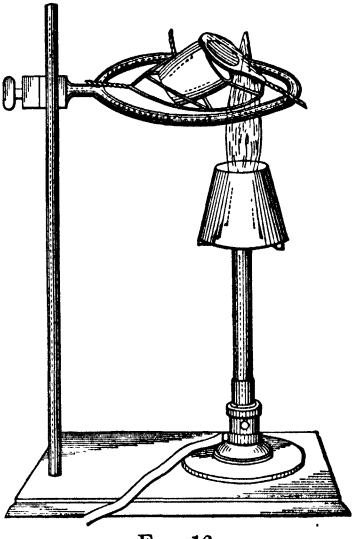


FIG. 16.

Always in igniting precipitates care should be taken to raise the temperature slowly. The object in keeping the flame near the mouth of the crucible at the start is to make sure that the contents of the crucible are dried from the outside. If the flames were placed at the base of the crucible at the start, there would be more danger of loss by spattering.

When the contents of the crucible are dry, the flame should be removed to the base of the crucible and it is better to use a small flame

* In Fig. 16, the inner triangle is platinum wire, the outer triangle is heavy iron wire. Triangles of fused silica or of nickel-chromium alloy are suitable, but platinum alloys with iron, so that a hot crucible should never be placed in contact with iron wire.

near the crucible than to use a large flame with the crucible raised. Care should be taken not to let the paper take fire, except when the bulk of the precipitate has been removed from it and is ignited separately. When the paper burns rapidly in the crucible there is danger of a slight mechanical loss due to the rapid escape of the products of combustion.

Too rapid heating of a paper filter may cause two other errors. Often the temperature is raised rapidly enough to fuse a little salt around the ash of the paper and carbon inside such a fused coating is hard to burn off because it is out of contact with the air. This is true for example in the case of a silica precipitate which is likely to retain a little adsorbed alkali salt. If the precipitate is heated rapidly a little carbon is likely to remain even after long ignition over the blast lamp.

Another serious error is sometimes caused by an undesirable reduction taking place. If the filter paper is smoked off slowly at a low temperature it is possible to heat magnesium ammonium phosphate in a platinum crucible or to heat ferric hydroxide without getting any magnetite formed. If however a precipitate is heated too rapidly there may be a reduction of enough phosphorus to ruin a platinum crucible and often considerable magnetite is formed from ferric hydroxide.

In the case of the magnesium ammonium phosphate it is quite likely that the reduction may be caused by ammonia as well as by carbon. The same principle holds, however, for if the ammonia is expelled slowly at a low temperature there is less danger of a harmful reduction than when the precipitate is decomposed rapidly by strong heating.

When the price of platinum was low, chemists were accustomed to use platinum vessels freely. Thus platinum evaporating dishes, platinum crucibles, platinum filtering cones, platinum spatulas and heavy platinum wire were used in nearly every chemical laboratory. Since platinum has become more expensive, the chemist is learning how to get along without much of it. Glass ware and porcelain are now made of better quality and can be used in chemical work without much contamination. Alloys such as palau or even nichrome are being used more and more. Most ignitions can be made in a porcelain or quartz crucible as well as in platinum. More time is required to cool these crucibles after they have been heated but the chemist learns to do something else during that time and in the end gets more work done by using a number of porcelain crucibles than he used to do with a few platinum ones.

Palau is the trade name of an alloy containing about 80 per cent of gold alloyed with palladium. It melts at 1370° which is about 400° lower than the melting point of platinum. When heated to 1200°

the loss in weight is less than that of platinum alloyed, as it is likely to be with iridium. A crucible made of this material can be used satisfactorily in place of platinum except for fusions with potassium pyrosulfate.

Rhotanium is a trade name for another series of palladium-gold alloys, some of which contain rhodium. These alloys and their advantages have been described by Fahrenwald.*

Alundum† represents a refractory form of aluminium oxide. It does not fuse below 2050°. Crucibles can be obtained which are similar to porcelain crucibles although they are not well glazed. Other alundum crucibles are made more porous so that they can be used for filtering purposes instead of a Gooch or Munroe crucible. Some of them make very rapid filters but it is hard to dry them and errors due to adsorption are much more serious than with a platinum or porcelain Gooch crucible.

The Properties and Care of Platinum

Platinum melts at 1770° but does not soften much until this temperature is nearly reached. It resists the action of all common acids except aqua regia and solutions containing chlorine. Long contact with acid ferric chloride solution is also injurious. It forms alloys with easily reducible metals and platinum crucibles are ruined when such alloys are formed. Long contact with hot carbon injures platinum forming some carbide. For this reason a crucible should always be heated with an oxidizing flame; the flame should never show a luminous tip and the top of the inner cone should be below the bottom of the heated platinum vessel.

Fusion with alkali hydroxides injures platinum but the metal will stand fusion with alkali carbonate. Compounds of phosphorus are likely to be reduced by hot carbon and the crucible is ruined when phosphide of platinum is formed.

Iridium has been used to harden platinum but the alloy is less resistant to the action of reagents than pure platinum and the iridium is volatilized appreciably by heating over the blast lamp. Even good platinum ware is likely to become frosted by strong ignition but the surface crystals which cause the frosty appearance should be fine and evenly distributed. A poor platinum alloy will often become covered with a whitish coating and with brown iron oxide stains. In buying platinum it is advisable to get *hammered* rather than *spun* ware as the latter is

* *J. Ind. Eng. Chem.*, **9**, 590 (1917).

† Saunders. *Trans. Am. Electrochem. Soc.* **19**, 333 (1922).

more likely to have surface cracks. It is well to specify that no marked, uneven discoloration should result from heating, that treatment with acid should show no test for iron after heating two hours, that the loss on heating at 1100° should not exceed 0.2 mg. per hour over a period of four hours and that 5 per cent of rhodium instead of iridium should be present as hardening agent.

Handle platinum carefully and avoid bending. Use clean tongs for handling hot crucibles and do not let the tongs come in contact with melted flux.

To clean, use chromic acid for removing organic matter, hydrochloric or nitric acid singly (never mixed) to remove insoluble carbonates or metal oxides. Fuse with sodium carbonate or borax to remove silica or silicates and with alkali pyrosulfate to remove metals or oxides that resist the action of acids.

Never heat platinum with the inner cone of the Bunsen flame touching the vessel; this will cause brittleness.

Do not heat compounds of lead, tin, bismuth, arsenic, antimony, or zinc in platinum. Do not ignite sulfides in platinum and avoid heating phosphorus compounds except with great care.

Do not attempt to remove fusions with knives, files, glass rods or other hard tools. Use rubber tipped rods or solvents.

Polish dull surfaces with sea sand or very fine carborundum powder.

Triangles

For use with platinum crucibles, platinum triangles are desirable. Figs. 17 and 18 represent two forms of these. The first is made of heavy platinum wire and is intended to rest on the ring of a lampstand.

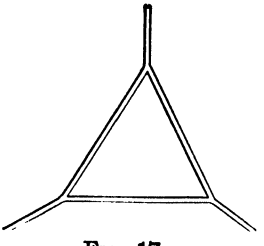


FIG. 17

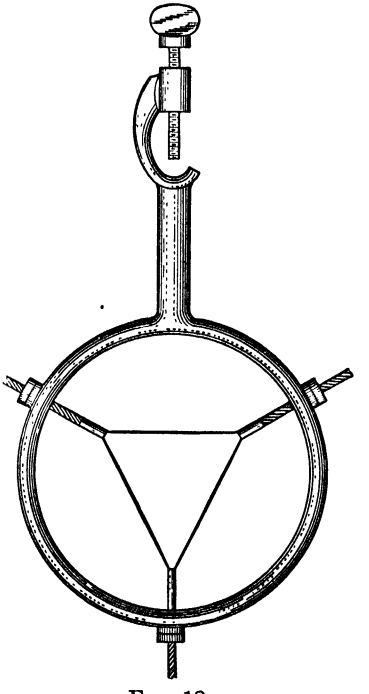


FIG. 18.

The second form is made so that it can be screwed on to the ring and thus kept in place.

Fig. 19 shows a clay triangle which can be used even for platinum crucibles and Fig. 20 represents a less expensive nichrome triangle.

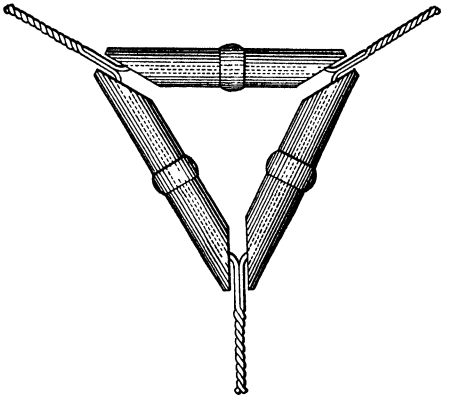


FIG. 19.

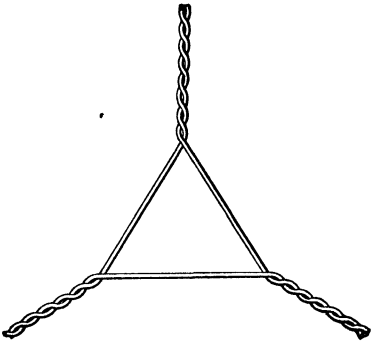


FIG. 20.

This may be used with platinum if it is kept clean and no flux is spilled upon it but there is some danger of staining the crucible with this kind of a triangle.

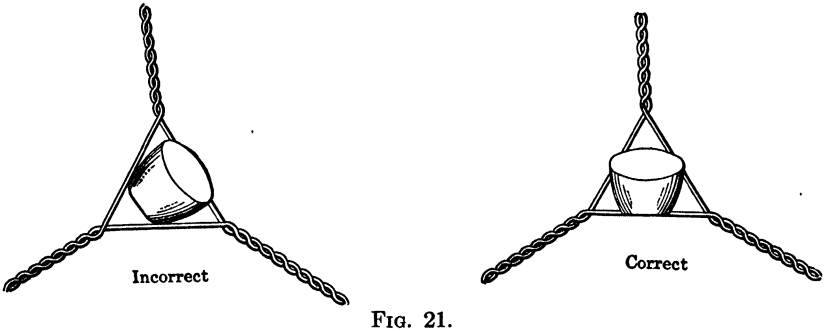


FIG. 21.

Triangles of fused quartz are also useful. Fig. 21 shows the correct and incorrect ways of placing a crucible on a triangle in an inclined position.

Burners

Besides the burners described in Volume I of this book, two other types deserve mention. The Tirrill burner is based upon the principle of the Bunsen burner but is an improvement in design. At the

base of the burner the flow of gas is regulated by a screw which operates a needle valve and the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more air to enter through the holes at the base.

The Méker burner provides for a similar adjustment of gas and of air but the shape of the burner tube is different. The tube is narrowest near the base and widens out at the top. As a result the delivery of the gas under pressure into the inverted cone causes a greater reduction of pressure within the tube and a greater inflow of air than is the case with other burners which do not operate with a blast. There is a more perfect mixing of the gas with air and a greater combustion of gas within a given space. At the top of the burner tube is fitted a nickel grid and the gas burns in a great many small flames with the tip of each inner reducing cone about one millimeter above the top of the burner. The many small flames unite to give a very hot and highly concentrated flame which is oxidizing in character except below the tips of the tiny flame cones. A crucible placed just a little above these tiny flames is heated nearly as hot as by a blast lamp.

Distilled Water

Various forms of stills are in common use. It is important that the vessel containing the boiling water should be so separated from the condenser that there is little danger of spray entering the latter. The boiler may be of any material but the condensing worm and supply pipes should be of pure tin.

Distillation does not free water from carbon dioxide, oxygen, nitrogen and ammonia and supply tanks are likely to become slimy after a time. For water analysis and in any work involving the use of water free from nitrogenous compounds, it is necessary to distil the water a second time with permanganate in the boiler. The first and last runnings are then rejected.

Transfer of Liquids

In pouring out a reagent from a bottle never place the stopper on the work bench. Pick up the stopper, hold it between the first two fingers of the right hand with the palm up, grasp the bottle with the same hand and the palm over the label and pour from the bottle with the label up so that there is no danger of any liquid falling upon the label. With printed labels it is advisable to cover them with thin coatings of gum sandarac dissolved in alcohol. In pouring liquids it is always advisable to pour against a glass rod so that none of the liquid is spilt. In

removing the rod do not move it upwards and scrape off a little liquid thereby. It is well to give the rod a slight downward motion on taking it away.

Reagents and Glassware

One of the greatest sources of trouble for the analytical chemist is the presence of impurities in reagents and the action of solutions upon glassware. It is desirable to use the purest possible reagents but the chemist should always take care to test them. Even if the reagents are perfectly pure, they often become contaminated by solutions remaining in glass bottles. In every analysis, therefore, errors are likely to arise from impurities that were in the reagents or from glassware that has been somewhat dissolved. Solutions of strong acids and bases when kept for some time in bottles will always give a slight test for silica if sufficient reagent is taken for the test.

Today it is possible to buy glassware which is much less acted upon by reagents than that formerly used. Such glass is essentially a borosilicate of sodium, zinc and aluminium.*

It is well sometimes to run through blank analyses to see if any weighable precipitates are obtained when the reagents alone are used in an analysis. Such analyses are often misleading because the precipitates are so small that they may be overlooked or they may be so fine that they need some other precipitate to adsorb them and prevent their passage through the filter.

The Evaporation of Liquids

Liquids are usually evaporated upon the water-bath. In order to prevent anything from falling into the evaporating-dish it is well to cover it with an evaporation-funnel, as shown in Fig. 22.

The funnel is suspended above the dish by means of a porcelain fork fastened to the iron rod (covered with hard rubber) which is attached to the water-bath.

In case the laboratory is provided with

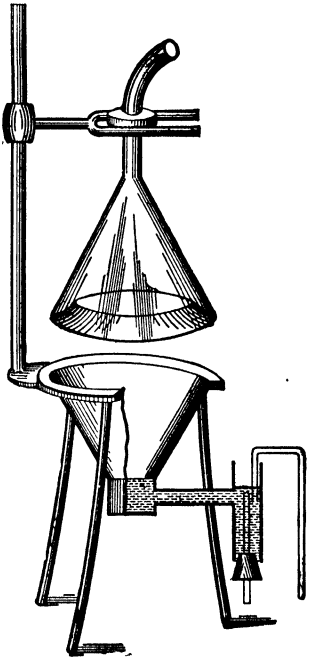


Fig. 22.

* In *Bur. Stand. Tech. Paper*, 107 (1908), the result of some tests on glassware are given. Since then several other good glasses have been developed.

a glass-covered hood with a good draft the use of the funnel is unnecessary.

If, however, the hood is directly connected with the chimney it often happens that on a windy day a considerable amount of dust falls into the hood.

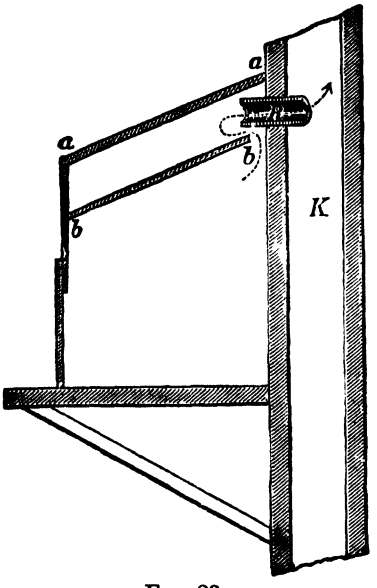


Fig. 23.

To prevent this, the hood in the Zurich laboratory is provided with a glass roof, *aa*, Fig. 23, and about 15 cm. below there is a second glass plate *bb* which does not quite touch the inner wall of the hood but is about 3 cm. away from it throughout its whole length. Between the two plates there projects a clay pipe *R*, about 15 cm. in diameter and about 5 cm. above the inner edge of the lower glass plate, leading directly into the chimney *K*, in which there is a small gas-flame (not shown in the illustration). Any dust, sand, etc., from the chimney falls upon the plate *bb*; none can get into the hood.

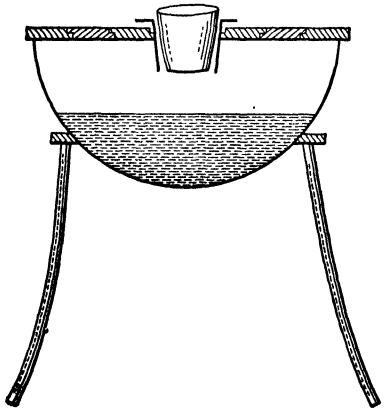


Fig. 24*a*.

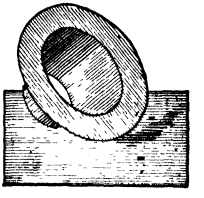


Fig. 24*b*.

In the evaporation of liquids on the water-bath in weighed platinum crucibles or dishes, the platinum should not come in contact with copper or glass rings. As a rule, porcelain rings should be used. In case the

crucible is smaller than the ring, use is made of a truncated brass cone turned back at the base (Fig. 24), and lined with thin platinum foil. This is suspended in the ring and the crucible placed within the cone (Fig. 24*a*).

During evaporation many substances have the property of " creeping " over the edge of the crucible or dish, often causing a slight loss of the substance; furthermore there is often " bumping," so that in some

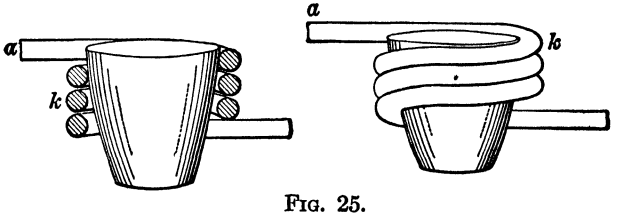


FIG. 25.

cases the entire contents are thrown out of the crucible (cf. the determination of boric acid according to the method of Gooch). Both of these phenomena can be readily prevented as follows:

Place the crucible, at the most not more than two-thirds filled with liquid, in a cylindrical tin or brass spiral *kk* (Fig. 25). The first two windings of the metallic spiral come into close contact with the sides of the crucible *above the liquid, while the remaining windings should not touch the crucible.* When steam is passed through the spiral the upper part of the crucible is warmed first, so that there is no spattering, and furthermore by keeping the upper edge hot during the whole of the evaporation all " creeping " of the substance is avoided. In this way it is possible to evaporate off alcohol rapidly without boiling the liquid.

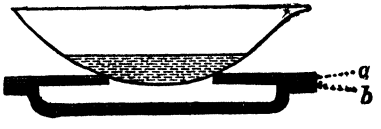


FIG. 26.
a = asbestos ring.
b = asbestos plate.

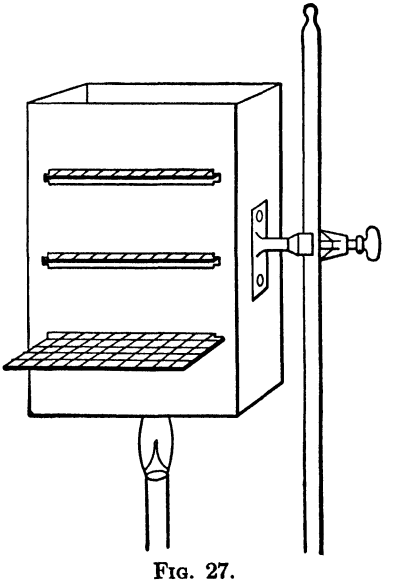


FIG. 27.

In case it is desired to evaporate high-boiling liquids, such as sulfuric acid, amyl alcohol, etc., either heat the crucible cautiously over the free flame (continually moving it back and forth) or else place the crucible in an air-bath, which can be prepared in some such way as is represented by Fig. 26.

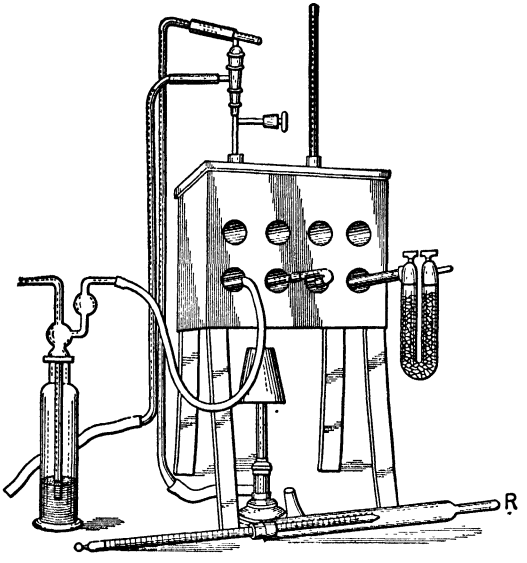


FIG. 28.

The Finkener tower, Fig. 27, is very useful for evaporating solutions to dryness and for heating the residue moderately as in silica determinations. It consists of a rectangular, sheet metal box with several openings in which are placed pieces of wire gauze. The casserole is placed on top of the tower and the heat is increased or diminished by removing or inserting layers of the wire gauze.

Drying Substances in Currents of Gases

Substances may be dried at a high temperature in a current of air or of carbon dioxide in a number of different ways. An oil-bath provided with a number of copper tubes (Fig. 28) may be used. Place the substance in a small

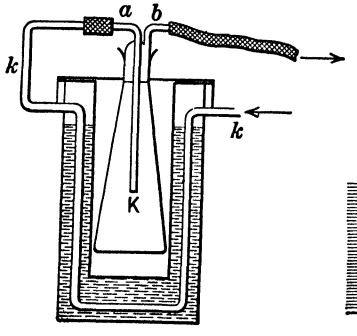


FIG. 29*a*.

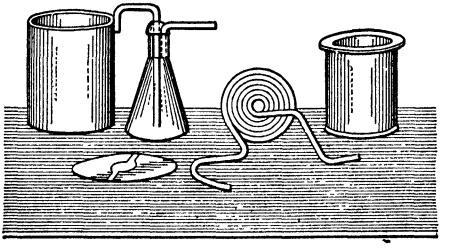


FIG. 29*b*.

"boat," put this in a glass tube and insert the latter into one of the copper tubes. Pass the gas through one or more of the empty

tubes (so as to warm it), and then through the tube containing the substance.

In case it is desired to evaporate off a liquid in a flask and to ignite the residue at a given temperature it is well to proceed as follows:

Place the solution in an open Erlenmeyer flask *K*, Fig. 29*a*, and evaporate as far as possible over the free flame. Then place the flask in a metal beaker suspended in a oil-bath (Fig. 29*a*), and aspirate dry air through the spiral copper tube *kk* as shown in the illustration. Fig. 29*b* shows the separate parts of the apparatus.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS

It is very difficult to give general rules for the preparation of substances for analysis, for it is necessary to proceed differently in different cases. If it is desired to determine the atomic composition of a substance, it is necessary to choose pure material for the analysis. Although this sounds so simple it is often one of the most difficult conditions to fulfill. Many substances are hygroscopic and absorb moisture from the air, which can be removed by heating the substance or by simply allowing it to stand in a desiccator over calcium chloride, provided the substance itself undergoes no change by this treatment. Many substances containing water of crystallization cannot even be dried in a desiccator, but must be analyzed air-dry. In all cases it is necessary to determine whether the substance to be analyzed possesses a constant weight.

Many commercial salts are prepared pure and can be analyzed directly; in most cases, however, they have stood for some time in the air and have been handled somewhat, so that they are not so pure as when freshly prepared. Consequently, in case it is desired to test the accuracy of an analytical process, the purity of a commercial sample should never be taken for granted. If the substance is soluble in water it can be purified by recrystallization.

Dissolve ten or fifteen grams of the commercial salt in the least possible amount of hot water (it is best to use not quite enough water to dissolve the substance *completely*) and pour the hot solution through a plaited filter contained in a funnel with the stem broken off (Fig. 30). This serves to remove all dust or other insoluble impurity. Catch the filtrate in an evaporating-dish and cool it rapidly, while stirring constantly, by placing the dish in a larger one containing cold water.

By means of the rapid cooling and constant stirring, the salt is ob-

tained in the form of a crystalline powder.* Filter off the crystals and drain them by suction. A perforated porcelain plate covered with filter paper may be used in the funnel, or an ordinary filter may be used placed in a perforated filter cone or in a small hardened paper, to prevent tearing the paper by suction. Test the purity of the substance qualitatively by means of some suitable reaction. In case it is still not quite pure, repeat the same process of recrystallization until the presence of no impurity can be detected.

Place the pure, moist crystals upon a layer of several thicknesses of clean filter-paper, cover with another sheet of filter-paper and allow the crystals to stand for twelve hours at the ordinary temperature. Then weigh out one or two grams of the substance upon a tared watch-glass, place it upon a dry glass plate, cover loosely with another watch-glass and allow it to stand for several hours more. If the substance

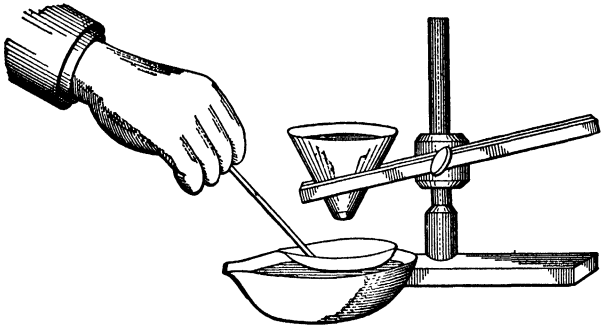


FIG. 30.

shows no change in weight it is ready for analysis. Otherwise it must be dried in the air until it no longer shows a change in weight. It is not permissible to dry the substance in a desiccator except in those cases in which the substance will not lose water of crystallization. Deliquescent substances of course should not be allowed to remain exposed to the air for very long. Such substances must be quickly dried upon a porous plate and transferred as soon as possible to a flask provided with a closely fitting, ground-glass stopper.

For *technical analyses*, the purpose being to determine the cost or selling price of an article or to control its manufacture, the substance must be analyzed *as it is*. In such a case the sample should represent as far as possible the average composition of the product.

* Large crystals would be obtained by allowing the solution to cool slowly, but they are undesirable, as they usually contain more enclosed mother-liquor than do the smaller crystals. Most water-soluble salts are much more soluble in hot water than in cold water.

The selection and preparation of representative samples for analysis is a matter of so great importance that it has been discussed in over 1100 papers* written between 1892 and 1922. The quantity of material from which the sample for analysis should be taken varies with the nature of the material. If it is homogeneous it is merely a matter of grinding a portion until it is of suitable fineness.

The Influence of Fine Grinding on Composition

The rate at which a substance dissolves increases as the amount of surface exposed to the solvent is increased and for this reason solid substances always dissolve more quickly when reduced to a fine powder. Moreover, when a material undergoes chemical attack, an insoluble substance is often formed and, during the process of solution, the insoluble substance may form a protective coating over particles of material that have not been acted upon. This danger is diminished if the material is in the form of a fine powder. For these reasons the chemist usually prefers to grind a solid substance to an impalpable condition before attempting to analyze it.

This practice, while desirable in most cases and absolutely necessary in others, is accompanied by certain disadvantages. If the material is hard there is always some contamination from the material of which the grinding apparatus is constructed. Thus when the sample is ground in a steel mortar or in a steel ball-mill, it will be contaminated with a little iron and if ground in an agate mortar with a little silica.† Again, if the sample readily undergoes slight decomposition, such a chemical change is likely to take place during the operation of grinding. In this way the determination of moisture, of ferrous iron, and of sulfur may be influenced very appreciably.

A number of investigators have pointed out the effect of grinding upon the moisture content of a sample. If the sample is practically dry, it is likely to absorb considerable moisture when dried in the air. Thus Hillebrand‡ found that a piece of unglazed porcelain contained no moisture originally, but showed 0.62 per cent of water when ground. If the substance is very hygroscopic, this danger becomes greater. On the other hand, grinding often causes loss of moisture. This is notably true in the case of substances containing water of crystallization or

* Cf. W. J. Sharwood and M. M. Bernewitz, *Bibliography of the Literature on Sampling*, Bureau of Mines Publication. Serial No. 2336.

† Hempel (*Z. Angew. Chem.* **1901**, 843) found that an agate mortar and pestle lost 0.052 g. in grinding 10 g. of glass to a fine powder.

E. T. Allen found a loss of 0.145 g. of agate in grinding 200 g. of quartz.

‡ *The Analysis of Silicate and Carbonate Rocks*, Bull. 700, U. S. Geol. Survey.

superficial moisture. Thus grinding can easily reduce the moisture content of a sample of gypsum from twenty to five per cent, and a sample of coal may show several per cent of moisture when large lumps of it are tested and very little moisture after it is reduced to a fine powder.

The heat produced by grinding may not only serve to expel moisture from the sample, but it may cause chemical change. Thus Mauzelius* has shown, and the experiment has been repeated by Hillebrand,† that the ferrous iron content of a rock becomes smaller on account of grinding it to a fine powder. It has also been found that some sulfur may be lost by long grinding of a sample of pyrite.

The effect of grinding, therefore, accounts for many cases of divergent results obtained in the hands of different chemists who have analyzed the same original material.

Sampling a Shipment. To prepare a representative sample from a large mass of material, such as a shipment of ore or of coal, special precautions are necessary. It is never safe to take samples from the top of a large pile of material but portions should be selected from all parts. The easiest way to do this is in the loading or unloading of the shipment, taking out portions at regular intervals either by a shovel, trowel or mechanical sampler. In sampling coal, the U. S. Gov't.‡ takes, as a rule, 1000 pounds from each shipment of 500 tons or less. The size to which ore must be crushed for sampling depends on (1)§ the weight of material given to the chemist from the shipment, (2) the relative ratio of the richest mineral value and the average value of the ore, (3) the density of the richest material and (4) the number of particles of the richest mineral. The more "spotty" the ore the larger must be the original weight selected. The results of Brunton's work show that it is necessary to crush the sample before "cutting it down" and advisable after each "cutting" to crush it still finer.

Crushing the Sample. After enough material has been taken from a shipment to guarantee a representative sample, the next operation is to crush it so that the largest particle is not larger than a certain definite size. Thus with a sample of coal weighing 1000 pounds, it is all broken up so that the diameter of the largest piece is not over one inch. This may be done by a mechanical grinder|| or by hand with an

* *Sveriges Geol. Undersökning*, Årsbok 1 (1907).

† *J. Am. Chem. Soc.*, **30**, 1120 (1908).

‡ G. S. Pope, *Methods of Sampling Delivered Coal*, Bur. of Mines, Bull. 116.

§ D. W. Brunton, *The Theory and Practice of Ore Sampling, Trans. Am. Inst. Min. Eng.*, **25**, 827 (1895).

|| W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey, Bull. 700.

iron tamping bar or sledge. In mineral analysis, where smaller samples are usually taken, samples are often broken up by pounding on a hardened steel surface with a hardened hammer of the best tool steel.*

Mixing and Coning. To mix the sample, it is customary to shovel it into a conical pile. Each shovelful should fall upon the apex of the cone and the material should be thrown so that the cone is not pushed away from its original position and the shoveler should walk around the cone as he shovels. This serves to bring the finer material near the center of the pile and the coarser pieces run down the sides. Of the first cone usually one half is rejected. This can be done by shoveling away the cone from the bottom, while walking around the cone, and rejecting every other shovelful. Or, the cone may be flattened and quartered.

Quartering. The top of the cone is flattened out and divided into quarters. Opposite quarters are taken for the next crushing.

The mixing, coning, quartering and crushing should continue until finally a sample of 100–200 g. is obtained. When the samples are small enough, the mixing is best done on a sheet of glazed paper, rubber or oil cloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. In weighing out an ore it is always well to mix it by rolling back and forth unless it is extremely fine, when it is not likely to segregate on standing. Segregation takes place when particles are of different sizes and densities.

If in the sifting of an ore, metallic particles are left on the screen, it is necessary to analyze these particles separately and make a proper allowance in the final calculation. It is necessary then to know the weight of the entire sample and the weight of metal that does not pass through the screen.

In sifting samples, wire screens are commonly used but inasmuch as a little metal is introduced into the sample, it is better to use silk bolting cloth.

The **cutting, or dividing,** at the several stages of the sampling process is best done by mechanical means. Some machines, of the riffle type, constantly deflect a part of the material that passes through them.

* Mechanical grinders should be made of specially hardened steel and should be built so that they can be kept clean easily. For laboratory grinding, a modified McKenna ore grinder has been recommended by Hillebrand. (*Bull.* 700, U. S. Geol. Survey.)

Others, which in some cases are more desirable, change the direction of the fall of the ore at regular intervals. Buckets are constructed so that as ore is poured into them, half of it is retained and half rejected. Split shovels, consisting of a series of parallel troughs with equally wide spaces between them, are made of various sizes. The ore retained by the shovel, or that which passes through, may be taken for the sample. In using such shovels, of which the smallest size is useful for weighing out samples that are not perfectly homogeneous, allow a thin stream of ore to fall back and forth over the riffle. The distance between riffles should be at least three times the diameter of the largest particles of ore.

In sampling metals and alloys it is necessary to remember that they are seldom homogeneous. During solidification the part that solidifies last is usually different from that which first separates on cooling. As a rule, the outside of an ingot solidifies first and some of the impurities are likely to be concentrated or segregated in the interior. In the case of a steel rail, microscopic examination often shows that the head, the foot and the web are not exactly the same. The sample used for analysis should consist of borings taken from all over the rail, or, better still, it should be obtained by planing over the entire cross section. A macroscopic* survey of the entire cross-section after it has been treated with a suitable etching agent, such as an 8 per cent solution of cupric ammonium chloride or a 6 per cent solution of iodine in alcohol for steel specimens, will often show where segregation has taken place. When metals break under strain, the crack usually starts at some place where the material is defective, usually due to a little enclosed slag. The analysis of the entire material will often fail to indicate a defective material and the cause of the fracture can only be shown as a result of metallographic examination of polished specimens under the microscope and the chemical analysis of portions where segregation has been revealed by the microscope.†

* Magnifications of less than ten diameters are often classed as macroscopic, although strictly speaking, they are not included in an exact definition of the term.

† Cf. Hall and Williams, *Chemical and Metallographic Examination of Iron, Steel and Brass.*

PART I

GRAVIMETRIC ANALYSIS

A. GRAVIMETRIC DETERMINATION OF THE METALS (CATIONS)

METALS OF GROUP V

POTASSIUM, SODIUM, LITHIUM, AMMONIUM, AND MAGNESIUM

POTASSIUM, K. At. Wt. 39.10

Forms:* KCl, K_2SO_4, K_2PtCl_6, and $KClO_4$

1. The Determination as Chloride

This compound is chosen for the determination of potassium when it is already present as such, or in case the salt to be analyzed may be changed to chloride by evaporation with hydrochloric acid. If the potassium is present as sulfate it may be transformed to chloride by precipitation *of the sulfate* with barium chloride (see Silicate Analysis); if it is present as the phosphate, the phosphoric acid may be precipitated as basic ferric phosphate (Vol. I); or, finally, if it is present as chromate the $CrO_4^=$ ions may be reduced to chromic ions by evaporation with hydrochloric acid and alcohol and then precipitated by ammonia and filtered off.

In almost all of these cases it is a question of separating the potassium chloride from the aqueous solution and in most cases of separating it from ammonium chloride as well.

Procedure. — Evaporate the solution to dryness on the water-bath in a platinum or thin *porcelain* dish stirring frequently as soon as the salt begins to separate out, in order to hasten the evaporation of the enclosed water. In spite of long-continued heating and continual stirring, however, it is not possible to expel all of the water enclosed within the crystals; to accomplish this, heat the covered dish in a hot closet or drying oven for at least an hour at 130°–150°. Then remove the watch glass and heat carefully over a small flame until no more vapors are evolved, taking care not to heat too strongly because of the danger of volatilizing some potassium chloride. Usually there is a little carbon

* Under this heading will be given in every case the symbols of the compounds suitable for the determination of the element in question.

in the residue, due perhaps to a little pyridine in ammonia used in the analysis. Treat the residue with a little water and filter through a small filter into a weighed crucible or dish, preferably of platinum. Add a few drops of hydrochloric acid, carefully evaporate to dryness and remove the last traces of moisture by drying and heating as before. Cool, weigh and repeat the heating until a constant weight is obtained.

In all the methods of gravimetric analysis described in this book it will be understood that when a crucible is " heated " and " weighed " the operations should be repeated to see if the weight is constant. As a general rule, a weight may be regarded as constant when it agrees within 0.3 mg. with the previous weight or when the difference is less than one-thousandth part of the entire weight.

The above method of analysis is capable of yielding exact results and is suitable to give beginners in quantitative analysis.

Example. — Determination of Potassium in Potassium Bichromate.

Dissolve 0.5–0.6 g. of the powdered salt (weighed to the nearest tenth of a milligram) in a 300 ml. porcelain casserole. Add 10 ml. of concentrated hydrochloric acid and 5 ml. of alcohol. Cover the dish with a watch glass and heat on the water bath until all the bichromate is changed to chromic salt as shown by the emerald green color of the solution. Remove the watch glass and rinse off the under surface into the casserole to remove any salt that may have spattered upon it during the evolution of chlorine. Evaporate to dryness, add 2 ml. of concentrated hydrochloric acid and 200 ml. of water. Heat just to the boiling point and to the hot solution add enough dilute ammonia to precipitate all the chromium but avoid an excess. Filter and wash the chromic hydroxide precipitate until a little of the filtrate gives no test for chloride with silver nitrate solution.

Evaporate the filtrate and weigh the residual potassium chloride taking all the precautions described on the previous page. If a little chromic hydroxide is deposited during the evaporation, it must be filtered off and the precipitate washed with hot water until free from chloride.

From the weight of potassium chloride, compute (*a*) the per cent of *K*, (*b*) the per cent of K_2O and (*c*) the percentage purity of the sample. The computation is explained in the Appendix. It is advisable to carry out all analyses in duplicate. The results should agree within two parts in one thousand* and should not be far from the truth, although a little potassium is adsorbed by the chromic hydroxide precipitate.

* Considerable misunderstanding often arises with regard to the meaning of a " check within two parts in one thousand or within two-tenths of one per cent." The agreement should always refer to the value itself and not to the percentage of

2. Determination of Potassium as Potassium Sulfate

This method is chosen when the potassium is already present in solution as the sulfate, or when it is in such a form that it can be readily changed to sulfate by evaporation with sulfuric acid; it is most frequently used for determining the amount of potassium in combination with organic acids.

Since the sulfate of potassium is much less volatile than the chloride, it is advisable to choose this method in case no other metal is present. On the other hand, when it is necessary to separate potassium from sodium, it is preferable to have the potassium in the form of the chloride.

Example. — Determination of Potassium in Potassium Bichromate. Weigh 0.5 g. of the powdered salt into a 300-ml. porcelain evaporating-dish, and treat with 20 ml. of a freshly-prepared, saturated, aqueous solution of sulfur dioxide* and 5 ml. of 2-normal sulfuric acid. Cover the dish with a watch glass and heat on the water-bath until there is no more evolution of gas. Then remove the cover glass, rinse it off, and evaporate the solution almost to dryness. Add 200 ml. of water and precipitate the chromium as in Method 1. Filter off the precipitate and wash it with hot water until a little of the filtrate gives no test for sulfate with barium chloride. Evaporate the filtrate containing potassium and ammonium salts to dryness, heat in the hot closet and expel the ammonium salts as described in Method 1. In this case, however, there is less danger of vaporizing the potassium salt. After weighing the cold dish or crucible, add a small piece of solid ammonium carbonate, about the size of a pea, to decompose any $K_2S_2O_7$ and heat again until a constant weight is obtained.

From the weight of K_2SO_4, compute the percentages of K, K_2O and of $K_2Cr_2O_7$ in the original salt.† There is a slight adsorption of potassium by the chromic hydroxide precipitate.

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the weight of sample. Thus if two analyses of $K_2Cr_2O_7$ give values 31.95 and 32.01 per cent K_2O, the check is two parts in one thousand or 0.2 per cent of the value found.

* The solution of sulphur dioxide may be prepared as follows: Take 150 ml. of saturated $NaHSO_3$ solution in a 300-ml. Erlenmeyer flask and slowly add concentrated sulfuric acid from a drop-funnel. Pass the evolved SO_2 gas into a small wash-bottle containing water and then into another wash-bottle containing distilled water, which is kept cool by placing it in a larger vessel filled with cold water. When the evolution of the SO_2 begins to slacken, it can be accelerated by gentle warming.

† In quantitative analysis it is customary to report results in the form of the most representative oxide. This method of representation is based upon the Dualistic theory. There are several reasons why the analytical chemist continues to express his results in these terms. (1) It furnishes the most convenient way of properly apportioning the element oxygen which is practically never determined directly when

To determine the quantity of potassium in an organic salt, treat the weighed salt in a large, weighed crucible with a little concentrated sulfuric acid. Heat exactly as in the case of igniting a moist precipitate (see p. 39) placing the crucible in an inclined position and directing the flame against the cover of the crucible. Thick, white fumes of sulfuric acid are soon evolved; as soon as these begin to diminish in quantity gradually move the flame toward the base of the crucible, and finally heat to dull redness until no more vapors are given off. The mass remaining in the crucible now consists of K_2SO_4 and $K_2S_2O_7$. The latter compound can be converted by stronger ignition into K_2SO_4 with loss of SO_3, but as this procedure involves a slight loss of potassium it is preferable to add a little solid ammonium carbonate, by means of which the excess of sulfuric acid is converted into ammonium sulfate, which is readily volatile and can be decomposed at a much lower temperature.

2. Determination of Potassium as K_2PtCl_6 and as $KClO_4$

These determinations are only employed when it is necessary to effect a separation of potassium from sodium. They will be discussed under the Separation of Potassium from Sodium.

SODIUM, Na. At. Wt. 23.00

Sodium, like potassium, is determined in the form of its chloride and of its sulfate, and the same precautions which were discussed under

present in a compound. Thus in the analysis of bichromate it is more satisfactory to report the per cent K_2O and per cent CrO_3 than it is to subtract the K and Cr contents from 100 and call the difference oxygen, or to report the Cr as Cr_2O_7 and thus arbitrarily make the accuracy of the chromium determination the only factor governing the oxygen content. (2) When reported in this way, the analysis of salts of all oxygen acids should add up to 100 per cent and this furnishes a fairly satisfactory check on all the determinations made. If a salt of a binary acid is present, *e.g.*, a sulfide or halide, the results should add up to more than 100 per cent if the metal of the sulfide or halide is reported as oxide. In such cases, it is customary to deduct a weight of oxygen equivalent to the weight of sulfide or halide. Thus mineral analyses made in the laboratories of the U. S. Geological Survey often close with the statement " Less oxygen for fluoride, sulfide, etc." (3) The statement that a substance contains K_2O and CrO_3 does not mean that these constituents are present in an uncombined condition but it shows that the chromium is present as chromate or dichromate and not as chromic salt. The statement that a substance contains FeO and SO_3 means that the substance contains iron as a ferrous salt and sulfur as a sulfate. (4) The continuance of this system of reporting analyses makes it easy to compare results with those made fifty years ago even although the Dualistic theory has been abandoned.

potassium hold in the case of sodium. It may be mentioned, however, that NaCl and Na_2SO_4 are more difficultly fusible and less volatile than the corresponding potassium compounds.

Separation of Potassium from Sodium

The solution should contain salts of no other metals with the exception of ammonium salts. In order to separate the sodium and potassium they should both be present as chlorides, the combined weight of which being first ascertained. The mixture is then dissolved and the potassium precipitated out either as chloroplatinate or as perchlorate. From the weight of the precipitate, the corresponding amount of potassium chloride can be calculated, which value is deducted from the weight of the combined chlorides; this gives the weight of sodium chloride originally present. The sodium, therefore, is determined by difference. It is important that no ammonium salt be present as otherwise insoluble ammonium salts will precipitate with the potassium.

A. Separation of the Potassium as K_2PtCl_6

Principle. — Potassium chloroplatinate is practically insoluble in absolute alcohol, whereas the corresponding sodium salt is soluble. On the other hand, sodium chloride is insoluble in absolute alcohol, so that it is necessary to convert both the potassium and the sodium into chloroplatinates, as otherwise the potassium chloroplatinate obtained will be contaminated with sodium chloride and too high a value will be found for the amount of potassium present.

Procedure. — Dissolve the weighed chlorides (0.2 g. or less) with a little water in a small porcelain dish. Add enough chloroplatinic acid to combine with all the alkali present, assuming, to be on the safe side, that the sample is all sodium chloride. Of the usual reagent, containing 10 g. of dissolved platinum in 100 ml., 1.7 ml. should be used for each 0.1 g. of chloride. Enough water should be present to dissolve any precipitate of K_2PtCl_6 when the contents of the dish are heated on the water bath.

Evaporate the solution nearly to dryness on a water bath.* Stop evaporating when the contents of the dish solidify on cooling. Drench the residue with a little 80 per cent ethyl-alcohol and break up the mass of crystals into a fine powder by means of a stirring-rod or a platinum spatula. Decant the liquid through a filter moistened with alcohol, and repeat the treatment of the residue with alcohol until the filtrate runs through completely colorless and the salt remaining in the dish

* A convenient bath is obtained by placing the dish on a beaker half filled with water, which is kept just below the boiling point by a flame beneath the beaker.

assumes a pure, gold-yellow color without any orange-colored particles being present ($Na_2PtCl_6 + 6\,H_2O$).

Try not to get much if any of the precipitate upon the filter. Dry the dish and filter a few minutes to remove the alcohol, transfer the precipitate to a weighed crucible or very small dish and wash out the original dish with several small portions of hot water poured through the above-mentioned filter. Evaporate to dryness on the steam bath and heat for 30 minutes in an air bath at 135°, with the crucible or dish covered to avoid loss by decrepitation. Cool and weigh. From the weight of the K_2PtCl_6, compute the corresponding weight of KCl.

Remark. — Treadwell recommends the use of absolute alcohol because it has been claimed that anhydrous sodium chloroplatinate is more soluble in absolute alcohol.* This claim has been disputed. † Treadwell also recommends the use of the empirical factor 0.3056 for computing the KCl content, instead of the theoretical value

$$\frac{2\,KCl}{K_2PtCl_6} = 0.3068$$

but according to the directions given here with drying at 135° instead of 160° and with the 80 per cent alcohol, the true factor seems more suitable. Results about 0.3 per cent too high have been explained on the assumption that the precipitate contains besides K_2PtCl_6 a little $KHPtCl_6OH$.

Modification of Chloroplatinate Method

Instead of weighing the K_2PtCl_6, the dry precipitate may be heated in a stream of hydrogen, when HCl and H_2O will be given off and a mixture of platinum and potassium chloride will remain behind.

1. If the evolved hydrochloric acid is determined and from this the weight of potassium chloride is computed the result will be too low because less hydrochloric acid is evolved than corresponds to the equation:

$$K_2PtCl_6 + 2\,H_2 = 4\,HCl + Pt + 2\,KCl$$

2. If the mixture of platinum and potassium chloride remaining in the dish is weighed and from this the amount of potassium chloride is calculated, too low a result will be obtained.

3. Finally, if the mixture of platinum and potassium chloride is treated with water and, on the one hand, the weight of the platinum remaining undissolved and, on the other hand, the weight of the potassium chloride

* Cf. Fresenius, *Z. anal. Chem.*, **1882**, p. 234. Also F. Dupré, "*Die Bestimmung des Kaliums als Kaliumplatinchlorid*," Inaugural Dissert., Halle, 1893. Also W. Dittmar and McArthur, *J. Soc. Chem. Ind.*, **6**, 799, and *Ber.*, **1888**, Ref. 412.

† Cf. W. F. Hillebrand, *Bull.* 700, *U. S. Geological Survey*, p. 211. The method here described corresponds to that recommended by Hillebrand.

which goes into solution (by evaporating the solution and weighing the residue) is determined, then the amount of potassium chloride calculated from the weight of the platinum again gives a result which is too low; but the amount of potassium chloride found in the aqueous solution corresponds to the amount of potassium chloride originally present.

Inasmuch as the precipitate of potassium chloroplatinate possesses a constant composition it is possible to determine experimentally by working with pure materials the exact ratio which exists between (*a*) the amount of hydrochloric acid evolved, (*b*) the mixture of potassium chloride and of platinum remaining after the ignition, (*c*) the weight of platinum remaining undissolved after treatment of the residue with water and the amount of potassium chloride originally present. According to Dupré, if the amount of platinum determined according to *c* is multiplied by the factor 0.7614 the true amount of potassium chloride will be obtained.

As an example of the modified chloroplatinate method we have the

Neubauer-Finkener Method*

This method does not require that the sodium and potassium shall be present as chlorides. It depends upon the precipitation of potassium chloroplatinate in the presence of ether-alcohol, igniting the precipitate (K_2PtCl_6, Na_2SO_4, etc.) in hydrogen, washing out the soluble salts, and weighing the residual platinum.

Procedure. — Pour the aqueous solution containing about 0.5 g. of substance into a large porcelain casserole and add a few drops of hydrochloric acid. Add a little more than enough chloroplatinic acid to precipitate the potassium and evaporate the solution on the water-bath until its volume does not appear to diminish perceptibly; avoid an unnecessarily long heating. Cool, moisten the mass with about 1 ml. of water and carefully crush the crystals with the end of a flattened stirring-rod. Add at least 30 ml. of alcohol (93–96 per cent by volume) in portions of 10 ml., each time crushing the crystalline mass with the rod. If considerable sodium or potassium is present, the mass toward the end assumes a soft, cheesy consistency but eventually becomes hard and crystalline. Allow the covered casserole to stand for half an hour, rubbing the precipitate from time to time. Then pour the supernatant liquid through a platinum Gooch crucible and wash the precipitate by decantation with alcohol. After each addition of alcohol, crush the crystals with the rod. As soon as the filtrate passes colorless through the filter, transfer the precipitate to the crucible using alcohol to rinse out the dish. Remove the alcohol by washing six times

* *Z. anal. Chem.*, **1900**, 485.

with ether, and evaporate the ether by sucking air rapidly through the crucible. Cover the crucible and through an opening in the cover introduce hydrogen (or illuminating-gas)* and heat the crucible at first very gently, to avoid losses by decrepitation. After five minutes increase the heat so that the bottom of the crucible just shows a faint redness in the center,† and maintain this temperature for at least twenty minutes. Cool, moisten the contents of the crucible with cold water, and suck hot water through the crucible fifteen times to remove all of the soluble salts. To remove calcium sulfate, or other difficultly soluble salt, fill the crucible with 5 per cent nitric acid (not HCl), and allow it to act for about half an hour, from time to time replacing with a little fresh acid. Then wash with hot water, dry and weigh the residual platinum. From the weight of platinum compute the corresponding weights of KCl and of K_2O.‡

If hydrochloric acid were used instead of nitric acid in the above treatment, the platinum would subsequently run through the filter in a colloidal condition.§

Lindo-Gladding Modification

In determining potassium it is usually necessary to remove ammonium salts by volatilization before precipitating with chloroplatinic acid. Since the alkali chlorides are more volatile than the sulfates it is safer to remove ammonium salts by heating the sulfates than to ignite the chlorides. Sodium sulfate, however, is insoluble in alcohol and will contaminate the precipitate of potassium chloroplatinate unless precautions are taken to remove it. In the Lindo-Gladding method, which is much used in the United States, the precipitate of potassium chloroplatinate is washed with alcohol to remove the excess of platinum and then with a solution of ammonium chloride which is saturated with potassium chloroplatinate.

Procedure. — To the slightly acid solution, add 1 ml. of 18 *N* sulfuric acid, evaporate to dryness and ignite till a white residue is obtained and all ammonium salts are decomposed. Dissolve in a little hot water and proceed with the precipitation of potassium chloroplatinate as described on page 59. Wash the precipitate thoroughly with 80 per cent alcohol until all the excess chloroplatinic acid is dissolved and then with

* As in the determination of copper as cuprous sulfide.

† The crucible should be placed upon a piece of platinum foil so that the flame does not come directly in contact with the perforation in the bottom of the Gooch crucible.

‡ According to Neubauer the coefficient 0.7612 must be used in the presence of sulfates, and Dupré found that the factor 0.7614 holds in the case of chlorides. Similarly, Dittmar and McArthur (*Z. anal. Chem.*, **28**, 767) state that the factor 0.7611 applies in the presence of much magnesium.

§ Kling and Engels, *Z. anal. Chem.*, **45**, 315 (1906).

five 10 ml. portions of 20 per cent ammonium chloride which is saturated with potassium chloroplatinate.* Again wash with 80 per cent alcohol, dry 30 minutes at 100° and weigh.

Concentrate the solution as much as possible without causing deposition of salt and saturate it with hydrogen chloride using a delivery tube with enlarged end not quite touching the surface of the liquid as shown in Fig. 31. Add 2 ml. of water for each 100 ml. of solution, allow the precipitated sodium chloride to settle and filter through a Gooch crucible or other form of suction filter. Wash the salt three times by decantation with 95 per cent alcohol and three times on the filter. In the solution there remains all of the potassium, some sodium, and possibly calcium, magnesium, and sulfuric acid.

Evaporate the solution to dryness on the water bath and finally heat over a free flame to expel sulfuric acid if it is present. Weigh the residue, add 3 ml. of 2-normal hydrochloric acid and more than enough chloroplatinic acid to precipitate all of the potassium. Evaporate to a paste and stir this into 20 ml. of absolute alcohol. After five minutes, add 5 ml. of ether and allow to stand half an hour under a bell jar. Filter, reject the filtrate, and purify the precipitate as follows; dissolve the air-dry precipitate in a little hot water, add a few drops of chloroplatinic acid and repeat the above treatment. The second precipitate should be nearly pure K_2PtCl_6 but may contain a little sodium chloride and sulfate. Wash it with a mixture of alcohol and ether until the liquid runs through the filter colorless. Dry the precipitate, moisten it with hot water, and digest on the water-bath with a few drops of chemically-pure mercury,† constantly stirring with a glass rod, until the liquid appears perfectly colorless.

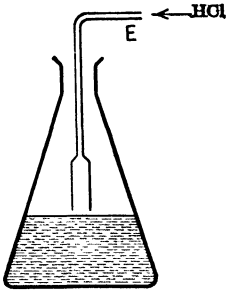


FIG. 31.

By means of this treatment the potassium chloroplatinate is decomposed with separation of platinum:

$$K_2PtCl_6 + 4\,Hg = 2\,KCl + 2\,Hg_2Cl_2 + Pt$$

Dry the mixture on the water-bath and gently ignite until the mercury is all volatilized; this heating also changes the platinum to a denser form which can be readily washed by decantation. After cooling, treat the mass with water, decant the aqueous solution through a filter, wash the residual metal with hot water, dry, and cautiously heat.

* Dissolve 200 g. of NH_4Cl in 500 ml. of water and shake the solution with at least 5 g. of pure K_2PtCl_6.

† Sonnstädt, *Z. anal. Chem.*, **36**, 501.

Burn the filter separately in a platinum spiral, add its ash to the main portion of the platinum in the crucible, ignite and weigh. From the weight of platinum compute the per cent of K, K_2O, or potassium salt.

Separation of Potassium from Sodium by the Perchlorate Method*

Principle. — This separation depends upon the insolubility of potassium perchlorate and the solubility of sodium perchlorate in 97 per cent alcohol. Ammonium salts and sulfates must not be present on account of the difficult solubility of ammonium perchlorate and of sodium sulfate in alcohol, but a little phosphate does no harm, as both sodium perchlorate and phosphoric acid are soluble in alcohol.

Many experiments by the agricultural chemists of the United States show that the method is nearly, if not quite, as accurate as the chloroplatinate method. It requires a little more attention to details. Since 1914 the price of platinum has been so high that it has interfered seriously with its use in the chemical laboratory.

In the analysis of fertilizers, the Association of Official Agricultural Chemists recommends placing 2.5 g. of sample on a 12.5 cm. filter paper in a funnel and dissolving the soluble salts by treating with small portions of hot water until about 200 ml. of filtrate are obtained. Then 5 ml. of concentrated hydrochloric acid are added and the sulfate precipitated. The solution is diluted to exactly 250 ml. in a calibrated flask and, after mixing thoroughly, a little of the solution is filtered through a dry filter and exactly 50 ml. of filtrate taken for the rest of the analysis.

By taking a fairly large portion for analysis and then using an aliquot part, a more representative analysis is obtained if the sample is not perfectly uniform. It is assumed that the actual volume of precipitate can be neglected and no attention is paid to adsorption of solute by the precipitate or by the filter paper. Such effects must be considered when pure substances are to be analyzed with the greatest possible accuracy but when the weight of precipitate is small or the percentage of desired constituent low, it is permissible to neglect the volume of precipitate and adsorption, especially as the errors tend to compensate one another.

Procedure. — If the solution to be analyzed contains sulfate, it is advisable to remove it. To about 70 ml. of solution (containing not more than 0.5 g. of potassium salt) add 1 ml. of concentrated hydrochloric acid, heat to a gentle boil and add hot, 0.5 *N* barium chloride solution drop by drop until no further precipitation occurs. Wait fifteen minutes, filter off the barium sulfate and wash it with hot water.

If ammonium salts are present, evaporate to dryness and ignite carefully till all ammonium salts are decomposed. Cool, rinse down the sides of the dish with a little water and again evaporate and ignite

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* Schlösing-Wense, *Z. angew. Chem.*, **4**, 691; **5**, 233; **6**, 68; *Landw. Ver. Sta.*, **59**, 313; **67**, 145; *J. Am. Chem. Soc.*, **36**, 2085. Cf. also *U. S. Chemical Bulletin* 152; Baxter and Kobayashi, *J. Am. Chem. Soc.*, **39**, 249 (1917); **42**, 735 (1920); Davis, *J. Agr. Sci.*, **5**, 52 (1912); Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917); T. D. Jarrel, *J. Assoc. Off. Agri. Chem.*, **4**, 76–7 (1920–21).

at a temperature below redness.* Dissolve the residue in about 20 ml. of water.

Add 5 ml. of perchloric acid, *d.* 1.12 containing 20 per cent $HClO_4$, and evaporate carefully till salts separate. Add 10 ml. of hot water, 5 ml. more of perchloric acid and again evaporate on a water bath and finally on a sand bath. If dense fumes of perchloric acid are not evolved, repeat the addition of water and perchloric acid until dense fumes are obtained by evaporation. Cool to below room temperature† and add 20 ml. of 97 per cent alcohol containing 0.2 per cent of perchloric acid and saturated with potassium perchlorate.‡ Crush the precipitated $KClO_4$ with the end of a stirring rod and allow to stand for 30 min., preferably with the dish resting in ice water. Filter through a Gooch or Munroe crucible that has been dried at 120–130° and weighed.

If only a small precipitate is obtained, it is safe to wash and weigh it at once without purification provided no considerable quantity of other salt is present in the alcoholic solution. Unless the absence of much sodium or other salt is assured, decant the solution through the filter and wash the crystals three times with small portions of alcohol containing 0.2 per cent of perchloric acid. Then dissolve the crystals in a little hot water, add 1 ml. of perchloric acid, evaporate and treat as before. Transfer the pure potassium perchlorate to the weighed filtering crucible and wash with small portions of cold alcohol§ which is saturated with $KClO_4$ besides containing 0.2 per cent of $HClO_4$. Dry at 130° for an hour and weigh.

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* It has been recommended to evaporate and ignite after the addition of perchloric acid. (Cf. Jarrell, *loc. cit.*) If there is any organic material present there is likely to be an explosion and it is, therefore, safer to remove ammonium salts and organic matter before the addition of any perchloric acid.

† It is not safe to add alcohol to *hot* perchloric acid. After the addition of the alcohol *do not heat!* It is perfectly safe to evaporate an aqueous solution of perchloric acid but a bad explosion may result by heating the alcoholic solution.

‡ 100 ml. of the alcohol containing perchloric acid will dissolve 2.8 mg. of $KClO_4$. If there is considerable $NaClO_4$ present it tends to salt out a little $KClO_4$ from the saturated alcoholic solution. When considerable sodium salt is present, therefore, it is advisable to wash the first precipitate with a little alcohol containing no potassium perchlorate, dissolve the precipitate in a little water and repeat the precipitation. The small quantity of sodium salt adhering to the partially washed $KClO_4$ precipitate will do no harm the second time. (Cf. Davis, *J. Agr. Sci.*, **5**, 52, 512; Gooch and Blake, *Am. J. Sci.*, **44**, 381; Baxter and Kobayashi, *J. Am. Chem. Soc.*, **42**, 735.

§ Baxter and Kobayashi have shown that it is advisable to cool the wash alcohol to 0° and to keep the volume of the washings as small as possible.

Remark. — The precipitation of potassium as perchlorate can be accomplished in the presence of most other cations except ammonium. The precipitate should be easily soluble in hot water. In the analysis of fertilizers it is often recommended to dissolve the precipitate in hot water, dry and weigh again to see if any other insoluble substance was present with the precipitated potassium perchlorate. In former editions of this book, Kreider's* method of preparing perchloric acid was given but it is now easy to purchase this chemical.

Determination of Potassium as Cobaltinitrite

Sodium cobaltinitrite is probably the most sensitive precipitant of potassium ions in aqueous solution. Biilmann† was able to detect 0.0009 mg. of potassium in the presence of 4000 equivalents of sodium. Since de Koninck‡ recommended the reaction in 1881, the quantitative determination of potassium as cobaltinitrite has been studied by many chemists,§ most of whom have been able to get satisfactory results. Since 1881 the price of platinum has increased enormously and cobalt compounds are easier to obtain; this accounts for the popularity of the cobaltinitrite method.

Produced under ideal conditions the precipitate, formed in dilute acetic acid solution with a considerable excess of the reagent, corresponds to the formula, $K_2NaCo(NO_2)_6$, with 17.93 per cent of potassium, equivalent to 21.37 per cent K_2O.

The reagent, sodium cobaltinitrite, is not very stable and the composition of the precipitate varies somewhat when produced under different conditions. For this reason, Vürtheim and others have recommended the use of empirical factors and the Association of Official Agricultural Chemists have abandoned the method although many of their co-operating chemists obtained excellent results.

The precipitate can be filtered, dried at 110° and weighed without decomposition, it may be dissolved and the cobalt determined electrolytically,|| the nitrite may be determined volumetrically,¶ or the volume of the precipitate may be measured in a graduated centrifuge tube.**

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* *Z. anorg. Chem.*, **9**, 342.

† *Z. anal. Chem.* **39**, 284 (1900).

‡ *Ibid*, **20**, 390 (1881).

§ Gilbert, *Ibid* **38**, 184 (1899); Van Leent, *Ibid* **40**, 569 (1901); Adie and Wood, *J. Chem. Soc.* **77**, 1076 (1900); Drushel, *Am. J. Sci.* [4], **24**, 433 (1907); Mitscherlich, Celichowski and Fisher, *Landw. Vers. Sta.* **76**, 139 (1912); Mitscherlich and Fisher, *Ibid* **78**, 75 (1912); Zaleski, *Ibid* **83**, 221 (1914); Van der Horn and van den Bos, *Chem. Weekbl.* **10**, 182 (1913); de Wildt and Dekker, *Compt. rend. de XI Congr. intern. d. pharm., II*, 685–90 (1913); Garola and V. Braun, *Ann. fals.* **10**, 572–5 (1917); Wenger and Hemén, *Ann. chim. anal. chim. appl.* **2**, 198–9 (1920); E. Sherrill, *Ind. Eng. Chem.* **13**, 227 (1921); Vürtheim, *Rec. trav. chim. Pays-Bas* **40**, 593–9 (1921), Clerfeyt, *Bull. soc. chim. Belg.* **31**, 417 (1922).

|| Dissolve the precipitate in dilute hydrochloric acid, boil to decompose the nitrite, and carry out the electrolysis as described under Cobalt.

¶ Boil the washed precipitate with dilute sodium hydroxide, filter off the cobaltic hydroxide, make the filtrate acid and titrate with permanganate as described under *Volumetric Analysis, Analysis of Nitrous Acid;* 1 ml. of 0.1 *N* $KMnO_4$ = 0.000785 g. K_2O. Another method, — Wash the precipitate into a measured volume of hot permanganate solution diluted with ten times as much water. After 5–6 minutes make acid with 5 *N* H_2SO_4 and titrate the excess permanganate with standard oxalate solution. In this case, 1 ml. 0.1 *N* $KMnO_4$ = 0.000856 g. K_2O.

** Cf. Sherrill, *loc. cit.*

Reagent. — Dissolve 28.6 g. of cobaltous nitrate crystals and 50 ml. of glacial acetic acid in enough water to make 500 ml. of solution. Dissolve 180 g. of sodium nitrite in 500 ml. of water. Keep these two solutions separate until the day before the analysis is to be made, then mix equal volumes, shake or stir well, allow to stand over night in a glass-stoppered bottle and filter just before using.

Procedure. — The potassium solution should contain the equivalent of 0.25 g. KCl, or less, in a volume of 25 ml. For this weight of potassium salt use 40 ml. of the filtered reagent. For smaller quantities of potassium, use less solution and less reagent but never less than 10 ml. of either. Shake the mixture vigorously for several minutes, or, better still, stir mechanically for 30 minutes and allow to stand over night. Filter through a Gooch crucible, wash with 10 per cent acetic acid until the filtrate comes through colorless and then with 95 per cent alcohol. Dry at 110° for two hours.

Remark. — The presence of sodium salts in considerable excess does no harm. Most other cations can be removed by adding sodium carbonate solution. Ammonium salts should be removed, when present, by evaporating to dryness and gently igniting the residue. In fertilizer analysis, a fairly large sample should be taken and an aliquot part used for the potassium determination after the removal of ammonium salts and precipitation of other cations with sodium carbonate. Clerfeyt tested the method and obtained satisfactory results with materials containing from 5 to 62 per cent of K_2O. In most cases the agreement between the cobaltinitrite method and the chloroplatinate method was nearly, if not quite, as good as is usually obtained with duplicate analyses by the chloroplatinate method. When these directions are followed, the method appears to be rapid, exact and economical.

Determination of Potassium in a Silicate*

Most silicates are decomposed by treatment with hydrofluoric acid in the presence of a dehydrating agent such as sulfuric acid, concentrated hydrochloric acid or perchloric acid. The perchlorates of all the common cations, except those of potassium and ammonium, are soluble in alcohol.

Procedure. — To about 0.3 g. of silicate in a platinum crucible add 1.5 ml. of 2 *N* $HClO_4$ and 3–4 ml. of 48 per cent HF. Evaporate to dense fumes of $HClO_4$ heating at a low temperature on a sand bath in a larger crucible (Fig. 14) or in a wire gauze chamber made by bending some fairly fine-meshed copper or bronze gauze and inserting a triangle to hold the crucible. Cool, add water to fill about two-thirds of the crucible, heat just to boiling, filter and wash thoroughly with hot water. Evaporate the filtrate till fumes of $HClO_4$ are again obtained. Cool† and add 25 ml. of 97 per cent alcohol. Break up the residue with a stirring rod‡

* J. J. Morgan, *J. Ind. Eng. Chem.* **13**, 225 (1921); M. M. Green, *Ibid* **15**, 163 (1923).

† It is dangerous to add the alcohol to *hot* perchloric acid!

‡ This is important. If the crystals are not fine, it will be necessary to repeat the following purification process.

and filter through a Gooch crucible. Wash the precipitate with 1 per cent perchloric acid in alcohol. Transfer the washed precipitate and the asbestos mat to a filter and wash thoroughly with hot water to dissolve the $KClO_4$. Some insoluble salts are usually left on the filter. To the filtrate add 1 ml. more of perchloric acid, evaporate to fumes and treat with alcohol when cold. Usually the precipitate is now pure $KClO_4$. Filter, wash with one per cent perchloric acid in alcohol, dry for one hour at 110° and weigh as $KClO_4$.

LITHIUM, Li. At. Wt. 6.94

Forms: Li_2SO_4 and LiCl

The determination of lithium in the form of the above salts is carried out in practically the same way as in the case of potassium. It should be mentioned, however, that on evaporating a lithium salt with concentrated sulfuric acid the acid salt, $LiHSO_4$, is formed, which on gentle ignition (even without the addition of ammonium carbonate) is changed to difficultly volatile Li_2SO_4.

Since lithium chloride is a very hygroscopic salt, it is necessary to weigh it out of contact with moist air. To accomplish this, place the platinum crucible, after being gently ignited, together with a glass stoppered weighing beaker in a desiccator which is provided with a calcium chloride tube. After both crucible and beaker have assumed the temperature of the room, quickly place the former within the latter and stopper. Allow the weighing beaker to stand for 20 minutes in the balance case and then weigh. Place the salt in the crucible and repeat the above process.

Determination of Lithium, Potassium, and Sodium in the Presence of One Another

After determining the weight of the combined chlorides, determine the potassium in one portion as K_2PtCl_6, $KClO_4$ or $K_2NaCo(NO_2)_6$ and in a second portion determine the lithium according to one of the following methods:

(*a*) *Gooch's Method**

Principle. — Anhydrous LiCl is soluble in anhydrous amyl alcohol (10 ml. of cold amyl alcohol dissolve 0.66 g. LiCl) while KCl and NaCl are difficultly soluble in this liquid (10 ml. dissolve 0.3 mg. NaCl and 0.4 mg. KCl).

Procedure. — Place the concentrated solution, containing not more than 0.2 g. LiCl, in a 50 ml. Erlenmeyer flask, add 5–6 ml. of amyl alco-

* *Proc. Am. Acad. of Arts and Sciences* **22** [N. S. 14], 177.

hol (boiling point 132°) and carefully heat on an asbestos plate. The aqueous solution at the bottom of the beaker soon begins to boil and the water vapor escapes through the upper layer of amyl alcohol. To prevent loss by bumping at this point, it is well to pass air through the liquid during the boiling; the water evaporates more quickly and without bumping. As soon as all the water has been boiled off, the chlorides of sodium and potassium separate out and nearly all of the lithium chloride dissolves in the alcoholic solution. During the evaporation of the aqueous LiCl solution, however, some LiOH is formed by hydrolysis, and the latter compound is insoluble in amyl alcohol. To dissolve this, add 2–3 drops of concentrated hydrochloric acid, boil two or three minutes and filter while still warm through a small asbestos filter. The insoluble residue is composed of sodium and potassium chlorides. Wash it with hot amyl alcohol, which has been boiled. Evaporate the filtrate to dryness, and dissolve the residue in a little water and a little dilute sulfuric acid. Filter off the carbonaceous residue into a weighed platinum crucible, evaporate as far as possible on the water-bath, remove the excess of sulfuric acid by gentle heating over a flame (the crucible being placed in an inclined position) and then weigh. The lithium sulfate thus obtained will contain small quantities of potassium and sodium sulfates if the corresponding cations are present. To correct for these impurities subtract 0.00041 g. for every 10 ml. of the filtrate (exclusive of the alcohol used in washing the residue) in case only sodium chloride is present, 0.00051 if only potassium chloride is present, and 0.00092 if both sodium and potassium chlorides are present.

If only 10–20 mg. of lithium chloride were present in the original salt mixture, then, after filtering and washing with amyl alcohol, dissolve the residue in a little water, repeat the above treatment, and determine the lithium in the combined filtrates.

(*b*) *Rammelsberg's Method* (*Modified by F. P. Treadwell*)

Principle. — Anhydrous lithium chloride is soluble in a mixture of equal parts alcohol and ether which has been saturated with hydrogen chloride gas, whereas the chlorides of sodium and potassium are practically insoluble.

Procedure. — Evaporate the solution of the chlorides to dryness in a small Jena flask which is provided with a ground glass, two-way stopper (p. 48 Fig. 29*a*). During the evaporation pass a current of dry air into the flask through the long tube *a* and out through the short tube *b* As soon as the residue has become dry place the flask in an oil-bath and heat for half an hour at 140–150° while passing dry hydrogen chloride gas through the flask. Allow the flask and its

contents to cool with the hydrogen chloride still passing through the flask. Treat the cold residue with a few milliliters of absolute alcohol, which has been saturated with hydrogen chloride gas and thereupon diluted with an equal volume of absolute ether. Tightly stopper the flask and allow it to stand with frequent shaking for 12 hours. Pour the solution through a filter which is wet with the ether-alcohol mixture, and wash the residue three times by decantation with ether-alcohol. Add a little more ether-alcohol to the contents of the flask and again allow it to stand for 12 hours; pour off the liquid and wash the residue with ether-alcohol until a trace of the residue tested in the spectroscope shows the absence of lithium. Carefully evaporate the ether-alcohol extract to dryness on a water-bath containing lukewarm water, moisten the residue with a few drops of dilute sulfuric acid, dissolve in as little water as possible, transfer to a weighed crucible and treat with sufficient sulfuric acid to transform the lithium chloride into sulfate. Evaporate the solution as far as possible on the water-bath, then cautiously over the free flame, gently ignite and weigh the residue of lithium sulfate.

Remark. — In the presence of considerable sodium and potassium salts it is advisable to remove the greater part of these by precipitation with hydrochloric acid gas (cf. p. 63), filtering through asbestos and washing the precipitate with concentrated hydrochloric acid until the residue no longer gives the lithium spectrum. The results obtained by this method are satisfactory.

Besides the above methods for the separation of lithium from sodium and potassium there are two other methods to be mentioned; that of W. Mayer* and that of A. Carnot.† According to Mayer the lithium is precipitated in the presence of NaOH as Li_3PO_4, which, after being washed with ammonia water, is ignited and weighed. Rammelsberg, however, claims that the Li_3PO_4 always contains some sodium, so that the method is inaccurate. A great many experiments tried in the author's laboratory have led to the same conclusion.

According to Carnot the lithium is separated as the fluoride and then transformed to the sulfate. Walter‡ claims that this method is accurate but tedious.

Example for practice: Lepidolite analysis. (See Index.)

Indirect Determination of Lithium and Sodium

The mixture of the two chlorides is weighed and the chlorine determined either gravimetrically or volumetrically. (See p. 2.)

Indirect Determination of Lithium and Potassium

The method is the same.

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* *Ann. Chem. Pharm.*, **98**, 193, and Merling, *Z. anal. Chem.*, **18**, 563.

† *Z. anal. Chem.*, **29**, 332.

‡ *The Analyst*, **16**, 209.

AMMONIUM, NH_4. Mol. Wt. 18.04

Forms: NH_3, NH_4Cl, $(NH_4)_2PtCl_6$, Pt, N_2

There are two cases to distinguish: (1) The ammonium is present as chloride in aqueous solution. (2) The ammonium is present in solution together with other cations and anions.

1. *The solution contains only* NH_4^+ *and* Cl^- *ions.* In this case the solution can be evaporated to dryness and the residue of ammonium chloride weighed; or the ammonium can be precipitated as $(NH_4)_2PtCl_6$ and the precipitate weighed; or the ammonium chloroplatinate can be ignited and the residue of platinum weighed.

(*a*) Determination as NH_4Cl

Add concentrated HCl to the aqueous solution and evaporate to a small volume on the water-bath at as low a temperature as possible, transfer the solution to a crucible, evaporate on the water-bath to dryness, and heat the covered crucible to constant weight in a drying-oven. Good results are obtained, but they are always a little low. On evaporating the aqueous solution some NH_4Cl is driven off, and the amount lost increases in proportion to the quantity of water used and the temperature at which the evaporation takes place. In cold, aqueous solution, ammonium chloride is largely ionized, $NH_4Cl \rightarrow NH_4^+ + Cl^-$. As the temperature is raised, hydrolysis takes place to an appreciable extent, $NH_4Cl + H_2O \rightarrow NH_4OH + HCl$ and NH_3 evaporates from the ammonium hydroxide noticeably faster than does hydrogen chloride.

If, however, a little hydrochloric acid is added to the solution the hydrolysis is prevented and the loss of NH_3 is reduced to a minimum. The ammonium chloride must be dried in a covered crucible as otherwise a small quantity of the salt will be lost, but this loss is small in comparison with the possible loss during the evaporation.

(*b*) Determination as $(NH_4)_2PtCl_6$

On heating $(NH_4)_2PtCl_6$ to 130° the salt is unchanged. An aqueous solution containing HCl and an excess of H_2PtCl_6 can be evaporated to dryness without appreciable loss of NH_3. To the aqueous solution of ammonium chloride, therefore, add an excess of chloroplatinic acid and a little hydrochloric acid. Evaporate to dryness at as low a temperature as possible. Pour absolute alcohol over the residue to dissolve the excess of H_2PtCl_6, break up the crystals with a stirring rod and filter through a Gooch crucible. Dry at 130° and weigh.

(*c*) Determination as Platinum

Instead of weighing the $(NH_4)_2PtCl_6$ as such, it can be decomposed by ignition and the weight of the residual platinum determined. As ammonium chloroplatinate decrepitates strongly on being heated, the ignition must take place in a large porcelain crucible, which is provided with a close-fitting cover. The precipitate must be heated gradually at first to prevent loss. It is best ignited according to the directions of Rose. Place the precipitate and filter in the crucible with the filter-paper on top, cover the crucible and heat over a small flame until the paper is completely charred without allowing the vapor to escape visibly from the crucible. Then heat the crucible with a hotter flame, allowing free access of air into the inclined crucible, until the charred filter is completely consumed.

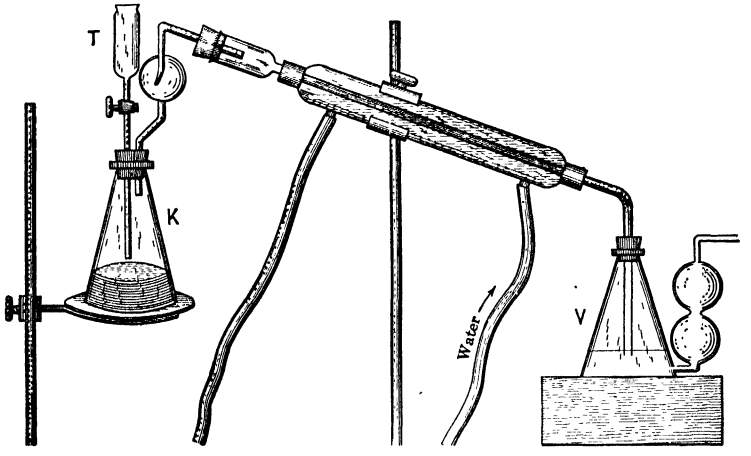


FIG. 32.

2. The Ammonium is Present Together with Other Cations and Anions in Solution or in Solid Form

The solution is distilled after the addition of a strong base (NaOH or $Ca(OH)_2$), the ammonia evolved is absorbed in hydrochloric acid and the resulting solution is analyzed according to 1.

Procedure. — Place about 0.5 g. of the substance to be analyzed in the 400–500 ml. Erlenmeyer flask *K*, Fig. 32, dissolve it in 200 ml. of water, add a few drops of litmus or phenolphthalein indicator* solution,

* An excess of strong caustic alkali solution will decolorize phenolphthalein. Only a little more than enough NaOH to turn the phenolphthalein pink is necessary

and in case the solution reacts acid, slowly add through T some 12 *N* sodium hydroxide solution (which has been previously boiled to expel traces of ammonia) until the color of the solution (well-mixed by shaking) shows a basic reaction; then add 5 ml. more of the caustic soda solution.* Heat the liquid to boiling and carefully distil 100 ml. into the receiver *V*, containing 30 ml. of 0.5 *N* hydrochloric or sulfuric acid. To make sure that no ammonia escapes from the receiver it is well to connect it with a second absorption flask containing 5 ml. of 0.5 *N* acid and some distilled water.

After 100 ml. of the liquid have distilled over, all the ammonia will be found in the receiver and can be determined according to 1 (*a*) or 1 (*b*); preferably the latter. The determination can be carried out much more quickly, however, if the receiver contains a measured amount of standardized acid and the excess is determined after the distillation by titration with methyl orange or methyl red as indicator (cf. Alkalimetry).

It is also possible to make an accurate determination of the amount of ammonia present by measuring the volume of the gas.†

Colorimetric Determination of Ammonium

For the determination of such small quantities of ammonia as occur in drinking-water, the above methods are not suited. In this case the procedure is the same as was described in Vol. I, under *Ammonium.* (In the case of mineral waters it is necessary to add more than one drop of the soda solution; the amount necessary being determined by adding litmus to a definite volume of the water and then adding the soda solution until the litmus changes to blue.) Receive the distillate in 50 ml. graduated Nessler tubes (in the fourth one there is usually no ammonia to be detected) and Nesslerize these. To do this, mix 50 ml. of distillate with 2 ml. of Nessler solution and compare the color produced with the colors obtained similarly from a series of tubes containing known amounts of ammonia. When a standard is found of the same shade as the solution tested, then the two solutions contain the same amount of ammonia.

Prepare the ammonium chloride standards as follows: Dissolve 3.141 g. of ammonium chloride, which has been dried at 100°, in 1 liter of water free from ammonia (cf. Vol. I, under *Ammonium*). The solution now contains 1 mg. of ammonia (NH_3) per milliliter; this, however, is too strong for most purposes. Take 10 ml. and dilute

* The separatory funnel *T* should be roughly calibrated before setting up the apparatus, by pouring water into it, one milliliter at a time, and marking with a pencil the level of the liquid on the glass.

† Cf. Part III, Gas Analysis.

to 1 liter. Of this solution 1 ml. contains 0.01 mg. NH_3. If the water to be analyzed contains considerable ammonia, a smaller portion should be taken for the analysis than in ordinary cases (500 ml.) as otherwise the first distillate (50 ml.) would give too intense a color with the Nessler solution. In such a case use only 50 ml. of the water for the analysis, dilute to 500 ml. with water free from ammonia and then distilled.

To determine how much should be taken for the analysis, make the following experiment:

Place about 100 ml. of the water to be tested in a narrow cylinder (which is provided with a ground-glass stopper), add 2 ml. of a strongly alkaline sodium carbonate solution* to precipitate the calcium which may be present, shake the mixture vigorously and allow the precipitate to settle. From the clear supernatant liquid pipet off 50 ml. into a Nessler tube, treat with 2 ml. of Nessler solution and mix.† If a strong yellow color, or even a precipitate, is obtained, then take only 50 ml. of the water for analysis. If, on the other hand, there is not more than a faint coloration apparent, use 500 ml. for the determination.

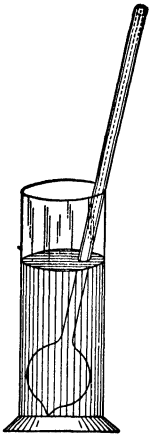


FIG. 33.

For the Nesslerization, place the three cylinders each containing 50 ml. of the distillate over a sheet of white paper, add 2 ml. of the Nessler reagent, and mix. Beside them place a series of similar cylinders containing respectively 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 ml. of the standard ammonium chloride solution diluted to 50 ml. Treat these also with 2 ml. of the Nessler reagent and match the colors obtained in the test with those obtained from known amounts of ammonia.

The Nessler reagent should give a distinct coloration with 500 ml. of water containing 0.005 mg. NH_3; if this is not the case, it must be made more sensitive by the addition of mercuric chloride solution.

For mixing the liquid in the cylinders it is convenient to employ a stirrer such as is shown in Fig. 33, the diameter of the bulb on the end being only slightly less than that of the cylinder. By moving this stirrer up and down twice the liquid becomes thoroughly mixed.

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* 50 g. NaOH and 50 g. Na_2CO_3 (calcined) dissolved in 600 ml. of pure distilled water and the solution boiled until the volume is only 500 ml.

† In the case of mineral waters rich in magnesium sulphate, the addition of the 10 ml. of sodium carbonate solution often fails to prevent a turbidity on adding the Nessler reagent, which would render a colorimetric determination impossible. In this case add 10 ml. of a boiled $BaCl_2$ solution (120 g. $BaCl_2 \cdot 2H_2O$ in 500 ml. H_2O) before treating the water with the sodium carbonate solution.

Kjeldahl's Method for Determining Nitrogen

The methods which have been described thus far are suitable only for the determination of nitrogen when it is in solution in the form of NH_4^+ ions. It is, however, of great importance to be able to determine nitrogen when it is present other than as an ammonium compound (in protein, coal, etc.). The Kjeldahl method converts such nitrogen into ammonium salt.

By heating nitrogenous organic substances with concentrated sulfuric acid, potassium permanganate, mercuric oxide, etc., the organic matter is destroyed and the nitrogen is completely changed to ammonium and held as ammonium acid sulfate, from which the ammonia can be readily distilled.

Procedure. — Place from 0.7 to 3.5 g. of substance, according to the nitrogen content, in a 500–600 ml. Kjeldahl digestion flask. This is made of difficultly-fusible potash glass and has a long neck to act as a condenser during the digestion process. Add about 0.7 g. of HgO or 0.065 g. of Hg, and 2–30 ml. of concentrated sulfuric acid. Place the flask in an inclined position and heat very gently until the substance is thoroughly wet with the acid and frothing ceases. Then, gradually raise the temperature until the acid boils and is nearly, if not quite, colorless. Usually 90 minutes digestion is sufficient.

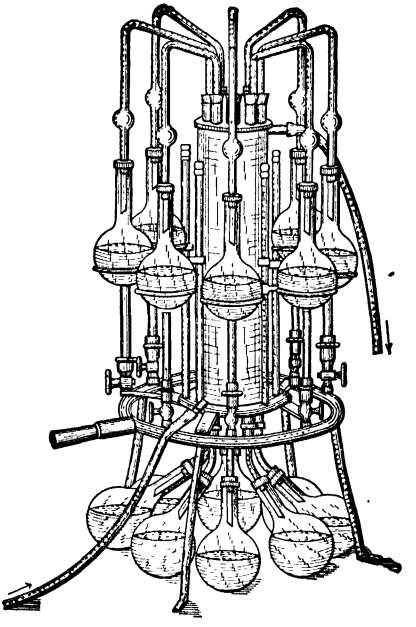


FIG. 34.

Allow to cool, dilute to about 200 ml., add a few pieces of zinc or pumice to prevent bumping, and 25 ml. of potassium sulfide solution (40 g. to the liter). This causes the precipitation of black HgS. Add sufficient strong sodium hydroxide solution to make the solution alkaline (80 ml. of 12 *N* NaOH should be sufficient), pouring it down the side of the flask so that it does not mix with the acid. Quickly connect with a condenser and distil off the ammonia into a measured volume of standard acid as in the analysis of an ammonium salt.

Fig. 34* shows how a series of analyses can be carried out simultaneously in a busy laboratory. The Hopkins' distillation tubes used

* From Scott's *Standard Methods of Chemical Analysis.*

to connect the distilling flasks with the condensers are useful in preventing errors by bumping.

Always make a blank test with all the reagents using about 1 g. of sugar for the digestion. The sugar serves to reduce any nitrates that are present in the reagents.

Gunning's Method for Determining Nitrogen

Instead of using mercuric oxide or mercury as a catalyzer in the digestion of organic materials, Gunning has recommended the use of 10 g. of pure potassium sulfate. Usually the digestion is accomplished just as quickly and it is unnecessary to add potassium sulfide. The solution is, therefore, clear during the distillation and there is less danger of bumping. The procedure is the same otherwise.

The Kjeldahl and Gunning methods will usually give the nitrogen present as nitrate if the original digestion is made with 30. ml.of concentrated sulfuric acid containing 1 g. of salicylic acid. Allow the acid mixture to stand 30 minutes with frequent shaking, add 5 g. of $Na_2S_2O_3$ and heat 5 minutes. Then add 10 g. of K_2SO_4 (or Na_2SO_4) and digest in the usual way.

Phelps* has studied the determination of nitrogen in organic compounds which are difficult to decompose and recommends for azo compounds the use of $SnCl_2$ solution or of formaldehyde previous to the digestion with acid. He also recommends the use of both HgO and K_2SO_4 in the digestion.

MAGNESIUM, Mg. At. Wt. 24.32

Forms: $MgSO_4$, MgO, $Mg_2P_2O_7$

(*a*) Determination as $MgSO_4$

This method for the determination of magnesium can always be employed when the magnesium is combined with an acid which can be volatilized by heating with sulfuric acid, and when no other metal besides ammonium is present.

Place 0.5 g. of the substance in a crucible and add about 2 ml. of concentrated sulfuric acid. Substances which react violently with concentrated H_2SO_4 should be first treated with water, and dilute sulfuric acid added little by little. Evaporate on the water-bath as far as possible and remove the excess of sulfuric acid by cautiously heating the crucible, held in an inclined position, over a free flame. Finally,

* *J. Assoc. Off. Agr. Chem.*, **3**, 218–20; 306–15 (1920).

heat the dry mass just to redness in a covered crucible, cool in a desiccator and weigh as quickly as possible, as the anhydrous magnesium sulfate is hygroscopic.

(*b*) Determination as MgO

This method is seldom used in practice, and then only in case the magnesium is present in a form that can be readily changed to the oxide by ignition — *i.e.*, as carbonate, nitrate or salt of an organic acid.* The procedure consists simply of first heating carefully in a covered crucible, and finally with the full heat of the Teclu burner in a half-covered crucible.

(*c*) Determination as Magnesium Pyrophosphate

This, the most important of all the methods for the determination of magnesium, is always applicable and depends upon the following principles: If the solution of a magnesium salt is treated with an alkali orthophosphate solution in the presence of ammonium chloride and ammonia, the magnesium is completely precipitated as magnesium ammonium phosphate, which by ignition is changed to magnesium pyrophosphate:

$$2\,MgNH_4PO_4 = 2\,NH_3 + H_2O + Mg_2P_2O_7.$$

Formerly it was a common practice to precipitate magnesium ammonium phosphate in the cold. Neubauer† showed, however, that this sometimes leads to high results while at other times the results are low. The latter is the case when the precipitation takes place in strongly ammoniacal solutions containing but little ammonium salts, particularly when the phosphate solution is added slowly. Tribasic magnesium phosphate, $Mg_3(PO_4)_2$, contaminates the precipitate. On the other hand, the results are too high if the precipitation takes place in neutral or slightly ammoniacal solution in the presence of considerable ammonium salts. In this case more or less monomagnesium ammonium phosphate, $Mg(NH_4)_4(PO_4)_2$, is formed. This compound is changed to magnesium metaphosphate by gentle ignition.

$$2\,Mg(NH_4)_4(PO_4)_2 = 2\,Mg(PO_3)_2 + 8\,NH_3 + 4\,H_2O,$$

and the results are too high. When only a little of the metaphosphate is present, the temperature of the blast-lamp will eventually lead to

* Magnesium chloride can be changed to the oxide by ignition with mercuric oxide in a porcelain evaporating-dish. Mercuric chloride and the excess of mercuric oxide are volatilized. In this way magnesium can be separated from the alkalies.

† *Z. angew. Chem.*, **1896**, 439. See also Gooch and Austin, *Z. anorg. Chem.*, **20**, 121.

volatilization of some phosphorus pentoxide, so that nearly correct results are then obtained.

$$2\,Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5.$$

Neubauer recommends adding an excess of sodium phosphate to the slightly acid solution of the magnesium salt, then stirring in one-third of the solution volume of 10 per cent ammonia, filtering after four or five hours, washing with 2.5 per cent ammonia, dissolving the precipitate in a little dilute hydrochloric acid, adding a few drops of sodium phosphate solution, and precipitating by the addition of one-third volume of 10 per cent ammonia. This method, however, gives results which are a little too high (*e.g.*, 9.96 per cent instead of 9.87 per cent Mg in pure $MgSO_4.7\,H_2O$).

Correct results can be obtained by the method of B. Schmitz,* or of W. Gibbs.†

Method of B. Schmitz

Heat the acid solution, containing magnesium in the presence of ammonium salts,‡ to boiling, add an excess of sodium or ammonium phosphate and one-third the solution's volume of 6 *N* ammonia. Allow the solution to cool and filter through a Gooch or Munroe crucible after standing for several hours. Wash the precipitate with 1.5 *N* ammonia, dry and ignite very slowly, gradually increasing the heat until the precipitate is white. After cooling, weigh the $Mg_2P_2O_7$:

$$2\,MgNH_4PO_4 = 2\,NH_3 + H_2O + Mg_2P_2O_7.$$

From the weight of the latter, p, the amount of magnesium can be calculated as follows: $\frac{2\,Mg}{Mg_2P_2O_7} \cdot p$ = weight of magnesium.

The precipitate can be filtered upon an ordinary filter, but in all cases the ignition must be gradual, or it is almost impossible to obtain perfectly white pyrophosphate. By rapid ignition, some of the phosphorus is reduced by the ammonia. This reduction is likely to injure a platinum crucible. Often a black precipitate can be whitened by moistening with strong nitric acid and carefully heating. This treatment, however, should be avoided by carefully igniting the precipitate. With care, a moist precipitate can be ignited together with the filter paper.

* *Z. anal. Chem.* 1906, 512; cf. Jörgensen, *ibid.* 1906, 278.

† *Am. J. Sci.* (3), **5**, 114.

‡ Ammonium salts do no harm when the precipitation takes place in hot solution, but, on the contrary, cause the formation of a coarsely crystalline precipitate which is easy to filter.

Method of W. Gibbs

To the boiling hot, neutral, not too concentrated, solution of magnesium and ammonium salts add a normal solution of microcosmic salt, $NaHNH_4PO_4 + H_2O$, until no further precipitation takes place. Almost 90 per cent of the magnesium present is at once thrown down as amorphous magnesium hydrogen phosphate, $MgHPO_4$:

$$NaHNH_4PO_4 + MgCl_2 = NaCl + NH_4Cl + MgHPO_4.$$

Then, while stirring the hot solution, add about one-third volume of 6 *N* ammonia; whereby the amorphous precipitate is transformed into crystalline magnesium ammonium phosphate:

$$MgHPO_4 + NH_3 = MgNH_4PO_4$$

and the magnesium remaining in solution is thrown down almost completely.

After standing two or three hours, decant off the supernatant liquid and wash the precipitate three times by decantation with 1.5 *N* ammonia. Finally transfer the precipitate to the filter, wash completely with 1.5 *N* ammonia and dry in the hot closet. Transfer the dried precipitate to a weighed platinum crucible, burn the filter-paper in a platinum wire spiral, and add the ash to the main portion of the precipitate. Heat the covered crucible very gently at first until the ammonia is all dried off, then more strongly until the mass is snow white. Cool the crucible in a desiccator and weigh.

S paration of Magnesium from the Alkalies

The methods of Gibbs and of Schmitz serve to separate magnesium from the alkalies in those cases where the determination of magnesium alone is desired. If it is desired to determine magnesium and the alkalies in one and the same sample, it is best to use the Gooch and Eddy* modification of the

Schaffgottsche Method for Precipitating Magnesium†

The method is based upon the fact that magnesium can be precipitated quantitatively, by means of an alcoholic solution of ammonium carbonate, as crystalline magnesium ammonium carbonate, $MgCO_3.(NH_4)_2CO_3.6\,H_2O$.

Preparation of the Precipitant. — Saturate a mixture of 180 ml. concentrated ammonia, 800 ml. water, and 900 ml. absolute alcohol with commercial ammonium carbonate. Shake the mixture occasionally and after several hours filter off the excess of carbonate.

* *Z. anorg. Chem.*, **58**, 427 (1908).

† Pogg. Ann., **104**, 482 (1858).

Procedure. — Treat the neutral solution containing only magnesium and the alkalies (lithium must not be present), preferably in the form of chlorides, with an equal volume of absolute alcohol and then with an excess of the ammonium carbonate reagent. Stir vigorously for a few minutes and allow to stand for at least half an hour. Filter through a Gooch or Munroe crucible. Wash with the precipitant, dry, ignite, and weigh as MgO.

If considerable alkali is present the precipitate always contains a small quantity of it. In such cases dissolve the precipitate in hydrochloric acid, evaporate the solution to dryness, take up the residue in a little water, and repeat the precipitation.

Evaporate the combined filtrates to dryness and determine the alkali as described on page 59 *et seq.*

If, however, it is desired to separate magnesium from the alkalies in order that the latter may be determined, the magnesium may be precipitated as magnesium hydroxide, from a solution free from ammonium salts, by the addition of barium hydroxide solution.* The barium is then removed by ammonium carbonate and the alkalies determined in the filtrate. For the detailed description of this method see Silicate Analysis. Even in this case, however, the use of the Schaffgottsche method of separating magnesium from the alkalies is more satisfactory.

* Cf. footnote to page 77.

METALS OF GROUP IV

CALCIUM, STRONTIUM, BARIUM

CALCIUM, Ca. At. Wt. 40.07

Forms: CaO, $CaCO_3$, $CaSO_4$

1. Determination as Calcium Oxide (Lime), CaO

For the determination of calcium as CaO, it is best precipitated as the oxalate and converted to the oxide by strong ignition. The solution should contain no other cation besides magnesium and alkalies. Enough ammonium salt should be present to prevent the precipitation of $Mg(OH)_2$ upon adding ammonium hydroxide.

Procedure. — Heat the dilute, slightly acid solution to boiling and add a slight excess of hot ammonium oxalate solution. Slowly neutralize with ammonium hydroxide, while stirring, and allow the precipitate to settle for about 4 hours. Add a little more ammonium oxalate to make sure that the precipitation is complete. Decant off the clear liquid through a filter, cover the precipitate with boiling water containing ammonium oxalate,* allow to settle, filter, and repeat this washing by decantation three times. Finally transfer the precipitate to the filter and wash with a hot, very dilute solution of ammonium oxalate, until free from chloride. Place the moist filter in a platinum crucible and ignite carefully. Heat the precipitate cautiously at first, so that the too rapid evolution of carbonic oxide will not cause loss. After the filter is burnt and the precipitate is perfectly white, cover the crucible and heat strongly over a Méker burner or blast-lamp for twenty minutes.

Allow the crucible to cool to about 100° in the air and then for 15 minutes in a desiccator. Weigh as CaO. Heat for another 10 minutes over the Méker burner to make sure that all of the calcium carbonate has been decomposed and again weigh.

During the ignition, the following reactions take place:

(1) $CaC_2O_4 \rightarrow CaCO_3 + CO$ (at dull redness)

(2) $CaCO_3 \rightarrow CaO + CO_2$ (at about 1000°)

Remarks. — With an ordinary Bunsen burner and an open crucible but little calcium oxide is formed. It is difficult to convert the precipitate completely to oxide if a *porcelain* crucible is used but if loss of heat by radiation is partly stopped

* T. W. Richards found that the calcium oxalate precipitate is appreciably soluble in pure water but practically insoluble in a dilute solution of ammonium oxalate (*Z. anorg. Chem.*, **28**, 85 (1901)).

by covering the *platinum* crucible, it is possible to convert 0.5 g. of calcium carbonate to oxide by heating one hour over a Tirrill burner.

Most beginners make the mistake of heating precipitates too fast at the start. It is always easiest to get white products if the paper is smoked off and burned at as low a temperature as possible. To hasten the decomposition of the carbonate, the crucible may be heated within a much larger clay or graphite crucible. Saw off the bottom of the graphite crucible and make holes in the sides to hold nichrome wires, to support the crucible. Heating in such a mantle prevents some of the loss of heat by radiation and a temperature is obtained nearly as high as that in a crucible over a blast-lamp.

If the calcium oxalate is heated not above a dull red heat, only calcium carbonate is formed. This may be weighed. Then moisten the precipitate with ammonium carbonate and gently heat again to see if the weight is constant.

Calcium oxide is hygroscopic but when strongly ignited there is no difficulty in weighing it provided the above directions are followed. It is, however, never safe to assume that the first weight is correct. If the cold crucible and its contents apparently gain weight rapidly while on the balance pan, it is probable that a little calcium chloride is present, due to incomplete washing of the precipitate. This can be removed by moistening several times with ammonium carbonate and heating after each addition of carbonate.

Sometimes a little calcium sulfate is formed by allowing the gas flame to enter the crucible. This is not a serious source of error with the illuminating gas of most American cities.

Remark. — If both solutions are not boiling hot during the precipitation, the calcium oxalate forms very fine crystals; it then settles very slowly and passes readily through the filter.

Calcium oxalate is inappreciably soluble in water and dilute acetic acid containing dissolved ammonium oxalate, but readily soluble in mineral acids. One liter of pure water dissolves 10 mg. of calcium oxalate.

2. Determination of Calcium as Sulfate, $CaSO_4$

This method is chiefly used in the analysis of calcium salts of organic acids or for the conversion of calcium oxalate to sulfate in a porcelain crucible. For this purpose heat the calcium salt in a weighed crucible until the organic matter is destroyed. Then cover the crucible with a watch-glass, add some dilute sulfuric acid and heat upon the water-bath until there is no longer any evolution of carbon dioxide. Wash off the under side of the watch-glass and evaporate the liquid as far as possible on the bath. Then carefully expel excess of sulfuric acid by inclining the crucible and heating over the free flame (or in an air-bath) (cf. Fig. 14, p. 38). Ignite gently and weigh. By strong ignition calcium sulfate loses SO_3.*

Calcium may also be precipitated as calcium sulfate. Treat the

* 0.2052 g. $CaSO_4$ remained unchanged in weight after heating for one hour to dull redness; but on heating with the full flame of a Teclu burner, it lost 0.0004 g. in weight. On heating for one hour over the blast lamp it lost 0.0051 g. (J. Weber.)

neutral solution containing about 0.1 g. of calcium in 25 ml. with 2 ml. of 6 *N* sulfuric acid, add four volumes of alcohol, and allow the mixture to stand 12 hours. Filter, wash with 70 per cent alcohol, gently ignite in a crucible and weigh.

3. Determination of Calcium as Carbonate, $CaCO_3$

Only in rare cases is calcium precipitated as carbonate by ammonium carbonate in the presence of ammonia. Gently ignite the filtered and washed precipitate and weigh as carbonate. After weighing, moisten the residue with a little ammonium carbonate solution, evaporate to dryness on the water-bath, and again ignite gently. This is done in order to change small amounts of calcium oxide, which may have been formed during the burning of the filter-paper, back to carbonate.

In the presence of considerable ammonium chloride the precipitation of calcium by means of ammonium carbonate is never complete whereas the precipitation with ammonium oxalate always is.

STRONTIUM, Sr. At. Wt. 87.63

Forms: $SrSO_4$, $SrCO_3$, SrO

The determination as the sulfate is the most accurate.

Determination of Strontium as Sulfate, $SrSO_4$

Procedure. — To 100 ml. of the neutral solution containing not more than 0.5 g. of strontium add 5 ml. of 6 *N* sulfuric acid and as much alcohol as there is volume of solution. Stir well, allow the mixture to stand twelve hours, filter and wash, at first with 50 per cent alcohol, to which a little sulfuric acid has been added, and finally with pure alcohol until the wash water no longer gives the sulfuric acid reaction. Dry, ignite, cool and weigh.

Remarks. — Only about 0.014 g. of $SrSO_4$ dissolves in 100 ml. of pure water. The addition of a little sulfuric acid decreases the solubility but if too much acid is added, the precipitate dissolves appreciably.

It is very soluble in concentrated sulfuric acid and appreciably soluble in dilute hydrochloric and nitric acids, acetic acid, and in concentrated solutions of magnesium or alkali chloride.

If considerable acid is present it should be removed by evaporation.

Determination of Strontium as Oxide, SrO, or as Carbonate, $SrCO_3$

Precipitate the strontium as carbonate, or as oxalate, and change by ignition to the oxide as described under calcium.

Strontium carbonate is decomposed by heat more difficultly than calcium carbonate and the determination as carbonate is very satis-

factory. It is advisable to treat the precipitate as described under calcium, although it is usually unnecessary to heat with additional ammonium carbonate.

Solubility of Strontium Carbonate in Water according to Fresenius

18,045 parts of water at ordinary temperatures dissolve 1 part of $SrCO_3$. In water containing ammonium carbonate the salt is much less soluble; on the other hand, ammonium chloride and ammonium nitrate increase its solubility. In case calcium, strontium, magnesium and alkali salts are present together, as in minerals and in mineral waters, the calcium and strontium are both precipitated as oxalates and transformed by ignition into the oxides. Cf. pp. 81, 83.

Solubility of Strontium Oxalate in Water

12,000 parts of water at ordinary temperatures dissolve 1 part of $SrC_2O_4 + 2\frac{1}{2}\ H_2O$. The solubility is very much less in water containing ammonium oxalate.

BARIUM, Ba. At. Wt. 137.37

Forms: $BaSO_4$, $BaCrO_4$, $BaCO_3$

1. Determination as Barium Sulfate

Dilute the solution so that it contains not more than 0.15 g. of barium per 100 ml. Make slightly acid with hydrochloric acid, heat to boiling and add a slight excess of hot, normal sulfuric acid. Use about 3 ml. of normal acid for each 100 ml. of solution. After the precipitate has settled, add a little more sulfuric acid to make sure that the precipitation is complete. After standing an hour or more in a warm place, decant the solution through a filter and wash four times by decantation with 50 ml. portions of hot water containing a few drops of sulfuric acid. Finally transfer the precipitate to the filter and wash with hot water till free from acid. Ignite the wet precipitate and filter in a platinum or porcelain crucible. Do not heat over the blast lamp or Méker burner, because barium sulfate is decomposed at about 900°. Cool in a desiccator and weigh as $BaSO_4$.

The precipitate usually contains a little chloride and the results are likely to be a little low. Sometimes a low result is caused by too rapid combustion of the filter which causes the formation of barium sulfide. To correct both of these errors, moisten the precipitate with a few drops of 18 *N* sulfuric acid, carefully evaporate off the acid, gently ignite and weigh again. Repeat the treatment until two successive weighings agree within 0.3 mg.

Remark. — It is difficult to get pure precipitates of barium sulfate.* One liter of pure water dissolves only about 0.3 mg. of barium sulfate and it is less soluble in

* Cf. M. J. van't Krys, *Z. anal. Chem.*, **1910**, 393.

water containing a little sulfuric acid. It is appreciably soluble in solutions containing more than about 1 ml. of 6 *N* mineral acid per 100 ml. and is very soluble in concentrated sulfuric acid. A full discussion of the problem of producing pure precipitates of barium sulfate is given under Sulfuric Acid.

The formation of a little barium sulfide during the ignition of the precipitate does not usually cause error for it is easily roasted back to sulfate by heating the inclined crucible with a small flame at the back, so that there is ready access of air into the crucible.

2. Determination of Barium as Chromate

Dilute the neutral solution, containing not more than 0.4 g. of barium, to 200 ml., add 10 drops of 6 *N* acetic acid, heat to boiling and slowly add a slight excess of ammonium chromate solution. Prepare the reagent by dissolving 12.5 g. of ammonium dichromate in 100 ml. of water and adding ammonium hydroxide until the color is a clear yellow. Allow the precipitate of barium chromate to settle and make sure that the precipitation is complete by adding a little more reagent. When cold, filter through a Gooch or Munroe crucible and wash with hot water until 20 drops of the filtrate give scarcely any reddish-brown coloration with a neutral solution of silver nitrate. Dry the precipitate in the hot closet, and then heat within a larger porcelain crucible (cf. p. 38) until the precipitate becomes a bright yellow.* Cool and weigh as $BaCrO_4$.

Solubility of Barium Chromate†

87,000 ml. of water at ordinary temperatures dissolve 1 g. $BaCrO_4$.
23,000 ml. of boiling water dissolve 1 g. $BaCrO_4$.
50,000 ml. of a 0.75 per cent ammonium acetate solution(at 15°) dissolve 1 g. $BaCrO_4$.
45,000 ml. of a 0.5 per cent ammonium nitrate solution (at 14°) dissolve 1 g. $BaCrO_4$.
24,000 ml. of a 1.5 per cent ammonium acetate solution (at 15°) dissolve 1 g. $BaCrO_4$.
23,000 ml. of 0.5 per cent ammonium nitrate solution dissolve 1 g. $BaCrO_4$.
3,700 ml. of 1 per cent acetic acid solution dissolve 1 g. $BaCrO_4$.
2,600 " 5 " " " 1 "
2,000 " 10 " " " 1 "
1,800 " 10 " chromic acid solution dissolve 1 g. $BaCrO_4$.

The solubility of barium chromate, therefore, increases considerably with increasing concentrations of either acetic or chromic acids; the solubility is affected to a much less degree by solutions containing neutral ammonium salts. By the additions of small amounts of neutral ammonium chromate the solubility becomes much less.

* Often some of the precipitate is reduced to chromic oxide by traces of organic matter, whereby it appears slightly greenish. By long-continued ignition in an open crucible, the chromic oxide is changed back to chromate, and the precipitate appears a homogeneous yellow throughout.

† P. Schweizer, *Z. anal. Chem.*, **1890**, p. 414, and R. Fresenius, *ibid.*, **1890**, p. 418.

Separation of the Alkaline Earths from Magnesium and from the Alkalies

I. Separation of Calcium from Magnesium (and Alkalies)

The separation depends upon the different solubilities of the two oxalates. Calcium oxalate is practically insoluble in hot water, whereas magnesium oxalate is fairly soluble; 1500 ml. of cold water, or 1300 ml. of boiling water, dissolve 1 g. of $MgC_2O_4 \cdot 2\,H_2O$. In an excess of the precipitant, however, magnesium oxalate is much more soluble owing to the formation of complex salts.

If calcium is precipitated as oxalate from a dilute solution in the presence of magnesium, some magnesium oxalate is *occluded* by the calcium oxalate precipitate even when the solution is by no means saturated with magnesium oxalate, and high results are obtained for calcium. In such cases the error is usually compensated according to Fresenius, by dissolving the precipitate in hydrochloric acid and repeating the precipitation with ammonia and ammonium oxalate.

The work of T. W. Richards* has shown, however, that the quantity of magnesium oxalate occluded is dependent upon the concentration of the *undissociated* magnesium oxalate in solution, and upon the time in which the calcium oxalate is in contact with the solution. Consequently anything that prevents the dissociation of magnesium oxalate will tend to increase the amount of occlusion and thereby increase the result of the calcium determination. Anything that will cause the ionization of the magnesium oxalate serves to reduce the amount of error.

Concentrating the solution and increasing the amount of oxalate ions in solution by the addition of considerable ammonium oxalate, both tend to repress the dissociation of the magnesium oxalate. The dissociation of this compound is favored by the presence of hydrogen ions and by dilution.

A considerable excess of ammonium oxalate is necessary in the quantitative precipitation of calcium and, moreover, magnesium oxalate forms readily soluble complex salts with undissociated ammonium oxalate. It is desirable, therefore, to prevent the dissociation of the ammonium oxalate as much as possible, and this is accomplished by the addition of another ammonium salt, preferably the chloride.

Procedure. — Dilute the solution with hot water so that not more than 0.3 g. of calcium or 0.08 g. of magnesium is present in 300 ml. If not already present, add 12 ml. of *N* ammonium chloride solution, heat to boiling and add 50 ml. of a hot solution of 1.0 g. pure oxalic acid crystals and 5 ml. of 6 *N* hydrochloric acid. Introduce a little methyl orange into the boiling solution, and add ammonia until a yellow coloration is produced. The ammonia should not be added all at once, but in small quantities from time to time so that about half an hour is consumed in the operation.

After the neutralization, add 10 ml. of hot, normal ammonium oxalate solution, allow to stand four hours but not longer on account of the fact that the occlusion increases with the length of time, filter,

* *Z. anorg. Chem.*, **28**, 71 (1901).

and wash with hot, one per cent ammonium oxalate until the filtrate gives no test for chloride after acidifying a sample with nitric acid.

Although this precipitate contains a little magnesium (0.1–0.2 per cent) it is also true that an almost equal amount of calcium passes into the filtrate, so that it is not advisable to repeat the precipitation when made in this way. Ignite the calcium oxalate precipitate as described under Calcium.

If more than ten times as much magnesium as calcium is present, it is necessary to dissolve the calcium oxalate precipitate in dilute hydrochloric acid and repeat the precipitation as before. To dissolve the precipitate, first wash as much as possible back into the beaker in which the precipitation took place, then pour three 5 ml. portions of hot 3 *N* hydrochloric acid upon the upper edge of the filter, washing it down each time with a stream of hot water from the wash bottle, and catching the filtrate in the beaker with the precipitate. Finally wash the filter with hot water, neutralize the last traces of acid with a little ammonia and save the filter for the purified precipitate. Heat the acid solution in the beaker until the calcium oxalate all dissolves, adding a little more acid if necessary.

In the filtrate from the calcium oxalate precipitate, using both filtrates if a double precipitation was made, determine the magnesium as pyrophosphate after precipitation as magnesium ammonium phosphate, as already described under Magnesium.

Determination of Calcium and Magnesium in Limestone and Dolomite

Limestone is impure, native calcium carbonate. Dolomite is an isomorphous mixture of calcium and magnesium carbonates. Samples of limestone and dolomite usually contain small quantities of ferrous and manganous carbonates and a little silica or silicate. For most purposes, it is desired to know the calcium and magnesium present as carbonate rather than the total calcium and magnesium. In other words, a commercial analysis would not take into consideration any calcium or magnesium present in the residue insoluble in acid.

Dissolving the Sample. — Weigh out duplicate portions of about 1 g. of the finely-ground and well-mixed sample into 250 ml. casseroles. Moisten the powder with 5 ml. of water, cover the casserole with a watch-glass and add 10 ml. of 6 *N* acid in small portions. When effervescence has ceased, wash off the bottom of the cover glass, raise it a little by means of a glass triangle and evaporate to dryness on the water bath. Heat the residue in the hot closet at 120° for one hour to thoroughly dehydrate any silica that may be present. Moisten the residue

with 10 ml. of 6 *N* hydrochloric acid and warm gently. Dilute with about 30 ml. of water, heat to boiling and filter off the insoluble, siliceous residue. Wash the residue twice with 5 ml. portions of hot, 2 *N* hydrochloric acid and then with hot water till free from chloride. The residue may be ignited and weighed if it is desired to know the amount of insoluble residue.

Precipitation of Iron, Aluminium and Manganese. — To the filtrate and washings add bromine water until a slight excess is present as shown by the color of the solution. Boil and add 6 *N* ammonia solution until a slight ammoniacal odor persists after blowing away the vapors. Heat again just to boiling and promptly filter off the precipitate of $Fe(OH)_3$, $Al(OH)_3$ and $MnO_2.H_2O$. Wash the precipitate 6 times in the small portions of hot water. Reserve the filtrate for the calcium and magnesium determinations.

Sometimes the precipitate contains a little calcium carbonate from the carbon dioxide in the air and often a little magnesium hydroxide. Wash the precipitate back into the casserole and pour 5 ml. of hot, 3 *N* hydrochloric acid on the upper edge of the filter. Wash down with hot water, collecting the acid that runs through the filter in the proper casserole. Continue the treatment with acid and water until all the precipitate left on the filter is dissolved. Finally wash the filter with a little dilute ammonia. Precipitate with bromine water and ammonia just as before, and wash this second precipitate till free from chloride.

Make the combined filtrate slightly acid with hydrochloric acid, bring to a volume of about 400 ml. and determine the calcium and magnesium as described above. Report the percentages of CaO and MgO present.

II. Separation of Strontium from Magnesium

This separation finds practical application in the analysis of almost all mineral waters and of minerals containing strontium. In all these cases, however strontium occurs in relatively small amounts in the presence of large amounts of calcium and varying amounts of magnesium, so that it is a question, first, of separating calcium and strontium from magnesium. This separation is effected by the precipitation of the calcium and strontium as oxalates as described on p. 86.

The filtrate containing magnesium may also contain traces of strontium. Remove ammonium salts by evaporating to dryness and heating the residue, dissolve this in hydrochloric acid, add sulfuric acid and alcohol, and allow the solution to stand for twelve hours. Filter off any resulting precipitate, consisting of strontium or barium sulfate, and weigh. From this filtrate precipitate the magnesium as magnesium ammonium phosphate as described on pp. 78, 79, and weigh as the pyrophosphate.

III. Separation of Barium from Magnesium

In case it is desired to separate only barium from magnesium, make the solution (which must be free from nitric acid) acid with hydrochloric acid, heat to boiling, and precipitate the barium by the addition of boiling, dilute sulfuric acid (cf. p. 84). Precipitate the magnesium in the filtrate as magnesium ammonium phosphate in the usual way.

In most cases, however, a separation of barium, strontium, and calcium from the magnesium is involved. Precipitate the three alkaline earths as oxalates as described for the separation of calcium from magnesium. A few milligrams of barium will escape precipitation. To recover this, add a little ammonium sulfate to the hot solution, filter, wash and weigh as $BaSO_4$. In the filtrate, determine the magnesium as pyrophosphate (p. 78).

IV. Separation of the Alkaline Earths from One Another

Principle. — The mixture of the dry nitrates is treated with ether-alcohol, which dissolves calcium nitrate alone. The residue is taken up in water, the barium is precipitated as chromate, and the strontium is determined in the filtrate as sulfate.

PROCEDURE

(*a*) Separation of Calcium from Strontium and Barium according to Rose-Stromeyer-Fresenius

The three metals are assumed to be present together in solution in the form of their nitrates. Evaporate the solution in a small Erlenmeyer flask, as described under lithium, p. 69, while passing a stream of dry, warm air through the flask. When all the water is evaporated, raise the temperature of the oil-bath to 140° and maintain this temperature for one to two hours, still passing the current of warm air through the flask. Cool, treat the dry residue with ten times its weight of absolute alcohol, stopper the flask and allow it to stand with frequent shaking for one to two hours. Add an equal volume of ether, close the flask, shake, and allow it to stand twelve hours. Filter through a filter moistened with ether-alcohol and wash with ether-alcohol until a few drops of the filtrate evaporated on platinum-foil leave no residue.

Evaporate the filtrate to dryness on a lukewarm water-bath, dissolve the calcium nitrate in water, precipitate as the oxalate, and, after ignition, weigh as the oxide.

Remark. — If only a small amount of calcium is present (not more than about 0.5 g.) the above separation is complete. With large amounts of calcium, the residue of strontium and barium nitrates almost always contains some calcium. In this case evaporate the aqueous solution again to dryness in the same way as before and repeat the treatment with alcohol and ether. Determine the calcium in the combined filtrates.

(*b*) Separation of Barium from Strontium according to Fresenius*

Requirements. — 1. Ammonium bichromate solution. Dissolve 100 g. of ammonium bichromate (free from sulfate) in 500 ml. of water, add 135 ml. of 6 *N* ammonium hydroxide solution, filter if necessary and dilute to one liter.

2. Ammonium acetate solution. Dissolve 231 g. in one liter of water or mix equal volumes of 6 *N* acetic acid and 6 *N* ammonia, leaving the solution slightly ammoniacal rather than acid.

3. Acetic acid, 6-normal.

4. Nitric acid, 2-normal.

Procedure. — Dissolve the residue of strontium and barium nitrates obtained after the above treatment with ether-alcohol in a little water and dilute the solution until the concentration corresponds to about 1 g. of mixed nitrates in 300 ml., heat to boiling, add 10 drops of acetic acid and about 10 ml. of ammonium chromate solution (this should be an excess over the theoretical amount necessary) and allow to stand one hour. Wash the precipitate of barium chromate by decantation, with water containing 25 ml. of ammonium chromate solution per liter, until the wash water no longer gives a precipitate with ammonia and ammonium carbonate; then wash with hot water containing 25 ml. of ammonium acetate solution per liter until the last washing gives only a slight reddish-brown coloration with neutral silver nitrate solution.

The precipitate on the filter still contains a little strontium. Carefully wash it back into the vessel in which the precipitation took place, and dissolve any precipitate remaining on the filter in a little hot 2 *N* nitric acid allowing it to run through the filter vessel containing the precipitate. Wash the filter with hot water till free from acid. Heat the precipitate till it dissolves in the dilute nitric acid (about 6 ml. is usually sufficient). Dilute the solution to 200 ml., heat to boiling, add 5 ml. of ammonium acetate solution, little by little, and finally enough ammonium chromate solution to cause the disappearance of the odor of acetic acid from the solution (usually about 10 ml. are necessary). After standing one hour pour the liquid through a Gooch crucible, cover the residue in the dish with hot water, allow to cool, filter and wash with cold water until the filtrate gives only a slight opalescence with neutral silver nitrate. Dry the precipitate, ignite gently in an air-bath (cf. p. 38), and weigh as $BaCrO_4$.

Add 1 ml. of 6 *N* nitric acid to the filtrate, concentrate somewhat, and precipitate the strontium as carbonate by the addition of ammonia and ammonium carbonate. The precipitate always contains some strontium chromate. Wash it once with hot water, dissolve in hydrochloric acid, and determine the strontium as sulfate, according to p. 83.

The results obtained according to this method are very satisfactory.

* *Z. anal. Chem.*, **29**, 427 (1890), **44**, 742 (1906).

METALS OF GROUP III

ALUMINIUM, CHROMIUM, TITANIUM, IRON, URANIUM, NICKEL, COBALT, ZINC, AND MANGANESE

A. DIVISION OF THE SESQUIOXIDES

ALUMINIUM, CHROMIUM, IRON, TITANIUM, AND URANIUM

ALUMINIUM, Al. At. Wt. 27.0

Form: Al_2O_3

To determine aluminium as oxide, it is precipitated as the hydrated oxide which, as van Bemmelen has shown, is really $Al_2O_3.xH_2O$ rather than the hypothetical $Al(OH)_3$.

The hydrated oxide is amphoteric and also tends to form colloidal solutions. Because of its amphoteric nature it is best precipitated, as Blum* has shown, by keeping the hydrogen ion concentration at about 10^{-7}, as it is in pure water. Because of the colloidal nature of the precipitate it is advisable to have ammonium salt in the solution and to wash the precipitate with water containing ammonium salt. The ammonium salt also prevents the precipitation of magnesium hydroxide by repressing the ionization of ammonium hydroxide.

Procedure. — To the solution containing at least 5 g. of ammonium chloride per 200 ml., or an equivalent quantity of hydrochloric acid, add a few drops of methyl red indicator (0.2 per cent alcoholic solution) and heat just to boiling. Add 6 *N* ammonium hydroxide until the color of the solution changes to a distinct yellow. Boil for two minutes and filter promptly. Wash the precipitate thoroughly with hot, 2 per cent ammonium nitrate solution. Ignite in an open crucible, cool and weigh as Al_2O_3.

Remark. — The ammonia should be freshly distilled. When kept for any length of time in glass bottles it invariably contains a little dissolved silica and alumina and gives high results. Because of the solvent effect of acids and bases on glass only glass of the boro-silicate type should be used in the chemical laboratory.

Determination of Aluminium by the Method of Chancel†

In the determination of aluminium in a sample of alum by precipitation with ammonia, there are a number of difficulties to overcome. In the first place the precipitate always contains a little basic aluminium sulfate, and it requires long ignition to expel the last traces of sulfuric anhydride. It is, to be sure, possible to wash out all the sulfate by means of a solution of ammonia and ammonium nitrate but the operation is tedious and a large quantity of the wash liquid is required. Another

* *J. Am. Chem. Soc.*, **38**, 1282 (1916).

† *Compt. rend.*, **46**, 987; *Z. anal. Chem.*, **3**, 391.

disadvantage arises from the fact that the filtration takes place very slowly, even when the precipitate contains basic sulfate, on account of the slimy nature of aluminium hydroxide. By the method of Chancel and in the two following methods these difficulties are overcome.

The principle of this and the following methods consists in neutralizing, by salts of weak acids, the mineral acid that is set free in the hydrolysis of an aluminium salt; the weak acid is finally removed by boiling or neutralization. In the Chancel method the mineral acid is neutralized by sodium thiosulfate,

$$2\,Al^{+++} + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 6\,H^+$$
$$6\,H^+ + 3\,S_2O_3^{--} \rightarrow 3\,SO_2\uparrow + 3\,S$$

Procedure. — Add to the dilute, neutral solution (about 0.1 g. Al in 200 ml.) an excess of sodium thiosulfate and boil until all traces of SO_2 are expelled. Add 6 *N* ammonium hydroxide* until its odor is barely perceptible after blowing away the vapors, and continue boiling a little longer. Filter off the precipitate of $Al(OH)_3$ and S, wash it with hot 2 per cent ammonium nitrate solution, and ignite in a porcelain crucible. Such a precipitate of hydrated Al_2O_3 is much denser than that produced by direct precipitation with ammonia and it is very easy to filter and wash.

Remark. — This method is often employed for separating aluminium from iron. Ferric iron is reduced to ferrous salt by the sodium thiosulfate and is not precipitated. In this case, however, the final neutralization with ammonia, as prescribed in the above directions, should not be carried out or a little iron will come down. The separation of iron from aluminium in this way is inaccurate.

Determination of Aluminium by the Method of Alfred Stock†

The aqueous solution of the aluminium salt, which on account of hydrolysis always shows an acid reaction,

$$Al^{+++} + 3\,HOH \rightleftarrows Al(OH)_3 + 3\,H^+$$

is treated in the cold with a mixture of potassium iodide and potassium iodate. This mixture in the presence of acid is decomposed in accordance with the equation,

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,H_2O + 3\,I_2$$

whereby the equilibrium which existed in the hydrolysis of the aluminium salt is disturbed and the first reaction continues to take place until all the aluminum is precipitated. If now the iodine in the solution is made to react with sodium thiosulfate and the mixture is heated on the water bath for half an hour, the precipitation of the aluminium is complete and the precipitate is in such a condition that it can be quickly filtered and washed.

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* If the addition of ammonia is omitted, the solution will retain traces of aluminium.

† Ber., **1900**, 548.

Procedure. — The solution in which the aluminum is to be determined should be very slightly acid; if more acid is present add sodium hydroxide solution until a slight permanent precipitate is obtained. Redissolve by means of a few drops of hydrochloric acid. Add equal volumes of a 25 per cent potassium iodide solution and a saturated potassium iodate solution (about 7 per cent KIO_3). After about five minutes, decolorize the solution by the addition of a 20 per cent sodium thiosulfate solution and add a little more of the potassium iodide and iodate mixture to make sure that enough is present. Add 1 or 2 ml. more of sodium thiosulfate solution and heat the mixture half an hour on the water bath. The pure white precipitate settles out well, and can be filtered through a filter with relatively wide pores, washed with hot 2 per cent ammonium nitrate solution, ignited and weighed as Al_2O_3.

Remark. — The presence of calcium, magnesium and boric acid does not interfere with the above determination, but if phosphoric acid is present, aluminium phosphate is precipitated. It is obvious that the method cannot be employed in the presence of organic substances such as tartaric acid, citric acid, sugar, etc., which prevent the precipitation of hydrated alumina.

Determination of Aluminium by the Method of G. Wynkoop* and of E. Schirm†

Principle. — If a neutral solution of aluminium (iron, chromium, or titanium) is boiled with an excess of sodium or ammonium nitrite until no more fumes are evolved, aluminium hydroxide is precipitated in a form that can be as easily filtered as that of the last methods.

$$2\ Al^{+++} + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 6\ H^+$$

$$6\ H^+ + 6\ NO_2^- \rightarrow 6\ HNO_2 \qquad 6\ HNO_2 \rightarrow 3\ H_2O + 3\ NO + 3\ NO_2$$

Procedure. — If the solution is acid, add ammonia until the precipitate first formed dissolves only slowly on stirring. Add an excess of a 6 per cent solution of pure ammonium nitrite,‡ dilute the solution to 250 ml. and boil until no more fumes of nitrous oxides are evolved (about 20 minutes). Filter off the precipitate, wash with hot 2 per cent ammonium nitrate solution, ignite wet in a platinum crucible, and weigh as Al_2O_3.

Remark. — In the presence of more than 1 per cent of ammonium salts, these are hydrolyzed enough so that the solution remains acid and the precipitation of the aluminium is incomplete even after long boiling. In such a case, after the vapors of

* *J. Am. Chem. Soc.*, **19**, 434 (1897).

† *Chem. Ztg.*, **1909**, 877.

‡ Sometimes the reagent contains a little barium which should be precipitated with ammonium sulphate before using it in an analysis.

nitrogen peroxide are no longer visible, add 6 *N* ammonium hydroxide, drop by drop, until the odor is barely perceptible. Allow the precipitate to settle while the beaker is on the water-bath, and finish the analysis as above.

If the solution contains only aluminium in the form of its chloride, nitrate, or sulfate, it can be determined by evaporating the solution in a platinum crucible on the water-bath with the addition of a little sulfuric acid, the excess of the latter being finally removed by cautious heating over the free flame in an inclined crucible. The residue of aluminium sulfate can be changed to the oxide by strong ignition over the blast-lamp.

In the case of organic salts of organic acids, the oxide is readily obtained by careful ignition of the salt in a platinum crucible.

IRON, Fe. At. Wt. 55.84

Forms: Ferric Oxide, Fe_2O_3, and Metallic Iron

Determination as Fe_2O_3

1. By Precipitation with Ammonia

The precipitation of ferric iron by means of ammonium hydroxide can be accomplished as described under Aluminium but when only iron is present it is not necessary to keep the solution so near the neutral point because ferric hydroxide is not appreciably dissolved by an excess of ammonia and does not form a colloidal solution when washed with a moderate amount of hot water. The same precautions described under Aluminium should be taken with regard to the use of freshly-distilled ammonium hydroxide and the use of the best grades of glass that are not attacked to any extent by dilute bases. The precipitate is rather bulky; an ordinary 9 cm. filter will not hold but about 0.2 g. of iron as hydrated oxide.

Procedure. — Heat the solution to about 70° and at a volume of 200–300 ml., precipitate hydrated ferric oxide by the addition of a slight excess of 6-normal ammonium hydroxide. Allow the precipitate to settle and wash it twice by decantation with 50 ml. portions of hot water. Wash with hot water or hot 2 per cent ammonium nitrate solution until free from chloride. Do not wash with ammonium chloride solution because ferric chloride is volatile upon ignition. Ignite slowly and carefully in an open porcelain or platinum crucible and weigh as Fe_2O_3.

Remarks. — It is not advisable to heat the precipitate over the blast because Fe_3O_4 is formed at high temperatures. This magnetic oxide is also formed if the carbon of the filter is not consumed at a low temperature. When once formed it is very difficult to get it back to the less stable Fe_2O_3. The color of the ignited oxide does not indicate the presence of magnetite, for pure ferric oxide is nearly black after strong ignition. The ignited oxide is difficultly soluble in dilute hydrochloric acid but can be dissolved by long digestion with concentrated hydrochloric acid on the water bath.

The wash-bottle shown in Fig. 35 is useful for work with hot water or with bad-smelling wash-liquids. It contains two tubes like the ordinary wash bottle but at

the end of the tube A a Bunsen valve is placed. This is made by cutting a slit in a short piece of rubber tubing, placing this on the end of the tube through which one blows in using the bottle and sealing the other end of the rubber tubing with a piece of glass rod. On blowing the slit opens but closes to prevent escape of steam. The third tube C is closed by the finger when using the bottle or by means of rubber tubing and a pinch cock. After blowing through A, a stream of water is ejected at B if C is kept closed. When C is opened the stream stops. It is well to wind the neck of the wash bottle with heavy curtain cord, if it is to be used for hot water.

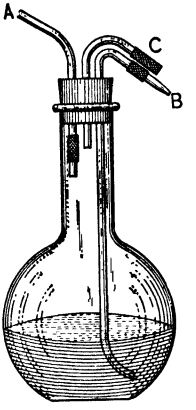


FIG. 35.

If the iron is in solution either as the ferrous or ferric salt of a volatile acid, it can be readily converted into ferric oxide by evaporation with sulfuric acid and ignition of the residue.

2. Determination as Metallic Iron

Iron may be determined by electrolysis, but this method offers no advantages over the gravimetric method just described or the following volumetric process, so that it will not be discussed in this book.

In the case of the analysis of oxidic iron ores or of mixtures of considerable iron oxide with comparatively little alumina, titanium dioxide, or silica, the following method is accurate and rapid.*

Weigh the finely-powdered† substance in a porcelain boat. Introduce the boat into a tube of difficultly fusible glass and heat to redness in a stream of dry hydrogen until no more drops of water condense on the cool, front end of the tube and the contents of the boat appear gray and not black. By this means the ferric oxide is reduced to metallic iron:

$$Fe_2O_3 + 3\,H_2 = 3\,H_2O + 2\,Fe.$$

After cooling in the stream of hydrogen, again weigh the boat and its contents after they have remained some time in a desiccator. The loss in weight p represents the amount of oxygen originally combined with the iron, from which the amount of iron can be calculated:

$$\frac{2\,Fe}{3\,O} \cdot p = 2.326\,p = \text{wt. of iron}$$

Remark. — In attempting to reduce ferric oxide to iron by means of hydrogen, it is very important to heat the oxide to bright redness. At a dull red heat, the oxide

* Rivot, *Ann. chem. phys.*, [3] **30**, 188 (1850); *Liebig's Ann.*, **78**, 211 (185).

† Ferric oxide after having been powdered and ignited is so hygroscopic that the porcelain boat should be placed within a weighing-beaker with ground-glass top immediately after removing it from the desiccator, and then weighed.

is to be sure reduced to metal, but in such cases black, pyrophoric iron is formed and the latter cannot be exposed to the air and weighed without becoming oxidized. By heating to a bright red heat, however, the iron becomes gray, is no longer pyrophoric, and can, if allowed to cool in the stream of hydrogen, which is subsequently replaced by carbon dioxide, be safely weighed in the air without fear of oxidation.

Although this method is extremely simple, and the corresponding oxides of aluminium, chromium, titanium and zircon, etc., are not reduced under the same conditions, it should be used with caution and only when the ferric oxide greatly predominates in a mixture of oxides. Otherwise the reduction of the iron is incomplete on account of some of the ferric oxide being enclosed within the particles of foreign oxide. This has been proved by the work of Daniel and Leberle* and by Treadwell and Wegelin. Moreover, the above computation shows that the error in determining the weight of reduced iron is multiplied by 2.33 in the computed weight iron.

It is more accurate to dissolve the metallic iron in dilute sulfuric acid out of contact with the air and determine the amount present volumetrically by titrating with potassium permanganate solution.

3. Volumetric Determination of Iron, according to Margueritte.†

Although the volumetric methods are discussed in the second part of this book, this determination is so important and is so often used to test the purity of the iron oxide produced by a gravimetric analysis that it seems proper to discuss it at this place.

Principle of the Method

Ferrous salts are oxidized by potassium permanganate in acid solution to ferric salts:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,Fe_2(SO_4)_3.$$

If, therefore, a potassium permanganate solution of known strength is slowly added to the solution of a ferrous salt, it will be decolorized as long as there remains ferrous salt to react with it. As soon as all of the ferrous salt has been oxidized, the next drop of the permanganate will impart a permanent pink color to the solution, whereby the *end-point* of the reaction is determined.

Preparation and Standardization of the Permanganate Solution

The concentrations of the standard solutions used in volumetric analysis are usually referred to the so-called *normal* concentration. A *normal* solution is one that contains *one equivalent weight in grams*

* *Z. anorg. Chem.*, **34**, 393 (1903).

† *Ann. chim. phys.* [3], **18**, 244 (1846).

per liter. It has been assumed throughout this volume that the abbreviation *N* signifies a concentration of one equivalent weight in grams per liter, that 6 *N* represents a solution 6 times as strong and 0.1 *N* represents a concentration of one-tenth an equivalent weight in grams per liter.

An equivalent weight of a salt *as precipitant* is determined by the valence of the characteristic ion. Thus the molecular weights of NaCl, $AgNO_3$ and KCNS and one-half the molecular weights of $BaCl_2$, $(NH_4)_2CO_3$, and $CaCO_3$ are equivalent weights.

An equivalent weight of an *acid* is determined by the number of replaceable hydrogen atoms in the molecule and of a base by the number of replaceable hydroxyl ions. Thus the molecular weights of HCl, HNO_3, KOH and NH_4OH and one-half the molecular weights of H_2SO_4, and $Ba(OH)_2$ are equivalent weights.

As an *oxidant* or as a *reductant* the equivalent weight is determined by the *change in valence* which takes place when the reaction of oxidation and reduction occurs. Thus, in the above equation which may also be expressed as follows:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$

the manganese is reduced from a valence of seven in permanganate to a valence of two in the manganous salt while the iron is changed from a valence of two to a valence of three.

Therefore, in the oxidation of a ferrous salt by permanganate the equivalent weight of permanganate is one-fifth the molecular weight and the equivalent weight of the ferrous salt is that weight which contains an atomic weight in grams of iron.

For titrations with permanganate a tenth-normal solution is commonly used. To make 0.1 *N* $KMnO_4$ solution take one-fiftieth of the molecular weight in grams, or 3.161 g. of $KMnO_4$.

Although it is possible to purchase very pure potassium permanganate, it is not advisable to take the trouble of weighing out just this amount of the substance and dissolving it in exactly enough water, for the distilled water in which the permanganate is dissolved almost always contains traces of organic matter oxidizable by the permanganate. Consequently it is better to weigh out on a watch-glass approximately 3.2 g. of permanganate, dissolve it in a liter of water, boil 10–15 minutes, allow to cool over night and then filter through asbestos.* After this time all of the oxidizable matter in the water will have been completely destroyed. Filter the solution through an asbestos filter and then standardize. The addition of 10 g. of KOH per liter increases the stability of the solution.

* Cf. Morse, Hopkins, and Walker, *Am. Chem. Jour.*, **18** (1896), p. 401.

Standardization of the Potassium Permanganate Solution

It is possible to standardize a solution of permanganate by a number of different methods. In this case the most natural way would seem to be to take a sample of pure ferrous salt or to make a ferrous solution from a weight of pure iron. Owing to the difficulty in procuring a sample of perfectly pure ferrous salt or of perfectly pure iron, it is generally considered better to standardize against pure sodium oxalate. Specially purified sodium oxalate can now be purchased from dealers in chemicals and can also be obtained from the United States Bureau of Standards at Washington, D. C.

Procedure. — Weigh to the nearest tenth of a milligram from 0.22 to 0.3 g. of pure sodium oxalate into a 300–400 ml. beaker. Add about 240 ml. of hot water and 12 ml. of 6 *N* sulfuric acid. Heat nearly to boiling and titrate the stirred solution slowly with the permanganate. The temperature should be between 80° and 90° at the start and not less than 60° at the end. At first the permanganate will be decolorized very slowly. Do not add a second drop until the first drop has been decolorized. After a little manganous salt is formed the reaction takes place more rapidly. The permanganate should not be added so fast that the drops cannot be counted and the color should be discharged as fast as the permanganate is added. Titrate slowly toward the last and make a blank to determine how much permanganate is required to color 250 ml. of hot water to the shade taken as the end point. Deduct this from the total volume of permanganate solution used in all titrations.

To compute the normal concentration of the permanganate, first find the weight of sodium oxalate oxidized by 1 ml. of permanganate by dividing the weight taken by the number of milliliters of permanganate used. From the reaction,

$$2\,MnO_4^- + 5\,C_2O_4^{--} + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,CO_2\uparrow + 8\,H_2O,$$

it is evident that the equivalent weight of sodium oxalate is one-half the molecular weight, or 67.00. One liter of normal permanganate, therefore, would oxidize 67 g. of sodium oxalate and 1 ml. would oxidize 0.067 g. of $Na_2C_2O_4$. To find the normal concentration of the permanganate, divide the weight oxidized by 1 ml. of permanganate solution by the milli-equivalent, 0.067 of sodium oxalate.

Thus if a gram of pure $Na_2C_2O_4$ reacted with t ml. of the given permanganate, then $\frac{a}{t \times 0.067}$ is the normal concentration or *normality* of the permanganate. To find the weight of any other substance which reacts similarly with the permanganate multiply by the milli-equivalent of the substance. Thus as the milli-equivalent of iron

when it is oxidized by permanganate from the ferrous to ferric condition is 0.05584 g. then using the above notation,

$$1 \text{ ml. of } \frac{a}{t \times 0.067} N \text{ } KMnO_4 = \frac{a \times 0.05584}{t \times 0.067} \text{ g. of Fe.}$$

Analysis of Ferric Compounds according to the Method of Margueritte

From what has already been said, it is evident that in order to determine the amount of iron present in a solution by titration with potassium permanganate, it is necessary for the iron to be present entirely in the ferrous condition. To apply this method therefore to the analysis of ferric compounds, it is first necessary to reduce them completely.

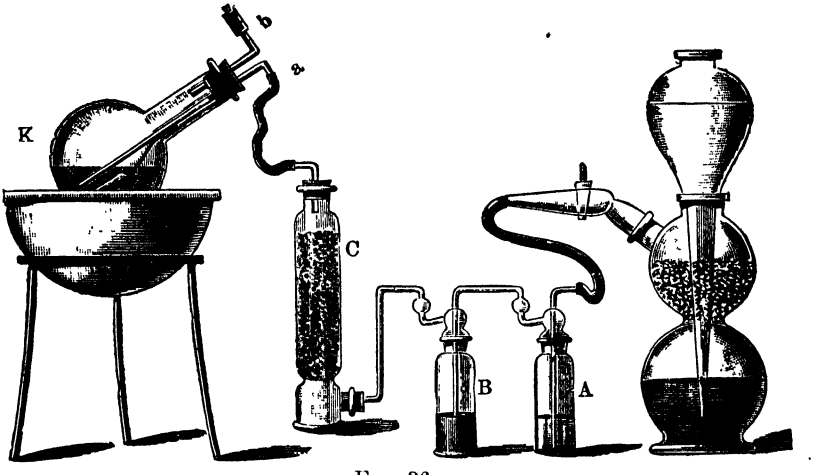


FIG. 36.

*Procedure.** — Transfer the solution to a 200 ml. flask (*K*, Fig. 36) which is fitted with a rubber stopper carrying glass tubes for the entrance and exit of gas. The volume of the solution should be approximately 100 ml. and it should not contain more than 0.15 g. of iron. Add 5 ml. of 18 *N* sulfuric acid and introduce hydrogen sulfide gas into the cold solution for 30 minutes and for 15 minutes as it is slowly heated to boiling. Then add 15 ml. more of 18 *N* sulfuric acid and continue the gentle boiling for at least 30 minutes, while a stream of carbon dioxide is bubbled through the solution. In the train shown in Fig. 36, the bottle *A* contains water, the bottle *B* a fairly strong solution of permanganate and the tower *C* pumice wet with copper sulfate solution. In this way all hydrogen sulfide or other reducing gas is removed from

* The conditions given in these directions are those recommended by Lundell and Knowles, *J. Am. Chem. Soc.*, **43**, 1565 (1921).

the carbon dioxide. After the excess hydrogen sulfide has all been removed and the volume of the solution reduced to about 50 ml., allow the solution to cool while the stream of carbon dioxide is still passing. Dilute with 200 ml. of cold water and titrate with standard permanganate solution.

The precipitate of sulfur formed during the reduction of the ferric salt by the hydrogen sulfide does no harm if the above directions are followed closely. If it is desired to remove any precipitated sulfide, the solution should be filtered before the last addition of acid and the filtrate given a further, short treatment with hydrogen sulfide.

If t ml. of permanganate were necessary to oxidize the solution completely and 1 ml. of the permanganate corresponds to a g. of iron, then the titrated solution evidently contains $a \cdot t$ g. of iron.

Besides hydrogen sulfide, a great many other substances can be used to reduce the ferric salt, *e.g.*, zinc, sulfurous acid, stannous chloride. The use of these substances will be discussed in the portion of this book devoted to Volumetric Analysis.

Remark. — The titration of a solution by means of potassium permanganate takes place preferably in a sulfuric acid solution; in the case of hydrochloric acid too high results will be obtained (due to the fact that the permanganate oxidizes some of the acid), unless the oxidation takes place in a dilute solution in the presence of a large excess of manganous sulfate. See Volumetric Analysis.

Determination of Iron in Ferrous Sulfate or Ferrous Ammonium Sulfate

The determination of iron is one of the best known of all the gravimetric methods of analysis and for many years it has been the custom to require most students of analytical chemistry in the colleges of the United States to carry out an analysis of ferrous sulfate or of ferrous ammonium sulfate. In a sulfate solution, there is always some basic ferric sulfate formed if the precipitation of ferric hydroxide is accomplished in accordance with the directions for precipitating aluminium with ammonia. It is the general practice, therefore, to dissolve the first precipitate in acid and repeat the precipitation with ammonia.

It has been shown, however, that the formation of basic sulfate can be prevented if a considerable excess of ammonium hydroxide is used.

Procedure. — Weigh out, to the nearest milligram, duplicate portions of about 1 g. into 400 ml. beakers. Moisten the sample with 5 ml. of 6 N hydrochloric acid, dilute with 50 ml. of water and heat, if necessary, to dissolve the sample. Heat nearly to boiling and to the hot solution add concentrated nitric acid, drop by drop, until the iron is all oxidized to the ferric condition. When the iron is partially oxidized, the nitric oxide combines with the excess of ferrous salt, forming a dark brown, unstable compound. Continue adding the nitric acid until the dark color fades and a clear yellow solution is obtained. Not more than

about 1 ml. of nitric acid should be necessary. Boil gently for about 3 minutes to remove the reduced nitrous compounds. Dilute to about 200 ml. and neutralize with ammonium hydroxide, finally adding 5–7 ml. of concentrated ammonium hydroxide in excess. Heat carefully to about 70° and allow the precipitate to settle. Filter, wash, ignite and weigh as described on page 94.

Determine the sulfate in the filtrate as described under Sulfuric Acid.

TITANIUM, Ti. At. Wt. 48.1

Titanium occurs very commonly in rocks but usually only in small quantities. It occurs together with zirconium, cerium and thorium and is very similar to zirconium in its chemical behavior.

For the determination of small quantities of titanium the colorimetric method is very satisfactory except when large quantities of iron, phosphorus, alkali salts, or even traces of vanadium are present. When these elements interfere it is not advisable to try the colorimetric determination until after they have been removed.

When titanium is unaccompanied by other cations of this group it is best to precipitate it with ammonia. The precipitate of $Ti(OH)_4$, or hydrated TiO_2, is not dissolved by an excess of ammonia and is easily converted into TiO_2 by ignition.

In most cases it is necessary to remove titanium from interfering elements and then, after the separation has been accomplished, it is best to determine the titanium volumetrically or colorimetrically.

Titanium is precipitated as hydroxide by boiling the dilute solution of the sulfate. Formerly, it was the common custom to precipitate titanium in this way but it requires such long boiling of the nearly neutral solution that it has been generally abandoned. The Gooch method depends upon adding alkali acetate and carrying out a basic acetate precipitation. The titanium precipitates in the presence of sufficient acetic acid to keep most of the aluminium in solution. The Baskerville method is based upon the fact that a nearly neutral solution of titanium and iron chlorides when boiled with sulfurous acid at moderate dilution gives a precipitate of titanium hydroxide while the iron remains in solution in the ferrous state. Thornton recommends the use of cupferron (ammonium nitrosophenylhydroxylamine). These methods will be discussed under the separations described a little farther on.

(*a*) Determination as Titanium Dioxide

Precipitate with ammonia in the manner described under Iron (p. 94) or, to the nearly neutral solution, add 10 g. of ammonium acetate and

10 ml. o. glacial acetic acid. Dilute to about 150 ml., heat to boiling and filter. Wash the precipitate with 7 per cent acetic acid, ignite and weigh as TiO_2.

(*b*) Determination of Titanium Colorimetrically; Method of A. Weller

(Suitable for small amounts of titanium.)

This determination depends upon the fact that acid solutions of titanium sulfate are colored intensely yellow when treated with hydrogen peroxide; the yellow color increases with the amount of titanium present and is not altered by an excess of hydrogen peroxide. On the other hand, inaccurate results are obtained in the presence of hydrofluoric acid (Hillebrand); consequently it is not permissible to use hydrogen peroxide for this determination which has been prepared from barium peroxide by means of fluosilicic acid.† The so-called " perhydrol " is excellent though other commercial brands of hydrogen peroxide are satisfactory. Furthermore, chromic, vanadic, and molybdic acids must not be present, since they also give colorations with hydrogen peroxide. The presence of small amounts of iron does not affect the reaction, but large amounts of iron cause trouble on account of the color of the iron solution.

Alkali sulfates have a marked bleaching effect unless considerable sulfuric acid is present and even then a slight effect is noticeable.

Preparation of the Standard. — Heat 0.600 g. of pure, recrystallized potassium fluortitanate, K_2TiF_6 with sulfuric acid in a platinum dish until all the fluorine is evolved. Add a little more sulfuric acid, evaporate to small volume but not to dryness and repeat the treatment several times. Finally dilute with 5 per cent sulfuric acid to 200 ml. One milliliter of this solution corresponds to 0.001 g. of TiO_2. To make sure that the standard is correct, dilute 50 ml. to about 150 ml., add a slight excess of ammonia, heat nearly to boiling, filter, wash with hot water till free from potassium, ignite and weigh as TiO_2.

Preserve the standard solution in a glass-stoppered bottle with the stopper coated with vaseline. Always withdraw the solution by means of a pipet, never by pouring it out.

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* *Ber.*, **15**, 2593 (1882).

† To test for fluorine, — Add a slight excess of sodium carbonate to 50 ml. of the reagent and heat to decompose the peroxide. Filter if a precipitate forms and add to the boiling solution an excess of calcium chloride. Filter and ignite the precipitate. Add acetic acid till the calcium carbonate is dissolved, filter, wash and ignite the residue gently. Test with sulfuric acid to see if a gas is evolved which will etch glass, or with sulfuric acid and silica to see if a gas is evolved which makes a drop of water turbid.

In making an analysis, take 5 ml. of the standard solution, mix with sufficient hydrogen peroxide to fully oxidize it (1 or 2 ml. of the 3 per cent reagent) and dilute with 5 per cent sulfuric acid to 50 ml. in a measuring flask. Each cubic centimeter of this diluted standard contains 0.1 mg. of TiO_2.

The Test Solution. — It is most convenient in rock analysis to determine titanium in the solution which has been used for the titration of the total iron after fusing Al_2O_3, Fe_2O_3 etc. with $K_2S_2O_7$. For accurate work, however, correction should be made for the iron and alkali content.

If necessary, evaporate the sulfate solution containing the titanium to less than 100 ml. It should contain 5 per cent or more of sulfuric acid. Add sufficient hydrogen peroxide to fully oxidize the titanium. Then, if the color is less than that of the standard, dilute to exactly 100 ml. If the color is deeper, dilute to 200 ml. or until the shade is weaker than the standard. Using a colorimeter or Nessler tube, dilute 10 ml. of the standard solution with 5 per cent sulfuric acid from a buret until the color matches, when viewed horizontally, that of the solution being analyzed. Repeat the comparison with several portions of the standard. Then, since the volume of the diluted standard and its titanium content are known, it is easy to compute the weight of TiO_2 per ml. of the solution being analyzed. Thus if a ml. of the standard (0.1 mg. per ml.) were diluted with b ml. of acid to make it correspond to the color of the tested solution, of which the total volume was A ml. then

$$\frac{0.1\,a \times A}{a+b} = \text{mg. } TiO_2 \text{ present.}$$

To correct for iron, it is usually sufficient to assume that the coloring power of 0.1 g. of Fe_2O_3 in 100 ml. of 5 per cent sulfuric acid is about equal to 0.2 mg. of TiO_2 in the same volume. It is more exact, however, to add to the standard a quantity of ferric alum solution that corresponds to the weight of iron in the sample. If A is the ml. of the test solution used in a preliminary test, made as just described, a the ml. of the standard used, b the ml. of acid used, p the weight of Fe_2O_3 corresponding to the iron in A and x the weight of iron (in terms of Fe_2O_3) which should be present in each milliliter of 5 per cent sulfuric acid used for diluting the standard, then since bx is the weight of Fe_2O_3 in $(a + b)$ ml. of diluted standard and $\frac{p}{A}$ is the weight of Fe_2O_3 per ml. of solution being tested, we have

$$\frac{p}{A} = \frac{bx}{a+b} \text{ and } x = \frac{p\,(a+b)}{Ab}.$$

To correct for the bleaching effect of alkali sulfate, a similar computation will show how much should be added to the 5 per cent sulfuric acid solution used in diluting the standard. In ordinary rock analysis, however, no correction need be applied for the alkali sulfate present if the TiO_2 content exceeds 0.02 g., when 6 g. of potassium pyrosulfate is used for fusing the ignited Al_2O_3, Fe_2O_3 etc., and the melt is dissolved in 100 ml. of 5 per cent sufuric acid. If the TiO_2 content is between 0.002 and 0.01 g., the weight of TiO_2 found by the test is too low by 0.0004 g.

If vanadium is present, precipitate the titanium (and vanadium) with ammonia and fuse with sodium carbonate. Sodium vanadate is formed which dissolves in water. Sodium titanate is hydrolyzed and none of it dissolves in water. After extracting with water, therefore, fuse the residue with $K_2S_2O_7$ and dissolve the melt in 5 per cent sulfuric acid.

Considerable phosphoric acid has a bleaching effect but the quantity present in rocks is too small to be serious. It is not advisable, however, to attempt to compensate the effect of ferric sulfate by adding phosphoric acid, although this practice has been recommended.

According to J. H. Walton, Jr.,* titanium in the presence of iron may be determined after fusing the finely powdered substance with two or three times as much sodium peroxide. On extracting with water, sodium pertitanate goes into solution and ferric oxide is left behind. Add sulfuric acid till 5 per cent of free acid is present and compare the color of the solution with that obtained by fusing a known weight of TiO_2 with Na_2O_2, etc.

CHROMIUM, Cr. At. Wt. 52.0

Forms: Chromic Oxide, Cr_2O_3; Barium Chromate, $BaCrO_4$

(*a*) *Chromic Compounds*

Determination as Chromic Oxide

1. *By Precipitation with Ammonia*†

If the chromium is present in solution as chromic compound it can be precipitated exactly as described under *Aluminium*, by means of the slightest possible excess of ammonia‡ in the presence of considerable

* *J. Am. Chem. Soc.*, **29**, 481 (1907).

† Cf. C. Rothaug, *Z. anorg. Chem.*, **84**, 165 (1914).

‡ An excess of ammonia prevents the complete precipitation of the chromium hydroxide, the filtrate is then colored pink. In such cases the filtrate must be boiled until the excess of ammonia is expelled, and the chromium is all precipitated.

ammonium salts (or better still, by the addition of freshly prepared ammonium sulfide solution to the boiling solution). Wash the precipitated $Cr(OH)_3$ with 2 per cent ammonium nitrate solution and ignite wet in a platinum crucible. Cool and weigh as Cr_2O_3. The results obtained are always a few tenths of a per cent too high on account of the formation of small amounts of chromic chromate. It is best, therefore, to heat the precipitate and allow it to cool in a stream of hydrogen. Use a Rose crucible and introduce hydrogen from a Kipp generator. Weigh as Cr_2O_3.

If phosphoric acid is present, it will be found in the precipitate. In this case fuse the dried precipitate in a nickel crucible with sodium carbonate and sodium peroxide, whereby sodium chromate and sodium phosphate are obtained. Determine the chromate volumetrically as described for the analysis of *chromite*.

2. *By Precipitation with Potassium Iodide-Iodate Solution. Method of Stock and Massaciu**

Carry out the determination as in the case of aluminium (cf. p. 92). Treat the slightly acid† solution, contained in a porcelain dish, with a mixture of potassium iodide and iodate, decolorize after a few minutes by means of sodium thiosulfate solution, treat with a little more iodide and iodate and then again with a few ml. of sodium thiosulfate, and heat half an hour on the water-bath. The flocculent precipitate of chromic hydroxide settles quickly. Filter, ignite in hydrogen and weigh as Cr_2O_3.

3. *By Precipitation with Ammonium Nitrite*‡

If the solution of the chromic salt is acid, neutralize with ammonia until a slight permanent precipitate is obtained. Dissolve this precipitate with a few drops of hydrochloric acid and add an excess of 6 per cent ammonium nitrite. Boil the liquid until all nitrous fumes have been expelled. By this means practically all of the chromium will have been precipitated, but in order to throw down the last traces, add ammonia, drop by drop, until the odor of free ammonia barely persists in the solution. Allow the precipitate to settle while the beaker remains on the water-bath, filter, wash with hot water, ignite wet in a platinum crucible in an atmosphere of hydrogen and weigh as Cr_2O_3.

* *Ber.*, **1901**, 467.

† If the solution is strongly acid, it is neutralized by the addition of pure KOH solution drop by drop, until a faint permanent turbidity is obtained.

‡ E. Schirm, *Chem. Ztg.*, **1909**, 877. Cf. p. 93. According to Schoeller and Schrauth (*ibid.*, **1909**, 1287) iron, chromium, aluminium, and zinc can be precipitated by means of aniline.

(*b*) *Chromates*

If the chromium is present in solution in the form of an alkali chromate, free from chloride and large amounts of sulfuric acid, it may be determined very accurately by precipitation with mercurous nitrate solution as mercurous chromate; on ignition the latter is changed to Cr_2O_3.

Procedure. — To the neutral or weakly acid solution add a solution of pure mercurous nitrate; brown, basic mercurous chromate, ($4\ Hg_2O.3\ CrO_3$), is formed. On heating to boiling, the precipitate becomes a beautiful, fiery red, being converted into the neutral salt Hg_2CrO_4. This red salt settles very quickly, and if the precipitation is complete the solution above the precipitate will be colorless. After cooling, filter the precipitate off, wash it thoroughly with water containing a little mercurous nitrate, dry and separate from the filter as completely as possible. Burn the filter in a platinum spiral and ignite the ash with the main portion of the precipitate, gently at first and finally strongly, in a platinum crucible under a hood with a good draft. Weigh the residue as Cr_2O_3.

The purity of the mercurous nitrate must be tested before using it. Five grams of the salt should leave no residue after being ignited.

This excellent method for the determination of chromium unfortunately permits only a very limited application. If the solution contains any considerable amount of chloride, mercurous chloride will be precipitated with the mercurous chromate, which, although volatile on ignition, renders the precipitate too bulky and the method inaccurate.

If, therefore, it is necessary to determine chromium present as chromate in a solution containing chloride, two other methods are at our disposal. The chromate may be reduced by boiling with sulfurous acid (or by evaporating with concentrated hydrochloric acid and alcohol) and analyzed according to (*a*), or it may just as accurately, and much more conveniently, be determined by precipitating as

Barium Chromate,

which is weighed after gentle ignition.

Procedure. — To the boiling neutral solution, or one weakly acid with acetic acid, add a solution of barium acetate, drop by drop,* and, after standing for some time, filter through a Gooch crucible (without using very strong suction, as otherwise the filter will soon get stopped up and the solution will filter extremely slowly). Wash the precipitate with

* If the barium acetate solution is added too quickly some of it will be carried down with the barium chromate, so that too high results will be obtained.

hot water till all soluble barium salt is removed, then with dilute alcohol and dry in the hot closet. Suspend the crucible in a larger one of porcelain by means of an asbestos ring (cf. page 38) and heat, at first gently, and finally over the full flame of a good Bunsen burner. After five minutes remove the cover and continue heating until the precipitate appears a uniform yellow throughout. Cool in a desiccator and weigh as $BaCrO_4$.

Sometimes the precipitate appears green on the sides of the crucible owing to a slight reduction (by means of dust, traces of alcohol, etc.) of chromic acid to chromic oxide. The latter gradually takes on oxygen from the air during the long-continued heating of the open crucible, so that the green color gradually disappears.

If a grams of chromate were taken for analysis, and the barium chromate precipitate weighed p grams, then the amount of chromium present may be calculated as follows:

$$x = \frac{100\ \text{Cr}}{BaCrO_4} \cdot \frac{p}{a} = \text{per cent Cr.}$$

Example for practice: Potassium bichromate, $K_2Cr_2O_7$, purified and dried as described on pages 49 and 50.

Weigh out about 0.5 g. of the salt. Dissolve in 300 ml. of water, add ammonia till neutral and then 10 drops of 6 *N* acetic acid. Heat to boiling, slowly add the barium acetate solution and continue as described above.

Chromium originally present as chromate, or obtained as such after suitable oxidizing treatment, may be determined accurately by volumetric methods described in Part II.

URANIUM, U. At. Wt., 238.2

Forms: U_3O_8 and UO_2

(*a*) Determination as U_3O_8

Uranium lis almost always precipitated by means of ammonia as ammonium uranate and changed to U_3O_8 by gentle ignition in a platinum crucible with free access of air. According to Zimmerman* this transformation is only complete when the precipitate is ignited in a stream of oxygen; the error is, however, so small that for ordinary purposes it can be neglected.

According to the temperature of ignition, the U_3O_8 appears dirty green or black, and is difficultly soluble in dilute hydrochloric or sulfuric

* *Ann. chim. phys.*, **232**, 287 (1886).

acids; in nitric acid it dissolves gradually. By heating with dilute sulfuric acid (1 vol. conc. H_2SO_4 + 6 vol. H_2O) in a closed tube at 150°–175° for a long time (W. F. Hillebrand),* the U_3O_8 is completely dissolved with the formation of uranous and uranyl sulfate:

$$U_3O_8 + 4\,H_2SO_4 = 2\,UO_2(SO_4) + U(SO_4)_2 + 4\,H_2O.$$

U_3O_8 is also readily soluble in dilute sulfuric acid in the presence of potassium bichromate. These two last facts are taken advantage of in the volumetric determination of uranium (which see).

(*b*) Determination as UO_2

Heat the ignited precipitate, obtained in exactly the same way as before, over a Méker burner, or the blast-lamp, in a current of hydrogen, until the precipitate is converted into UO_2 and a constant weight is obtained. This is the most accurate method for the determination of uranium.

The UO_2 thus obtained is a brown powder, insoluble in dilute hydrochloric and sulfuric acids, but soluble in concentrated sulfuric acid after long heating, best in a closed tube This oxide is also soluble in nitric acid.

Separation of Iron, Aluminium, Chromium, Titanium, and Uranium from Calcium, Strontium, Barium, and Magnesium

To the solution containing the above substances in the presence of considerable ammonium chloride in an Erlenmeyer flask, add a slight excess of freshly-prepared ammonium sulfide, free from sulfate and carbonate. After standing overnight filter off the precipitate and wash it with water containing ammonium sulfide. It contains the iron and uranium as sulfides, the aluminium, chromium, and titanium as hydroxides. In case large amounts of magnesium are present, some of it is almost always present in the precipitate, so that it is then necessary, after filtration, to dissolve the precipitate in hydrochloric acid and to reprecipitate with ammonium sulfide.

Instead of using ammonium sulfide, the separation can be accomplished satisfactorily with ammonia; the iron must then be in the ferric condition. Carry out the treatment as described for the precipitation of aluminium with ammonium hydroxide using methyl red as indicator.

Separation of Iron from Aluminium

(1) To a boiling solution of half-normal sodium hydroxide in a porcelain dish, add the dilute, acid solution of ferric and aluminium chlo-

* *Bull. U. S. Geol. Survey*, **78**, p. 90.

rides. After the solutions are all mixed make sure that an excess of alkali hydroxide is present so that the iron is all precipitated as $Fe(OH)_3$* and the aluminium all dissolved as $NaAlO_2$. Dilute with hot water and filter. For the iron determination, dissolve the precipitate in hydrochloric acid, reprecipitate with ammonia, † dry and weigh as Fe_2O_3 (see page 94). Precipitate the aluminium as hydroxide in the filtrate by acidifying with nitric acid and then adding ammonia. Filter, wash with 2 per cent ammonium nitrate solution and weigh as Al_2O_3.

(2) Add three times as much tartaric acid as corresponds to the weight of dissolved Fe_2O_3 and Al_2O_3 and pass hydrogen sulfide into the solution until it is saturated. Add a very slight excess of ammonia and allow the sulfide of iron to settle in a closed Erlenmeyer flask. Filter, wash with water containing ammonium sulfide, dissolve in hydrochloric acid, oxidize with a little potassium chlorate or nitric acid, and precipitate as ferric hydroxide by the addition of ammonia. Determine the aluminium in the filtrate by evaporating to dryness with the addition of a little sodium carbonate and potassium nitrate. Gently ignite the residue in a platinum dish to destroy the tartaric acid, dissolve the residue in dilute nitric acid, filter off the carbon, and precipitate the aluminium from the solution by the addition of ammonia.

(3) Add sodium carbonate solution to the neutral solution of the chlorides or sulfates (not the nitrates) until a slight permanent precipitate is formed; dissolve this by the addition of a few drops of hydrochloric acid. Dilute the solution to about 250 ml. for each 0.1 or 0.2 g. of the metals present, add an excess of sodium thiosulfate solution, and boil the solution until every trace of SO_2 has disappeared. By this operation the ferric salt is reduced to ferrous salt:

$$2\,Na_2S_2O_3 + 2\,FeCl_3 = 2\,NaCl + Na_2S_4O_6 + 2\,FeCl_2,$$

and the aluminium is precipitated as the hydroxide:

$$2\,AlCl_3 + 3\,H_2O + 3\,Na_2S_2O_3 = 6\,NaCl + 3\,SO_2\uparrow + 3\,S + 2\,Al(OH)_3.$$

Filter off the precipitate of aluminium hydroxide and sulfur, wash with hot water, dry, transfer as completely as possible to a porcelain crucible, burn the filter in a platinum spiral and add the ash to the crucible. Ignite gently until all the sulfur has been expelled and then more strongly over the blast, Méker or Teclu burner until the weight is constant. Cf. page 92.

* If the precipitate is large, it should be dissolved in hydrochloric acid and again precipitated with KOH.

† It is very hard to wash the KOH precipitate free from alkali so that the first precipitate should not be weighed.

To determine the iron, make the filtrate acid with hydrochloric acid, boil off the SO_2, filter off the sulfur, oxidize the solution with nitric acid and precipitate the iron as ferric hydroxide as described on page 94.

Or, add ammonia and ammonium sulfide to the filtrate from the $Al(OH)_3$ precipitate, filter and wash with hot water. Dissolve the iron sulfide in hot 2 *N* hydrochloric acid, oxidize to the ferric condition with concentrated nitric acid, dilute and precipitate with ammonia according to page 94.

(4) Precipitate both iron and aluminium with ammonia, filter, wash, dry, ignite in a porcelain or platinum crucible, and determine the weight of the combined oxides. After a constant weight is obtained, digest the mixed oxides with concentrated hydrochloric acid to which a little water has been added (10 HCl : 1 H_2O) in a covered crucible until the iron is completely dissolved. If ferric oxide predominates, as is frequently the case, the solution is effected in one or two hours. If, on the other hand, a relatively large amount of alumina is present, as is usually the case with silicates, and which can be predicted by the color of the precipitate produced by ammonia, the precipitate dissolves very slowly and in many cases only incompletely.

In the latter case instead of treating with hydrochloric acid, fuse the ignited oxides with 12–15 times as much potassium pyrosulfate, $K_2S_2O_7$ (cf. Vol. I).* The conversion of the oxides into sulfates is usually complete in 2–4 hours. Place the crucible together with its cover in a beaker, add water and a little sulfuric acid and dissolve the melt by warming gently and passing a current of air through the solution in order to keep the liquid in motion. A small amount of platinum is always dissolved by this treatment. After removing the crucible and its cover, heat the solution to boiling and reduce with hydrogen sulfide as described on page 99. After the iron is reduced, filter off the platinum sulfide, again introduce hydrogen sulfide and continue as described on p. 100, finally titrating the reduced iron with standard potassium permanganate in 250 ml. of cold acid solution. The aluminium is determined from the weight of the combined oxides after deducting the weight of Fe_2O_3 corresponding to the volume of permanganate used in the titration.

For the determination of iron in silicates the above process is most suitable (Hillebrand). The reduction of the ferric salt to ferrous salt by means of hydrogen sulfide possesses advantages over the reduction

* E. Deussen finds that fusion with KF.HF works better. The platinum is not attacked and the solution is effected more readily. — *Z. angew. Chem.*, **1905**, 815.

by means of zinc, for in the former case no foreign element is introduced, and furthermore zinc serves to reduce the titanium that is almost always present in rocks, and this will be again oxidized by the permanganate, so that too high an iron value will be obtained. When titanium is present, it is better to reduce with sulfurous acid as described in Part II of this book.

If the iron is all dissolved by treating the oxides with hydrochloric acid, evaporate the solution to dryness and treat the residue with a few milliliters of dilute sulfuric acid, evaporate on the water-bath as far as possible, and then heat over the free flame until fumes of sulfuric acid are evolved. After cooling, dissolve the sulfates in water and reduce the ferric sulfate to ferrous sulfate by introducing a piece of zinc, free from iron, into the crucible and covering the latter with a watch-glass. The reduction is complete in 20–30 minutes. Filter off the slight residue of platinum* with the excess of zinc, catching the filtrate in a flask already filled with carbon dioxide. Wash the residue with water that has been boiled, and titrate the solution with potassium permanganate solution.

The latter method is to be recommended for the determination of small amounts of iron in the presence of still less aluminium, as is the case in the analysis of mineral waters.

The following procedure leads to the same end, but the results are not quite so reliable:

Dilute the solution in which the iron and aluminium are to be determined to a definite volume (*e.g.*, 250 ml.) and take two aliquot portions by means of a pipet (usually 100 ml.).

In one portion determine the weight of the combined oxides of iron and aluminium by precipitation with ammonia and ignition of the precipitate as described on p. 91; in the other aliquot determine the iron by titration. If the solution contains hydrochloric acid, as is usually the case, it is best first to precipitate the iron with ammonia, filter, wash, and dissolve in dilute sulfuric acid. Reduce this solution and titrate as described above.†

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* Platinum is perceptibly attacked by long digestion with ferric chloride solution:

$$4\,FeCl_3 + Pt + 2\,HCl = H_2PtCl_6 + 4\,FeCl_2.$$

The chloroplatinic acid is reduced to platinum by the action of zinc.

† It is desirable to get rid of the hydrochloric acid on account of its action upon potassium permanganate (cf. Vol. Anal., under Iron). In the presence of hydrochloric acid, the Zimmermann-Reinhardt method of reducing with stannous chloride and titrating with permanganate is capable of giving good results. See Part II.

Separation of Iron, Aluminium, and Phosphoric Acid

Although the determination of phosphoric acid has not yet been described, its determination in the presence of iron and aluminium will now be discussed because this highly important separation is necessary in the analysis of almost all minerals containing iron and aluminium as well as in the analysis of many mineral waters. Two cases are to be distinguished:

1. The solution contains only a small amount (a few centigrams or less) of iron, aluminium, and phosphoric acid.
2. The solution contains large amounts of these substances.

1. In the first case the determination of all three constituents must be undertaken in the same portion, as otherwise errors would be introduced on account of the small quantities to be determined. First treat with ammonia as described on page 91 whereby the iron, aluminium and phosphoric acid are precipitated.*

Ignite the precipitate in a platinum crucible and weigh:

$$Fe_2O_3 + Al_2O_3 + P_2O_5 = A.$$

Fuse the oxides with six times their weight of a mixture consisting of four parts anhydrous sodium carbonate and one part pure silica. Heat the mixture over the blast-lamp or Méker burner. Cool, extract the melt with water, to which a little ammonium carbonate has been added and filter. The filtrate contains all of the phosphoric acid and a very little silicic acid, while the residue contains all of the iron and aluminium and considerable silica.

For the determination of the phosphoric acid, evaporate the filtrate to dryness with hydrochloric acid on the water-bath in order to remove the silica, moisten the residue with 6 *N* hydrochloric acid, take up in a little water, filter, and precipitate the phosphoric acid in the filtrate by the addition of ammonia and " magnesia mixture," as described under Phosphoric Acid. By igniting in a porcelain crucible change the precipitate of magnesium ammonium phosphate to magnesium pyrophosphate and from its weight p calculate the amount of phosphoric anhydride, P_2O_5 (= B):

$$B = \frac{P_2O_5}{Mg_2P_2O_7} \cdot p.$$

Subtract B from A to get the combined weight of the iron and aluminium oxides and then after determining the iron by titration the

* The phosphoric acid is usually present in such small amounts that the iron and aluminium are more than sufficient to effect the precipitation of all the phosphoric acid, on the addition of ammonia, as phosphates of these metals.

aluminium can be estimated " by difference." For the determination of the iron, take the insoluble residue, obtained after treating the product of the fusion with water and ammonium carbonate and digest it with hydrochloric acid in a small porcelain crucible until the iron oxide is completely dissolved. Add a little 18 *N* sulfuric acid, and evaporate first on the water-bath, and then over a free flame until fumes of sulfuric anhydride are evolved. After cooling, add water and digest on the water-bath for some time. Filter off the silica, reduce the solution by means of hydrogen sulfide (cf. p. 110, sub. 4), and, after removing the excess of hydrogen sulfide, titrate the iron with permanganate solution.* From the amount of permanganate used, the quantity of ferric oxide (C) can be calculated, and by deducting this from the weight of the combined oxides, the weight of the Al_2O_3 is ascertained:

$$A - (B + C) = Al_2O_3.$$

2. In case the solution contains large amounts of iron, aluminium, and phosphoric acid, divide it into three aliquot portions and in one determine the value of " A " by precipitation with ammonia; in the second determine the phosphoric acid by the molybdate method as described under Phosphoric Acid; and in the third determine the iron by titration.

Separation of Iron from Chromium

1. The chromium is oxidized in alkaline solution by means of chlorine, bromine or sodium peroxide to a soluble chromate, and the insoluble ferric hydroxide is filtered off. If the chromium alone is desired, it is often better to fuse with sodium carbonate and peroxide as described for the Analysis of Chromite.

Procedure. — Pour the solution of the chlorides into an Erlenmeyer flask of Jena glass, provided with a ground-glass stopper and tubes by which gas may enter and leave the flask, and add sodium hydroxide solution until strongly alkaline. Heat on the water-bath and conduct chlorine gas through the liquid, or add bromine water, until it becomes distinctly yellow and the ferric hydroxide has assumed its characteristic reddish-brown color. When the oxidation is accomplished by chlorine gas, 0.5 g. of the mixed oxides will be completely oxidized in fifteen to twenty minutes. Dilute the solution with water and filter. Carefully make the filtrate acid with acetic acid, precipitate the chromium by the addition of barium acetate, and treat the precipitate of barium chromate as described on p. 107. Dissolve the

* Instead of reducing the iron, the ferric salt may be titrated directly with titanous chloride or iodometrically (see Volumetric Analysis).

ferric hydroxide in hydrochloric acid, reprecipitate with ammonia as described on page 94 and weigh as ferric oxide.

Remark. — If the chromate is to be determined as barium chromate, the solution must contain no sulfuric acid. If the latter is present, reduce the chromate by evaporating with hydrochloric acid and alcohol. In the solution of chromic chloride thus obtained determine the chromium as chromic oxide after precipitation with ammonia as described on page 104.

In the case of a precipitate containing iron and chromic oxides, fuse with sodium carbonate and a little potassium chlorate. Extract the melt with water, and determine the chromium in the aqueous solution by precipitating with barium acetate as described on p. 106. Dissolve the residue from the aqueous extraction of the fusion in hydrochloric acid, precipitate with ammonia, and determine the iron as ferric oxide, according to p. 94.

If it is desired to precipitate the chromium as mercurous chromate, fuse the precipitate containing the iron and chromic oxides with sodium carbonate and potassium nitrate, extract the melt with water, neutralize the solution with nitric acid and precipitate with mercurous nitrate solution, as described on p. 106.

2. It has been proposed to analyze the mixture of ferric and chromic oxides by strongly igniting them in a stream of hydrogen whereby the ferric oxide is reduced to metallic iron, while the chromic oxide is unchanged. The iron could then be determined by the loss of weight. This method, although theoretically very simple, seems from experiments carried out in the author's laboratory to be absolutely inadequate, for the ferric oxide is so enveloped in chromic oxide that it is not even approximately reduced even when heated over the blast-lamp.

3. Iron may be separated from chromium by precipitating the former with ammonium sulfide from a solution containing sufficient ammonium tartrate to prevent the precipitation of the chromium. The separation is the same as was described under aluminium, p. 109, sub. 2.

Separation of Aluminium from Chromium

If the chromium is present as chromic salt, oxidize it to chromate by means of chlorine or bromine as described on page 113. Make acid with nitric acid, and determine the aluminium as oxide after precipitating with ammonia as described on page 91. In the absence of sulfuric acid the chromium can be determined in the filtrate as barium chromate (cf. p. 106). If sulfuric acid is present, reduce the chromate to chromic salt by the action of concentrated hydrochloric acid and alcohol, precipitate with ammonia, and weigh as the oxide (see page 105).

If, however, the chromium is already present as chromate, at once precipitate the aluminium, with ammonia as hydroxide, as described on page 91.

Separation of Iron from Titanium

It is frequently necessary to determine both iron and titanium in a precipitate produced by ammonia consisting of a mixture of these two oxides alone, but it is more often necessary to determine titanium in the presence of iron, aluminium, and phosphoric acid, all of which are precipitated by ammonia in the analysis of rocks.

For the separation of titanium from iron in the absence of alumina, the following methods are suitable:

1. Ignite the precipitate produced by ammonia and weigh the mixture of oxides. Fuse it in a platinum crucible with 15–20 times as much potassium pyrosulfate. This is a difficult fusion to make satisfactorily and requires time and patience. In the first place, the pyrosulfate should be anhydrous. Before starting the fusion, heat the pyrosulfate, or fused potassium acid sulfate, in a platinum crucible until it begins to evolve fumes of sulfuric anhydride. Fuse the oxides with this dehydrated pyrosulfate until they are converted to sulfates. Use a small flame and heat so that only a slight fuming is noticed when the crucible cover is raised. As the fusion progresses the color of the melt darkens and the melting point of the mass rises as the sulfuric anhydride escapes. When the fusion is finished, there should be no unattacked oxide visible in the melt. This treatment usually takes about an hour for 0.2 g. of oxide. If the temperature is raised too quickly, sulfuric acid escapes without reacting with the oxide and if all of the pyrosulfate is converted to sulfate, the mass expands on cooling and may crack the crucible. It is a good plan to add a little pyrosulfate at the last to prevent this. If the pyrosulfate is not anhydrous, the escaping steam will carry up some of the oxides to the top of the crucible and spatter them on the cover and these particles are likely to escape the action of the pyrosulfate.

When the fusion is finished, cool and dissolve the melt in *cold*, 2.5 per cent sulfuric acid, stirring mechanically to hasten the dissolving. If necessary, filter off any undecomposed oxide. Treat this with sulfuric and hydrofluoric acids to make sure that no silica is present and again fuse with pyrosulfate.

Dilute the solution thus obtained to a definite volume, mix and take an aliquot part for the determination of iron and another aliquot for the determination of titanium. For the iron determination reduce with hydrogen sulfide as described on page 99, and titrate the reduced solution with standard permanganate solution. For the titanium determination, treat the other aliquot with sodium carbonate until a slight, permanent precipitate is formed; dissolve this in as little sulfuric acid

as possible, saturate with hydrogen sulfide in the cold, add 5 g. of sodium acetate which has been neutralized with acetic acid* and dilute to at least 500 ml. Conduct carbon dioxide through the solution, heat to boiling, filter hot, wash with 7 per cent acetic acid containing hydrogen sulfide, ignite wet in a crucible, and weigh as TiO_2.

Remark. — If considerable iron is present, the titanic oxide thus obtained is likely to contain iron. Fuse it again with potassium pyrosulfate and repeat the precipitation exactly as before. In this way a precipitate free from iron is obtained.

2. The Chancel-Stromayer method of precipitating titanium is also satisfactory. Neutralize the solution obtained from the pyrosulfate fusion with sodium carbonate as described above, add an excess of sodium thiosulfate, dilute to about 400–500 ml. and boil for some time. In this way metatitanic acid and sulfur are precipitated, while iron remains in solution. During the filtration, however, the finely divided sulfur passes through the filter, so that the first method is preferable. In the presence of considerable iron the metatitanic acid obtained by this method is also contaminated with iron, so that the separation must be repeated.

Separation of Aluminium from Titanium

It has been proposed to separate aluminium from titanium by taking the slightly acid solution from the pyrosulfate fusion (page 115) diluting to a large volume and boiling for some time on the assumption that metatitanic acid will precipitate, leaving aluminium sulfate in solution. This method, however, is useless, for alumina is precipitated with the metatitanic acid unless the solution contains enough acid to prevent this hydrolysis, in which case a considerable amount of titanic acid remains in solution.

One of the best methods of separation is that of Gooch;† it consists in boiling a solution of the two elements containing considerable free acetic acid and alkali acetate; by this means all of the titanium and none of the aluminium is precipitated. If, however, the amount of aluminium present is large (as is usual in rock analysis), the precipitate will contain some aluminium, so that the separation must be repeated. In no case is there danger of the precipitation of the titanium being incomplete.

In practice it is almost always necessary to separate the titanium not from aluminium alone, but from iron and aluminium, so that the method of Gooch will be described for this more general case.

* Cf. footnote to page 154.

† *Chem. News*, **52**, 55 and 68.

Treat the solution obtained by dissolving the pyrosulfate melt in *cold*, dilute acid * with three times as much tartaric acid as the weight of the oxides, saturate with hydrogen sulfide gas, and make slightly ammoniacal. By this means all of the iron is precipitated as ferrous sulfide, while the aluminium and titanium remain in solution. Filter off the iron sulfide, acidify the filtrate with sulfuric acid, heat to boiling, and filter off the precipitate of sulfur and platinum sulfide (the latter from the platinum crucible in which the fusion with pyrosulfate was made). Boil the filtrate to expel the last traces of hydrogen sulfide and destroy the tartaric acid by adding $2\frac{1}{2}$ times as much potassium permanganate as there is tartaric acid present. Add sulfurous acid until the precipitated manganese dioxide is redissolved, after which add a slight excess of ammonia and 7–10 ml. of glacial acetic acid for each 100 ml. of solution. Boil the solution for one minute, allow the precipitate to settle, and decant the filtrate through a filter.† Finally transfer the precipitate to the filter, and wash with 7 per cent acetic acid and finally with a little hot water. Ignite the precipitate and weigh as TiO_2.

The precipitate contains manganese and aluminium, so that it must be purified. Fuse it with three times as much sodium carbonate. Leach the melt (colored green by the manganese) with cold water, leaving sodium metatitanate‡ and some alumina undissolved. Filter off the precipitate by means of a small filter, ignite this residue in a platinum crucible, and fuse again with *a little* sodium carbonate. After cooling, dissolve the contents of the crucible in 200 ml. of 0.1-normal sulfuric acid. Add 5 g. of sodium acetate and 20 ml. of glacial acetic acid. After boiling one minute and allowing to stand until settled, filter the precipitate, wash with 7 per cent acetic acid, then with water, dry, ignite and weigh. This precipitate sometimes contains aluminium. Fuse it again with sodium carbonate and treat the melt with sulfuric acid, etc., exactly as described above. This time the precipitate is usually free from aluminium, but the process should be repeated until a constant weight is obtained.

This analysis does not require much time if the quantity of titanium present is so small that the precipitates filter and wash quickly.

For the determination of very small amounts of titanium, it is advisable to use the colorimetric method proposed by Weller (cf. p. 102).

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* See pages 95 and 115.

† Schleicher & Schüll's filter-paper No. 589 is satisfactory for this purpose.

‡ The sodium metatitanate undergoes hydrolysis and forms a precipitate containing a much higher percentage of TiO_2.

The above method of Gooch is tedious and fails to take into consideration the fact that zirconium, if present, precipitates with titanium. Phosphoric and vanadic acids are also likely to precipitate with titanium and zirconium but these were removed by the fusion with sodium carbonate which forms water-soluble sodium vanadate and phosphate. The titanium precipitate is also likely to contain some adsorbed alkali ions but this error is slight in rock analysis. Thorium and cerium are also precipitated to some extent but in most cases these elements are present to such a slight extent that they may be neglected. To obviate the necessity of destroying the tartaric acid in the method of Gooch, W. F. Hillebrand* recommends the following procedure:

Thornton's† Method of Precipitating Titanium and Zirconium

To the filtrate from the iron sulfide precipitate, which was formed in an ammoniacal ammonium tartrate solution to prevent the precipitation of aluminium, titanium and zirconium by ammonia (cf. p. 117), add 40 ml. of 18 *N* sulfuric acid and boil to expel the excess of hydrogen sulfide. Cool to 15°, or below, dilute to 400 ml. and add a cold, 6 per cent solution of cupferron, with constant stirring (cf. p. 157). Allow the precipitate to settle and test the supernatant solution to see if the precipitation is complete; if this is the case, a white turbidity forms instead of a yellow precipitate. Filter and wash 20 times with cold 1.2 *N* hydrochloric acid. Place the precipitate and filter in a crucible and dry at 110–120°. Then ignite very cautiously with a small flame placed at the base of the inclined, partly covered crucible. There is likely to be a sudden gush of smoke when the oxidation of the organic matter starts. Gradually raise the temperature until all of the organic material is destroyed. Fuse the residue with sodium carbonate, extract the melt with water, filter and wash with dilute sodium carbonate solution. Dissolve the residue in dilute sulfuric acid and repeat the precipitation with cupferron. Ignite and weigh as TiO_2 and ZrO_2. The separation of titanium and zirconium will be discussed on page 123.

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* *Analysis of Silicate and Carbonate Rocks*, p. 166 (1919).

† W. M. Thornton, *Am. J. Sci.* [4], **37**, 407 (1914); *Chem. News*, **110**, 5 (1914); *Z. anorg. Chem.*, **87**, 375 (1914); Schroeder, *Z. anorg. Chem.*, **72**, 95 (1911); Thornton and Hayden, *Am. J. Sci.* [4], **38**, 137 (1914); *Chem. News*, **110**, 153 (1914); *Z. anorg. Chem* **89**, 377 (1914); Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919)

The Determination of Titanium Dioxide in Titanium-Iron Ore

(*a*) Modified Gooch-Baskerville Method*

Most titanium ores are very difficultly soluble in the usual solvents. The analysis of these ores is also complicated by the fact that aqueous solutions of titanium salts readily undergo hydrolysis, partly on account of the amphoteric character of titanium dioxide and partly because of the insolubility of this oxide. If sodium titanate, Na_2TiO_3, is prepared by fusion with sodium carbonate, it undergoes hydrolysis when treated with water and an acid titanate of sodium is precipitated, *e.g.*, $2\,Na_2O \cdot 9\,TiO_2 \cdot 5\,H_2O$. This acid titanate is soluble in hydrochloric acid, d. 1.12, but if the solution is diluted and heated to boiling, hydrolysis takes place, as with any other salt of titanium, and metatitanic acid, H_2TiO_3, is precipitated. A method for determining titanium after fusing with sodium carbonate and dissolving the sodium titanate in hydrochloric acid will be given after the Gooch-Baskerville method has been described.

One of the best methods for attacking titanium dioxide, or an insoluble titanium ore, is based upon the fusion of the ore with potassium pyrosulfate. This converts titanium into titanium sulfate,† $Ti(SO_4)_2$, which is soluble in *cold*, dilute sulfuric acid. (Cf. p. 115).

The following procedure is given, not because it gives the most convenient or the most accurate method for determining titanium in an insoluble ore, but because it is an especially good method for teaching the art of fusing with potassium pyrosulfate to advanced students in quantitative chemical analysis. The method will give excellent results when properly carried out, but is likely to give too low results if the ore is not entirely decomposed by the acid sulfate fusion, or too high results if the titanic metatitanic acid is not purified sufficiently and washed free from alkali salts.

Procedure. — Weigh out 0.4 to 0.6 g. of the finely-ground ore into a platinum crucible and fuse with 6 to 8 times its weight of sodium carbonate for at least 30 minutes. Extract the fused mass with hot water and, when the melt is all disintegrated, decant the solution through an ashless filter paper. Boil the residue with 25 ml. of normal sodium carbonate solution, transfer to the filter, and wash twice with dilute sodium carbonate solution and several times with hot water. This serves to remove the phosphoric acid as sodium phosphate,‡ and to convert titanium into sodium acid titanate; the iron is left with the titanium as insoluble ferric oxide.

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* F. A. Gooch, *Proc. Am. Acad. Arts and Sci.* [new series], **12**, 435 (1885); *Chem. News*, **63**, 267 (1891); T. M. Chatard, *Am. Chem. J.*, **13**, 106 (1891); *Z. anorg. Chem.*, **56**, 337 (1907).

† Titanium sulphate shows a tendency to form complex ions. Thus Warren, *Pogg. Ann.*, **102**, 449 (1857), obtained the salt $K_2Ti(SO_4)_3$ after fusing with potassium pyrosulfate. See also Schutte, *Z. anorg. Chem.*, **26**, 239 (1901).

‡ Phosphoric acid interferes with the precipitation of metatitanic acid by hydrolysis. It tends to precipitate with the titanium to some extent and also to render the precipitation incomplete.

Ignite the residue and filter in a platinum crucible at a low temperature until the carbon of the filter paper is all consumed. Fuse with about 6 g. of potassium pyrosulfate, as described on page 115. Finally, when the contents of the crucible are at a dull red heat and there is no sign of undissolved material, suspend a coil of platinum wire in the melt and allow to cool. When cold withdraw the fused mass by heating the sides of the crucible and gently pulling on the wire.

Suspend the melt in 200 ml. of cold water and 100 ml. of saturated sulfurous acid solution, and allow to stand in a cool place until solution is complete. The dissolving can be usually accomplished by allowing the dilute acid to stand over night with the melt suspended near the top of the liquid. The process may be hastened by stirring with a mechanical stirrer.

If necessary, filter the solution and treat the residue with sulfuric and hydrofluoric acids to expel silica, fuse with more potassium pyrosulfate, and add the melt to the solution previously obtained. Finally dilute the solution to 800 ml. in a large beaker, add 125 ml. of acetic acid, d. 1.04, and 20 g. of ammonium acetate and boil the solution five minutes. Just before boiling begins, add 25 ml. more of sulfurous acid solution.* When the precipitation is complete, allow the beaker to stand in a warm place for at least half an hour, and filter through a 9-cm. filter paper. Arrange a siphon long enough to extend to the bottom of the beaker, with the glass tubing bent upward so that the water will suck into the siphon from above without drawing much precipitate with it. Connect the longer end of the siphon by means of rubber tubing with a short piece of glass tubing which rests just below the upper edge of a 9-cm. washed filter paper. When the precipitated metatitanic acid has settled to the bottom of the beaker, start siphoning off the supernatant solution through the filter, regulating the flow by means of a small screw clamp placed on the short piece of rubber tubing, a little way above the funnel.

Wash the precipitate with 7 per cent acetic acid until most of the sulfate has been removed. Ignite the filter and its contents at as low a temperature as possible and repeat the fusion with potassium pyrosulfate. This time there should be no difficulty in getting a good fusion. Treat the melt exactly as before, but now wash the residue more carefully, until all the sulfate has been removed. Ignite and weigh as TiO_2.

The precipitate will contain zirconium, cerium and thorium if these elements are present, as they usually are in small quantities.

* The saturated aqueous solution of sulfurous acid should have been prepared recently. Old solutions are likely to be too weak and may contain enough sulfuric acid to interfere with the complete precipitation of the titanium.

(*b*) Method of Barneby and Isham*

This method is based on the volatilization of the silica by hydrofluoric acid in the presence of sulfuric acid, evaporation to dryness and fusion with sodium carbonate and a little potassium nitrate (which converts the iron and titanium to insoluble ferric oxide and sodium acid titanate), extraction with hot water to remove the soluble phosphates, sulfates and aluminates, solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether, reduction of slight traces of iron with sulfurous acid, precipitation of the titanic acid by boiling in acetic acid solution, filtration and ignition to titanium oxide (or the titanium may be determined colorimetrically). The method is accurate except that it fails to take into consideration the probable presence of zirconium and other rare earths which will precipitate with the titanium more or less completely. It is shorter than the preceding method.

Procedure. — Weigh out about 0.5 g. of ore into a platinum crucible, cover with a little water, and add 5 to 10 drops of concentrated sulfuric acid, and about 2 ml. of hydrofluoric acid. Heat the mixture carefully until finally no more sulfuric acid fumes are evolved. Add 5–10 g. of sodium carbonate and a *little* potassium nitrate† and fuse the mixture at least thirty minutes. Cool, place the crucible and cover in a beaker, add about 25 ml. of hot water, and heat until the melt is disintegrated. Ferric oxide and sodium titanate are left insoluble in hot water. Remove the crucible, and dissolve any adhering particles of ferric oxide and hydrolyzed sodium titanate in hot 6 *N* hydrochloric acid; save this solution. Filter off the residue in the beaker and wash with hot water.‡ Perforate the filter and carefully wash the residue into a clean beaker with 6 *N* hydrochloric acid. (No water is to be added from this stage of the analysis until after the subsequent treatment with ether.) Transfer the hydrochloric acid washings from the platinum crucible to the beaker and heat the entire solution on the hot plate until complete solution is effected and the total volume reduced to 15 or 20 ml. Cool, add 2 ml. of 12 *N* hydrochloric acid and transfer the solution to a separatory funnel, rinsing the beaker with 6 *N* hydrochloric acid (*d.* 1.10). Add an equal volume of ether, which has been saturated with concentrated hydrochloric acid solution, to the solution in the funnel, insert a rubber stopper in the top, invert the funnel, open the stop-cock, and shake thoroughly. Close the stop-cock, place the separatory funnel

* *J. Am. Chem. Soc.*, **32**, 957 (1910).

† The potassium nitrate is added to make sure that the crucible is not injured by any sulfide or reducible metal which may be present. Too much nitrate should not be added; it will injure the crucible and also cause the melt to effervesce badly.

‡ The residue should not be washed with too much hot water; the hydrolysis of the sodium titanate may go so far that the residue will not dissolve in hydrochloric acid.

in an upright position and allow to stand ten minutes. Then drain off the aqueous layer into a second separatory funnel. Rinse the ether twice by shaking well with 5 to 10 ml. portions of 6 *N* hydrochloric acid, and add the washings to the aqueous solution. Repeat the treatment with ether two or three times until the last portion of ether fails to show any greenish tinge due to the presence of dissolved ferric chloride.

Carefully heat the aqueous solution containing all the titanium in the presence of little, if any, iron and aluminium, on a water-bath containing warm water to expel the dissolved ether, add 20 ml. of 18 *N* sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved. Dilute the cooled solution to about 100 ml. and nearly neutralize with ammonia. Add 1–2 g. of ammonium bisulfite and heat the solution on the hot plate for half an hour. Now add 10–15 g. of ammonium acetate, with 5–10 ml. of glacial acetic acid, and boil the solution for fifteen minutes. Filter, wash with 7 per cent acetic acid, ignite and weigh as TiO_2.

Determination of Titanium in Ferrotitanium

Warm 0.5 g. of the finely divided material with 50 ml. of 7 *N* sulfuric acid. After some time, add 15 ml. of 6 *N* hydrochloric acid and 10 ml. of concentrated nitric acid. After a short time the substance will be decomposed completely by heating with this acid mixture and pure silicic acid will be deposited. Cool, dilute with water and determine the titanium according to the above method of Barneby and Isham. Usually the zirconia, ceria, etc., which precipitate with the titanium can be neglected.

The volumetric method for determining titanium (see Part II) is also very satisfactory.

Determination of Titanium in Iron and Steel*

Dissolve the sample (5 g.) in 40 ml. of hydrochloric acid (*d.* 1.10). Filter off the insoluble residue, wash with water, ignite in a platinum crucible and treat with hydrofluoric and sulfuric acids to eliminate silica. Fuse the residue with sodium carbonate, dissolve the fusion in water, filter, and dissolve the insoluble matter in sulfuric acid. Compare the amount of titanium in this solution with a standard solution by proceeding as follows: Add a sufficient amount of ferric alum to the standard titanium solution to give the same tint as the sample when they are at the same dilution. Add 2 ml. of 3 per cent hydrogen peroxide to the solution and standard respectively and compare in a colorimeter.

* Method used at the Bureau of Standards, Washington, D. C.

The Separation of Zirconium from Iron, Aluminium, Chromium, Titanium, Cerium and Thorium

Zirconium, although almost always present in small quantities in rocks, is an element seldom determined in the past by the analytical chemist. It is very similar to titanium in its properties but is much less common. Rocks rarely contain more than 0.2 per cent of this element and usually less than 0.05 per cent. Zirconium, like titanium, although to less extent, is used in steel-making so that the steel-works chemists are now interested in the determination of zirconium in ores and in the metals and alloys derived from them.

At present the most popular method for determining zirconium* consists in precipitating secondary zirconium phosphate, $ZrH_2(PO_4)_2$, from a cold or tepid solution containing 20 per cent by weight of concentrated sulfuric acid, by means of a large excess of diammonium phosphate. In the presence of hydrogen peroxide titanium is not precipitated. In this way zirconium can be precipitated in the presence of iron, aluminium, chromium, cerium and thorium.

Procedure. — For small quantities of zirconium (0.5 mg.) the volume of the solution should be reduced to 25 ml. before attempting to precipitate zirconium phosphate. With larger quantities, the volume should be increased and amount to 200 ml. for the precipitation of 0.1 g. of zirconium. To the neutral solution add concentrated sulfuric acid until 20 per cent by weight is present. Add sufficient hydrogen peroxide to change all of the titanium to pertitanic acid and at least 10 times as much ammonium phosphate as required theoretically to form $ZrH_2(PO_4)_2$. For small quantities of zirconium an excess of 100 times the theoretical quantity is desirable. Keep the solution at 40–50° for two hours, if more than 5 mg. of zirconium is present, and for at least six hours if the quantity of zirconium is smaller. Decant as much as possible of the supernatant liquid through a filter and wash with cold 5 per cent ammonium nitrate until the excess ammonium phosphate is removed. Do not wash with pure water as it causes hydrolysis of the precipitate, leaving less phosphoric acid in proportion to the zirconium. Moreover it is easier to get a white, ignited precipitate when the filter and precipitate contains some ammonium nitrate. Ignite very carefully in an open crucible using a low flame until all the filter paper carbon has been consumed: then raise the temperature to the full heat of a Méker burner or the blast lamp. Weigh as ZrP_2O_7.

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* Bailey, *J. Chem. Soc.*, **49**, 149, 481 (1886); Steiger, *J. Wash. Acad. Sci.*, **8**, 637 (1918); Nicolardot and Reglade, *Compt. rend.*, **168**, 348 (1919); Johnson, *Chem. Met. Eng.*, **20**, 588 (1919); Ferguson, *Eng. Mining J.*, **106**, 793 (1918); Hillebrand, *Analysis of Silicate and Carbonate Rocks*, p. 173 (1919); Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919) and *J. Ind. Eng. Chem.*, **12**, 562 (1920).

Determination of Zirconium, Aluminium and Titanium in Steel

Dissolve 5 g. of steel in 50 ml. of concentrated hydrochloric acid and add small portions of concentrated nitric acid until all the iron is oxidized to the ferric state. Evaporate to dryness, moisten the residue with 10 ml. of concentrated hydrochloric acid and repeat the evaporation, this time baking somewhat to remove any nitrates that may remain. Take up the residue in 50 ml. of 6 *N* hydrochloric acid and heat until all the ferric oxide and basic salts are dissolved. Filter, wash the impure silica residue with hot, 3 per cent hydrochloric acid and save the filtrate.

Ignite the impure silica and determine its weight if it is desired to know the silicon content of the steel. Treat with hydrofluoric acid as described under Silicic Acid. Fuse the slight residue with a little potassium pyrosulfate (see p. 115). Dissolve the melt in 15 ml. of 5 per cent sulfuric acid and add the solution to the acid extract obtained after the ether separation described in the next paragraph.

Evaporate the filtrate and washings from the silica determination to sirupy consistency, add 40 ml. of 6 *N* hydrochloric acid and extract with ether as described on p. 121. The ether extract will contain most of the iron and molybdenum and the acid extract will contain some iron and all of the zirconium, titanium, aluminium, manganese, chromium and copper, etc., that was present in the steel.

Evaporate the ether from the acid extract, add the sulfuric acid solution obtained from treatment of the impure silica, and heat with 0.5 ml. of concentrated nitric acid to make sure that all of the iron is in the ferric condition. Dilute to 200 ml. and precipitate the iron, zirconium and titanium, manganese, nickel, etc., by adding 20 per cent sodium hydroxide, adding 10 ml. in excess. The caustic alkali used should be pure and free from carbonate. Dissolve the precipitate in hot, 6 *N* hydrochloric acid and repeat the treatment with caustic soda solution. Use the combined filtrates for the aluminium determination and this last precipitate for the determination of iron and titanium.

Dissolve the precipitate in hot 6 *N* hydrochloric acid. Inasmuch as zirconium phosphate is not easily dissolved by acid, it is possible for some zirconium to be left on the filters used for retaining the sodium hydroxide precipitate. To recover this, ignite the filters in a platinum crucible, fuse the ash with sodium carbonate and extract the sodium salts in the melt by treatment with hot water. Discard this aqueous solution, dissolve the residue in hot, 6 *N* hydrochloric acid and add the solution to that containing the greater part of the zirconium.

Determination of Aluminium. In the absence of chromium, uranium and vanadium, add a few drops of methyl red indicator solution, neutralize with hydrochloric acid and add 4 ml. of concentrated acid in excess for each 100 ml. of solution. Make barely alkaline with ammonia, boil 3 minutes and set aside for 10 minutes. If no precipitate forms, the absence of aluminium is assured. If a precipitate is obtained, filter it off and discard the filtrate. Without washing the precipitate, dissolve it in as little hot 6 *N* hydrochloric acid as possible. Dilute to 50 ml., neutralize with ammonia and add 2 ml. of concentrated nitric acid. Heat to 50° and precipitate phosphorus with ammonium molybdate as described under the Determination of Phosphorus in Steel, by the Blair method. Filter and wash with ammonium acid sulfate solution and discard the precipitate of ammonium phosphomolybdate. Precipitate the aluminium hydroxide again with ammonium hydroxide as described above. Filter, discard the filtrate, redissolve in hot 3 *N* hydrochloric acid and reprecipitate. After washing with 2 per cent ammonium nitrate, ignite and weigh as Al_2O_3. After so much manipulation, this precipitate is certain to contain a little silica from the reagents and glassware. It should be treated with sulfuric and hydrofluoric acid to volatilize silicon fluoride as described under Silicic Acid or a blank may be made carrying out every operation described above with a solution containing no iron or aluminium.

If the steel contains chromium, proceed as above until the filtrate from the ammonium phosphomolybdate precipitate is obtained. Continue as above but before the first precipitation of the aluminium hydroxide and phosphate, add a little sodium peroxide to oxidize the chromite to chromate. Then use nitric acid instead of hydrochloric acid to neutralize the alkaline solution. The first precipitate produced by ammonia will then be free from chromium.

If the steel contains uranium, use ammonium carbonate instead of ammonium hydroxide for the final precipitation of the aluminium.

If the steel contains vanadium, the weighed Al_2O_3 will contain some vanadium. Fuse the precipitate with potassium pyrosulfate, extract the cold melt with 5 per cent sulfuric acid and determine the vanadium content as described under Vanadium. Make a corresponding deduction from the weight of impure alumina.

Determination of Zirconium and Titanium. Dilute the hydrochloric acid obtained after dissolving the sodium hydroxide precipitate in the preceding directions to 250 ml. Neutralize partly with ammonium hydroxide but leave about 5 per cent by volume of 6 *N* hydrochloric acid. Add 2 g. of tartaric acid and precipitate any copper by introducing hydrogen sulfide. Filter if necessary. Add ammonia to the

solution which is saturated with hydrogen sulfide and introduce more of the gas. Filter and wash with water containing 2 per cent of ammonium chloride and a little ammonium sulfide. If a precipitate forms in the filtrate, heat to boiling and filter through a new filter. The precipitate contains besides FeS, all of the manganese, nickel and cobalt as sulfide. It is advisable to determine these elements in another portion of the steel.

Neutralize the ammonium sulfide filtrate with sulfuric acid, adding 30 ml. of concentrated acid in excess. Digest on the steam bath until sulfur and sulfides have coagulated. Filter, wash with 100 ml. of ten per cent sulfuric acid by volume. Cool the filtrate in ice water.

Slowly add, with stirring, an excess of a cold 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine). The excess of the reagent is shown by the formation of a white cloud on adding the reagent and the cloud disappears instead of forming a permanent coagulated precipitate. After waiting 10 minutes, filter with gentle suction and wash thoroughly with 10 per cent hydrochloric acid. Discard the filtrate. Carefully ignite in a weighed platinum crucible and weigh the ZrO_2 and TiO_2.

Fuse the weighed oxides with potassium pyrosulfate and determine the titanium colorimetrically as described on page 102. Deduct the corresponding weight of TiO_2 from the weight of the two oxides.

Remarks. — Phosphorus does not interfere appreciably. Vanadium causes some trouble. If present in the steel, fuse the weighed cupferron precipitate with sodium carbonate and determine the vanadium in the water soluble extract. Fuse the insoluble residue with potassium pyrosulfate and determine the titanium colorimetrically.

Uranium may interfere slightly when present in the quadrivalent state. If this element is suspected, boil off all the hydrogen sulfide before the cupferron precipitation and oxidize the uranium to the sexivalent condition by means of permanganate and then proceed with the cupferron precipitation.

Thorium and cerium interfere but are not thrown down quantitatively with the zirconium and titanium. If these elements are suspected, proceed as follows, — Take the solution after the colorimetric determination of titanium and add an excess of potassium hydroxide solution. Filter and wash once or twice by decantation and then a few times on the filter with water. Transfer to a platinum dish, add hydrofluoric acid and evaporate nearly to dryness. Take up in 5 ml. of 5 per cent hydrofluoric acid (by volume). If no precipitate is visible, the rare earths are absent. If a precipitate is obtained, filter off the fluorides on a small filter resting upon a perforated platinum cone or a rubber cone. Wash the crude fluorides back into the platinum dish, add the ash of the filter and evaporate to dryness with a little sulfuric acid. Take up in hydrochloric acid and precipitate the rare earth hydroxides with ammonia. Filter, redissolve in hydrochloric acid, evaporate to dryness and treat the residue with 5 ml. of boiling hot, 5 per cent oxalic acid solu-

tion. After 15 minutes, filter, wash with less than 20 ml. of 5 per cent oxalic acid, ignite and weigh. Multiply the weight obtained by 1.18 to allow for an imperfect separation of the rare earths and deduct the weight from that of the ZrO_2 obtained by the above procedure.

Separation of Beryllium (Glucinium) and Uranium

These two elements rarely occur together except in a few minerals. Both of these elements are not precipitated in the cold by adding an excess of ammonium carbonate to the acid solution and in this way are different from iron and aluminium. By boiling the ammonium carbonate solution, however, basic beryllium carbonate is precipitated. If the boiling is continued long enough to make the precipitation of the beryllium quantitative, some uranium is thrown down, probably as ammonium uranate, $(NH_4)_2U_2O_7$. Hydroxylamine serves to prevent the precipitation of the latter compound by ammonium hydroxide but it does not prevent precipitation of beryllium hydroxide. Brinton and Ellestad,* found it possible to develop a satisfactory method of separating beryllium and uranium by using both ammonium carbonate and hydroxylamine hydrochloride.

Procedure. — To the hydrochloric acid solution containing 0.2 g. or less of beryllium and 0.3 g. of uranium in a volume of about 250 ml. add 5 g. of ammonium chloride, unless already present, and 5 g. of hydroxylamine hydrochloride. Add concentrated ammonium carbonate solution until the precipitated carbonates dissolve completely in the excess of reagent. Heat to boiling and continue boiling for 30–60 seconds after the heavy white precipitate of basic beryllium carbonate forms. Filter without delay and wash thoroughly with cold water. This precipitate will contain the greater part of the beryllium and should contain no uranium.

Add hydrochloric acid in slight excess to the filtrate and heat to remove all the carbon dioxide. Add one gram more of hydroxylamine hydrochloride and a slight excess of ammonium hydroxide after the solution has cooled. This causes the precipitation of the remainder of the beryllium as $Be(OH)_2$. Filter and wash with 2 per cent ammonium nitrate solution containing a little hydroxylamine hydrochloride. Ignite the two precipitates in a crucible, finally heating over the blast or Méker burner, and weigh as BeO.

To determine uranium, make the filtrate from the last precipitation acid with hydrochloric acid and to the cold solution add small portions of alkali bromate (keeping the beaker covered with a watch glass to prevent loss by spattering) until the solution shows the color of dissolved bromine. In this way the hydroxylamine is oxidized. Heat the solution to boiling and precipitate ammonium uranate from the hot solution

* *J. Am. Chem. Soc.*, **45**, 395 (1923).

by adding a slight excess of ammonium hydroxide. Wash with 2 per cent ammonium nitrate solution containing a little ammonia but no hydroxylamine hydrochloride. Ignite and weigh as U_3O_8.

Separation of Uranium from Iron and Aluminium

Treat the slightly acid solution, containing considerable quantities of ammonium salts, with an excess of ammonium carbonate and then with ammonium sulfide, allow to stand for some time in a closed flask, finally filter and wash with water containing ammonium sulfide.

The precipitate contains the iron as sulfide and the aluminium as hydroxide; in the filtrate is found all of the uranium as $(NH_4)_4UO_2(CO_3)_3$. Dissolve the precipitate in hydrochloric acid. Expel hydrogen sulfide by gently boiling, oxidize the ferrous salt to ferric salt by the addition of nitric acid, and determine the iron and aluminium by one of the methods described on pp. 108–112.

Evaporate the filtrate containing the uranium almost to dryness, make acid with hydrochloric acid, boil, and precipitate the uranium as ammonium uranate by the addition of ammonia. Filter off, wash with 2 per cent ammonium nitrate solution to which a little ammonia has been added, dry, ignite and weigh as U_3O_8.

The result obtained may be verified by heating the residue repeatedly in a current of hydrogen in a Rose crucible (see Copper Determination) until a constant weight is obtained; weighing as UO_2. The purity of the precipitate may also be tested volumetrically (see Volumetric Analysis).

B. DIVISION OF THE PROTOXIDES

MANGANESE, NICKEL, COBALT, ZINC

MANGANESE, Mn. At. Wt. 54.93

Forms: $MnSO_4$, MnS, Mn_3O_4, $Mn_2P_2O_7$

1. Determination as Manganous Sulfate, $MnSO_4$

This method, first proposed by Volhard* gives accurate results provided no other sulfate is present. Heating at 450–500° for an hour† is sufficient to remove all moisture and excess sulfuric acid. Long heating (17 hours) at 580° causes slight darkening but even then the results are accurate.

Dissolve the oxide obtained by the ignition of the carbonate, sulfide, or of manganous manganite, in as little as possible of strong sulfuric acid, and some sulfurous acid if necessary to reduce Mn_3O_4, in a porcelain crucible, evaporate as far as possible on the water-bath, finally remove the excess acid by heating in an electric oven, gradually raising the temperature to 450° and keeping it there for 30 minutes, or by heating in an air bath (Fig. 14, p. 38). When the air-bath is used, finally cover both crucibles and heat over a good Bunsen burner for ten minutes.

(*a*) Precipitation of Manganese as Carbonate

This method is suitable only for the determination of manganese in solutions of pure manganese salts containing nothing else except alkali and ammonium salts.

According to H. Tamm, the precipitation is best accomplished by means of ammonium carbonate. For this purpose treat the neutral solution (which may contain other ammonium salts) with a slight excess of ammonium carbonate, heat gently, and allow the beaker containing the solution to remain in a lukewarm water-bath until the precipitate has settled and the upper liquid has become clear.

Filter off the precipitate, wash with hot water, dry, ignite, and weigh either as sulfate according to 1 or as Mn_3O_4 according to 3.

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* *Ann. Chem. Pharm.* **198**, 328 (1879). Cf. Marignac, *Arch. sci. phys. nat.* [3]. **10**, 25 (1883); Meineke *Chem. Ztg.*, **9**, 1478, 1787 (1885); Friedheim, *Z. anal. Chem.*, **38**, 687 (1899); Gooch and Austin, *Am. J. Sci.*, **5**, 209; Blum, *J. Am. Chem. Soc.*, **34**, 1382 (1912).

† Blum recommends a longer period of heating but in his experiments he was working with 2.4 grams of manganous sulfate and considered the weight constant only when the variation was less than 0.3 mg. after heating for protracted periods.

‡ *Chem. News*, **26**, 37 (1872) and *Z. anal. Chem.*, **11**, 425 (1872).

Remark. — If either sodium or potassium carbonate is used to precipitate the manganese, the precipitate will always contain alkali carbonate that cannot be removed by washing. After the precipitate has been ignited, however, the alkali carbonate can be easily extracted by water. Furthermore, the precipitation is not quite quantitative; the filtrate always contains small amounts of manganese. In order to remove this, it is necessary to evaporate the aqueous solution to dryness, whereby the manganous carbonate is completely hydrolyzed into carbonic acid and manganous hydroxide, and the latter in contact with the air changes to brown manganic oxide, Mn_2O_3. Treat the residue obtained after the evaporation with water, filter off the small amount of brown manganese compound, ignite, and add to the main part of the precipitate.

(*b*) Precipitation of Manganese as Sulfide

This method is employed when it is necessary to separate manganese from calcium, strontium, barium, and magnesium. Two cases will be discussed:

(α) The solution contains, besides manganese, considerable alkaline earths or magnesium. (β) The solution contains only small quantities of the alkaline earths or magnesium.

(α) The manganese sulfide must be precipitated in the cold in the presence of considerable ammonium salts. To the solution in an Erlenmeyer flask containing not more than 0.3 g. of manganese in a volume of 200 ml., add 2 g. of ammonium chloride or nitrate. If the solution reacts acid, add ammonia until it is slightly alkaline, and then a slight excess of freshly-prepared, colorless ammonium sulfide solution. Fill the flask nearly full with cold distilled water that has been boiled, cork, and allow to stand twenty-four hours, or longer. Then carefully decant off the clear supernatant liquid through a filter,* taking pains not to disturb the precipitate and to keep the filter filled with liquid all the time. If the precipitate is at all bulky, wash it three times by decantation with a 2 per cent solution of ammonium nitrate to which has been added 1 per cent by volume of ammonium sulfide solution. Transfer the precipitate to the filter and wash with dilute ammonium sulfide water until 20 drops of the filtrate evaporated to dryness on a crucible-cover leave no residue. Now, for the first time, allow the filter to drain completely.† Dry, transfer as much of the precipitate as possible to a small porcelain crucible, burn the filter-paper in a platinum spiral, and add the ash to the main portion of the precipitate in the crucible. Heat the uncovered crucible over a small flame until the

* Schleicher & Schüll's filter-paper No. 590 can be used to advantage.

† It is often necessary to remove alkaline earth carbonate or magnesium hydroxide. To accomplish this, dissolve the precipitate in hot 2 *N* hydrochloric acid, evaporate to remove CO_2 and repeat the precipitation with ammonium sulfide.

greater part of the sulfur has been burned off. Treat with concentrated sulfuric acid and determine the manganese as sulfate, or ignite more strongly, finally heat over the Teclu or Méker burner and weigh as Mn_3O_4 (cf. p. 133). Manganous sulfide is readily changed to Mn_3O_4 if the amount of sulfide is comparatively small. In case more than 0.2 g. is present there is danger of getting a too high result on account of some manganous sulfate not being decomposed. In this case, it is better to proceed as follows: Dissolve the washed precipitate of manganous sulfide in dilute hydrochloric acid, evaporate the solution to dryness to remove all hydrogen sulfide, dissolve the residue in a little water, transfer the solution to a weighed crucible, and determine as sulfate. Manganous sulfide can also be weighed as such. (See p. 132.)

(β) In case only small amounts of alkaline earths are present, the following procedure can be used: heat the neutral solution to boiling, add an excess of ammonia and some ammonium sulfide and continue boiling until the manganous sulfide has become a dirty green. Allow the precipitate to settle, filter and wash with water containing a little ammonium sulfide. From this point the procedure is the same as described under (α).

(*c*) Separation of Manganese as Manganese Dioxide

If a dilute solution of a manganous salt is treated with bromine water and boiled, the reaction

$$MnCl_2 + Br_2 + 2\,H_2O \rightleftarrows MnO_2 + 2\,HCl + 2\,HBr$$

does not take place unless the halogen acids are neutralized as fast as they are formed. This neutralization can be accomplished by means of the salt of a weak acid, such as sodium acetate, even when the solution contains free acetic acid, which is very slightly ionized in the presence of its alkali salt. Thus in a solution such as is obtained after the removal of iron and aluminium by a basic acetate separation (cf. p. 153), the manganese can be precipitated quantitatively by boiling with an excess of bromine water. The oxide does not correspond exactly to MnO_2, although most of the manganese is in the quadrivalent condition.* When the precipitate has collected in large flocks, discontinue the boiling and allow the precipitate to settle; filter and wash with hot water. Some chemists ignite this precipitate and weigh as Mn_3O_4 but it is more accurate to dissolve the precipitate in a mixture of HCl

* The MnO_2 acts as the anhydride of metamanganous acid, H_2MnO_3, and some manganous manganite, $MnMnO_3$ or Mn_2O_3, is contained in the precipitate.

and H_2SO_3 and to precipitate the manganese finally as manganese ammonium phosphate. (See 4, p. 133.)

Chlorine, hydrogen peroxide, hypochlorites, etc., may be used instead of bromine, but these reagents have no especial advantages.

If the solution of the manganous salt also contains ammonium salts the precipitation of the manganese does not take place by the above procedure, because the sodium acetate serves rather to neutralize the acid set free by the following reaction:

$$2\,NH_4Cl + 3\,Br_2 = N_2 + 2\,HCl + 6\,HBr$$

Upon the addition of ammonia, however, the precipitation of the manganese can be effected. In this case, it seems fair to assume that the reaction goes through the following stages:

$$MnCl_2 + 2\,NH_4OH \rightleftarrows Mn(OH)_2 + 2\,NH_4Cl,$$
$$Mn(OH)_2 + Br_2 + 2\,NH_4OH = MnO(OH)_2 + 2\,NH_4Br + H_2O.$$

The precipitation with bromine and ammonia is not so satisfactory as with bromine alone because when ammonia or ammonium salt is present much of the bromine is used up in oxidizing the nitrogen. In that case there is considerable evolution of nitrogen, and, moreover, when an excess of bromine is added the solution may become acid enough to dissolve the precipitated manganese.

$$2\,NH_3 + 3\,Br_2 = 6\,HBr + N_2.$$

It is necessary, therefore, when ammonium salts are present to make sure that the solution is ammoniacal at the end of the operation.

This method of precipitating manganese from solutions possesses disadvantages which make it useless in many cases. If, besides manganese, the solution contains calcium, zinc, etc., manganites of these metals are precipitated with the manganese. In this case the precipitate must be dissolved in hydrochloric acid and the precipitation repeated several times, but even then it is not possible to obtain a precipitate altogether free from these metals. If the other metals are present only in small amounts, the results obtained by this method are sufficiently accurate. The precipitation of manganese as sulfide in the presence of other metals is always satisfactory and should be used in almost all cases.

2. Determination of Manganese as Sulfide

If the manganese has been precipitated, as described on p. 130 as sulfide, separate the precipitate from the filter as completely as possible, place in a Rose crucible (of unglazed porcelain), burn the filter in a platinum spiral, and add the ash to the main portion of the precipitate.

Add some pure sulfur which has been crystallized from CS_2 and heat the crucible and its contents in a current of hydrogen as described under the Determination of Copper as Sulfide. After the excess of sulfur has distilled off and burned, cool the crucible in the stream of hydrogen and weigh the precipitate as MnS.

3. Determination of Manganese as Mn_3O_4

Inasmuch as all the oxides of manganese, as well as those compounds which are converted into oxide on ignition (manganous salts of volatile organic and inorganic acids, with the exception of the halogen salts), are converted into Mn_3O_4* on being ignited in the air, at temperatures between 940° and 1100°, it follows that this method for the determination of manganese is quite generally applicable. It is nearly as accurate as the methods described under 1 and 2, if the ignition of the precipitate takes place in an electric furnace at about 1000°, and very good results are obtained if, as recommended by Gooch,† the porcelain crucible (containing the carbonate, manganous manganite, or sulfide) is entirely surrounded by the oxidation flame of a Teclu burner, whereby a moderately high heat is obtained without too much free access of air.

After the ignition, cool the crucible and its contents in a desiccator and weigh the M_3O_4.

4. Determination of Manganese as Pyrophosphate, $Mn_2P_2O_7$

This excellent method was recommended by W. Gibbs‡ and subsequently studied by Gooch and Austin.§

To the slightly acid solution, containing manganese equivalent to not more than 0.5 g. $Mn_2P_2O_7$ in 250 ml., and no other metals except alkalies, add 20 g. ammonium chloride, 5 to 10 ml. of a cold, saturated solution of sodium phosphate, and ammonia, drop by drop, until a *slight* excess is present. Heat the solution to boiling and keep at this temperature for three or four minutes, or until the precipitate assumes a silky, crystalline appearance. After cooling, filter the precipitate into a Gooch or Munroe crucible, wash with cold ammonium nitrate solution, dry, ignite within a larger crucible or in an electric furnace. Cool in a desiccator and weigh as $Mn_2P_2O_7$.

Manganese can be determined very accurately by volumetric methods (see Volumetric Analysis).

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* Cf. R. J. Meyer and K. Retgers, *Z. anorg. Chem.*, **57**, 104 (1908), at 530° the oxides of manganese are slowly but quantitatively changed into Mn_2O_3.

† *Anorg. Chem.*, **17**, 268 (1898).

‡ *Am. J. Science*, **46**, 216; *Z. anal. Chem.*, **7**, 101 (1868).

§ *Z. anorg. Chem.*, **18**, 339 (1898).

5. Colorimetric Determination of Manganese

Small amounts of manganese can be determined accurately and quickly by the *colorimetric method* but if more than 1.5 per cent of manganese is present, the results are unreliable. The method depends upon the oxidation of the manganese to permanganic acid, bringing the solution to a definite volume and comparing its color with another solution containing a known amount of manganese. If the solutions are colored exactly the same shade, then the amounts of manganese which they contain are the same. As oxidant, ammonium persulfate can be used. In hot nitric acid solutions containing silver cations, the following reaction takes place:

$$2\,Mn^{++} + 5\,S_2O_8^{--} + 8\,H_2O \rightarrow 2\,MnO_4^{-} + 10\,SO_4^{--} + 16\,H^{+}.$$

To illustrate the method, the procedure recommended by the American Society of Testing Materials for the routine analysis of steel will be described. The method is not as reliable as the bismuthate method (see Part II). A similar procedure can be applied to the estimation of small quantities of manganese in rocks, after a solution containing all of the manganese is obtained by suitable methods.*

Procedure. — Dissolve 0.1 to 0.3 g. of steel in 15 ml. of 25 per cent nitric acid in a small Erlenmeyer flask. Boil gently till a clear solution is obtained. Add 15 ml. of 0.08 *N* silver nitrate solution, and 1 g. of ammonium persulfate. Continue heating 30 seconds after the oxidation begins and bubbles of oxygen arise freely. Cool and compare the color of the solution with that obtained with a standard steel similarly treated, diluting until the colors match.

NICKEL, Ni. At. Wt. 58.68

Forms: Nickel Dimethyl Glyoxime, $NiC_8H_{14}N_4O_4$; Nickel, Ni; and Nickel Oxide, NiO

1. Determination as Nickel Glyoxime

Dimethyl glyoxime, $CH_3 \cdot CNOH \cdot CNOH \cdot CH_3$, was recommended by L.Tschugaeff† as a reagent for nickel and used by K. Kraut‡ for detecting the presence of traces of nickel in ashes. O. Brunck§ and others have also studied the reaction and found it to furnish a most rapid and accurate method for the quantitative estimation of nickel either by itself or in the presence of cobalt, zinc and manganese. If the

* H. Lührig, *Chem. Ztg.*, **1914**, 781, has described a method for the determination of small quantities of manganese in water.

† *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **38**, 2520 (1905).

‡ *Z. angew. Chem.*, **19**, 1793 (1906); *ibid.*, 20, 1844 (1907).

§ *Ibid.*, **20**, 834 (1907).

solution contains tartaric acid enough to prevent the precipitation of iron by ammonia, the nickel in a sample of nickel steel can be determined accurately within two hours and without the removal of any other metal.

When a dilute, neutral solution of a nickel salt is treated with an alcoholic solution of dimethyl glyoxime, a red, crystalline precipitate of nickel dimethyl glyoxime is formed.

$$\underset{}{NiCl_2} + 2\,\underset{\text{Dimethyl glyoxime.}}{(CH_3)_2C_2(NOH)_2} = \underset{\text{Nickel dimethyl glyoxime.}}{[(CH_3)_2C_2NOH \cdot NO]_2Ni} + 2\,HCl.$$

The salt is soluble in mineral acids so that precipitation is incomplete because of the acid set free in the reaction. It becomes quantitative, however, if the mineral acid is neutralized by ammonia or if sodium acetate is added, whereby the mineral acid is replaced by acetic acid in which the precipitate is practically insoluble. Large quantities of ammonium salts or of alkali acetate do no harm, but an excess of ammonia tends to retard the formation of the precipitate. The precipitate is distinctly soluble in absolute alcohol, but only traces dissolve in 50 per cent alcohol, and in more dilute alcohol it is even less soluble. When thrown down in the cold or in the presence of much free ammonia the precipitate is very voluminous and hard to filter.

Procedure. — Dilute the neutral or slightly acid* solution so that not more than 0.1 g. of nickel is present in 200 ml., heat nearly to boiling and treat with five times the theoretical quantity of an alcoholic 1 per cent solution of dimethyl glyoxime.† Carefully add ammonia until the solution smells slightly of it. Allow to stand an hour if convenient, filter, while still hot, into a Gooch or Munroe crucible, wash with hot water and dry at 110° to 120° for 45 minutes. The precipitate contains 20.31 per cent Ni.

The nickel salt of dimethyl glyoxime is red and crystalline. It contains no water of crystallization and sublimes at 250° without decomposition.

2. Determination of Nickel as Metal by Electrolysis

From strongly *acid* solutions nickel is not deposited upon stationary electrodes by a current of 1–3 amperes per square decimeter of electrode surface. From slightly acid solutions the deposition is not quantitative.

From *ammoniacal* solutions nickel is easily deposited quantitatively.

(*a*) Method of Gibbs‡

Nickel sulfate or chloride (but not the nitrate) is dissolved in an ammoniacal solution of ammonium sulfate and electrolyzed.

* If strongly acid, neutralize the solution with sodium hydroxide.

† The volume of the alcoholic solution should in no case be more than half that of the nickel solution, as the precipitate is soluble in alcohol.

‡ *Z. anal. Chem.*, **3**, 334 (1864). Cf. Fresenius and Bergmann, *Z. anal. Chem.*, **19**, 320 (1880).

The nickel is deposited upon a weighed cathode and, at the end of the electrolysis, the gain in weight represents the quantity of nickel.

Requirements and Procedure. — For this, as well as for all other electrolytic determinations, the apparatus shown in Fig. 37 may be used.

B represents a storage-battery, which is provided with the binding posts *MM*. The current is led first through the variable resistance *W*, then through the known resistance *W'* (a resistance of 1 ohm is most convenient to use*), and from here to the decomposition cell finally back to the battery.

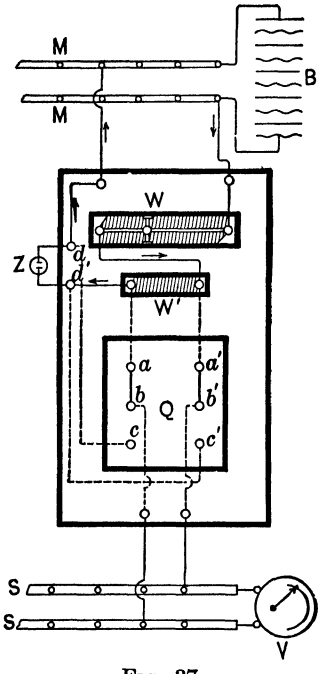


FIG. 37.

If at any time it is desired to measure the voltage between the electrodes of the cell, the voltmeter *V* is connected with the binding posts of the decomposition cell, by throwing the switch *Q*,† Fig. 38, so that *c* is connected with *b* and *c'* with *b'*. The strength of the current, on the other hand, is obtained by placing the switch in the opposite position with *a* united to *b* and *a'* to *b'*, as shown in Figs. 37, 38.

Since, according to Ohm's law, the

$$\text{Strength of current} = \frac{\text{Electromotive force}}{\text{Resistance}},$$

then if the strength of the current is expressed in amperes, the electromotive force in volts, and the resistance in ohms, we have amperes = volts/ohms. In case $W' = 1$ ohm, then $A = E$, and

* The resistance $W' = 1\ \Omega$ can be made from nickelin wire. The resistance of the wire is measured with the aid of the Wheatstone bridge and a length cut off corresponding to one ohm. This wire is wound around a wooden block and the ends fastened to binding posts.

† If a commutating switch is not available, one can be prepared by taking the cover of a pasteboard box, about 2 cm. deep, filling it with melted paraffin, and then, after cooling, making little cavities at *aa'bb'cc'* by pressing a test-tube, which is filled with hot water, against the cold wax. These cavities are filled with mercury and the switch finished with copper wire. Cf. Fig. 44, p. 179.

the voltmeter will show directly the strength of the current (amperes).*

It is arranged so that the current may be taken from different points along the bus bars *MM*, and it is thus possible to carry out a number

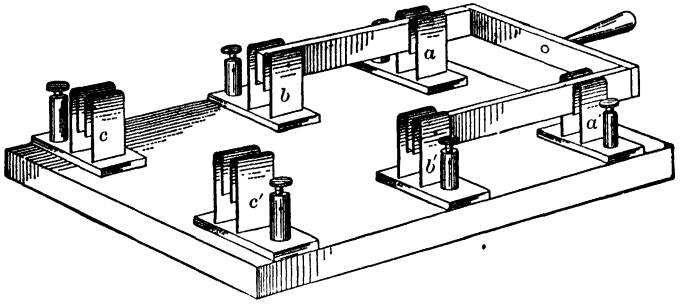


FIG. 38.

of electrolytic determinations at the same time, and the voltmeter *V* serves as measuring instrument for all the analyses that are in progress. By means of the bus bars *SS*, it is possible to connect easily the voltmeter with the different cells. While a measurement is being made at any cell, all other switches must be cut out of circuit.

The decomposition cell consists of a glass beaker in which is placed as cathode a wire gauze electrode (first recommended by Cl. Winkler) and as anode a platinum spiral. The electrodes must always reach to the bottom of the beaker and the top of the gauze electrode should be nearly covered by solution. In some cases it is desirable to use a platinum dish as cathode, as recommended by Classen. (See Fig. 44, p. 179.)

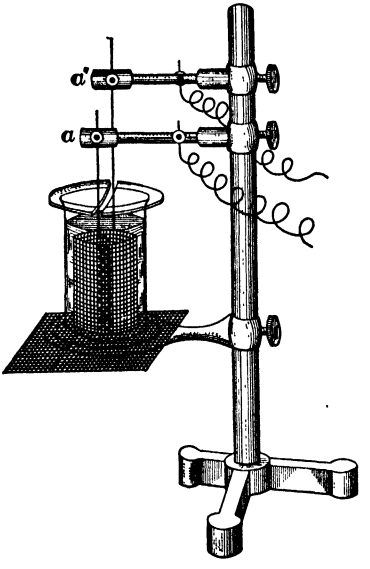


FIG. 39.

The electrodes are usually connected with two electrode stands on which metal arms are attached to an upright glass rod (Fig. 39). To prevent serious loss of electrolyte by spattering, cover the beaker with

* With weaker currents, the known resistance can be made $W' = 10\,\Omega$ so that the voltmeter will show ten times the actual current.

two halves of a watch-glass. This is not entirely satisfactory, as when much gas is evolved a little of the liquid is still carried off mechanically. This method of fastening the electrodes, moreover, has the disadvantage that when the electrolysis is carried out in a hot solution, acid or ammoniacal vapors, as the case may be, condense on the brass arms of the electrode support and in some cases the liquids thus condensed dissolve some brass and the resulting solution may drop into the beaker, and spoil the analysis. To prevent this, it is better to bend the ends of the electrodes to a right angle and connect with an electrode stand designed as shown in Fig. 40.

This electrode holder consists of two brass rods insulated from one another by means of an intervening layer of mica, and the rods are fas-

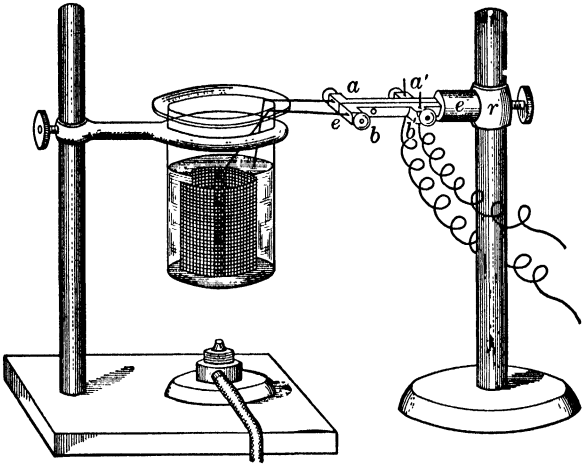


FIG. 40.

tened to the ring r through a piece of ebonite, e. The openings to hold the wires are cut wedge-shaped, so that any shape of wire can be inserted.

Since the ends of the electrodes leave the beaker in a horizontal direction, the beaker can be covered tightly by means of a whole watch-glass, and not only are losses by spattering avoided, but there is absolutely no danger of contamination from the outside.

The Electrolysis of Ammoniacal Nickel Solution

For every 0.25–0.30 g. nickel, present as sulfate or chloride but not as nitrate,* add 5–10 g. of ammonium sulfate and 30–40 ml. of

* It is possible to electrolyze ammoniacal nickel nitrate solutions but the electrolysis requires so much more time, due to the electrolytic reduction of nitrate, that it is better to remove nitric acid by evaporating the solution with sulfuric acid.

concentrated ammonia; dilute the solution with distilled water to a volume of 150 ml. Electrolyze this solution at the room temperature with a current of 0.5–1.5 amperes and an electrode potential of 2.8–3.3 volts. The electrolysis is finished in about two hours, as can be shown by adding a little water and allowing the current to pass through the solution for fifteen or twenty minutes longer. If at the end of this time no nickel has deposited upon the electrode surface which was wet for the first time by the last dilution, the determination is finished. If the solution is kept at a temperature of from 50°–60° C. only about one hour is necessary for the deposition and the deposit adheres better to the electrode and is bright, possessing almost the color of platinum.

As soon as the electrolysis is finished, remove the watch-glass, raise the electrode holder so that only the bottoms of the electrodes remain in the liquid, and wash the upper parts of the electrodes thoroughly with water from a wash-bottle. Then raise the electrodes entirely out of the solution and wash the bottoms immediately with water. Now turn off the current, rinse the cathode with absolute alcohol, and dry by holding it high above a gas flame. After cooling in a desiccator, weigh.

To clean the cathode, place it in a small beaker, add enough 6 *N* nitric acid to wet all the nickel, and heat for at least fifteen minutes. This treatment is absolutely necessary to remove the last traces of nickel. If this is not done, the electrode on being ignited becomes discolored, and it is then very difficult to clean the electrode by repeated treatment with acid followed by ignition. The addition of a little copper salt to the nitric acid helps to dissolve the nickel deposit. To make sure that all the nickel has been deposited from the electrolyzed solution, nearly neutralize the ammonia with hydrochloric acid and add a few cubic centimeters of a 1 per cent solution of dimethyl glyoxime in alcohol. When less than a tenth of a milligram of nickel is present, it will take several minutes for a yellow coloration to appear, and soon afterward the red crystals of nickel salt will be precipitated.

The nickel not deposited by an electrolysis may be estimated accurately by shaking the solution thoroughly and comparing the color produced by the addition of dimethyl glyoxime with that produced with a dilute nickel solution containing a known quantity of nickel. Naturally such a colorimetric test can be used only with very small quantities of nickel.

Remark. — The electrolysis of nickel from an ammoniacal solution should not be continued for too long a time, because the cathode slowly gains in weight even after all the nickel has been deposited from the solution. The anode is attacked,

causing platinum to go into solution, which is deposited upon the cathode, partially, at least.

The presence of too little ammonia often results in the formation of black $Ni(OH)_3$ at the anode; the analysis then comes out too low. Copper, cobalt and zinc will be deposited under the above conditions.

3. Determination as Nickelous Oxide

Heat the nickel solution in a porcelain dish with bromine water and an excess of pure potassium hydroxide; the nickel is precipitated as brownish-black nickelic hydroxide, $Ni(OH)_3$. Filter off the precipitate, wash by decantation with hot water, dry, and, after burning the filter, ignite and weigh as NiO. The grayish-green oxide thus obtained always contains small quantities of silicic acid and alkali,* whereby the results are too high. By treating the ignited mass with hot water, the greater part of the alkali can be removed. Drying and again igniting gives the weight of $NiO + SiO_2$. Treat the oxide in a porcelain crudible with hydrochloric acid, evaporate to dryness, moisten the dry residue with concentrated hydrochloric acid and then with hot water, filter through a small filter, wash with hot water, and ignite the filter together with the residue in a platinum crucible. The weight of this silica, SiO_2, subtracted from the former weight of $NiO + SiO_2$, gives good results.

Remark. — It is possible to precipitate nickel quantitatively as $Ni(OH)_2$ by means of caustic potash alone and the precipitate can be changed to NiO by ignition. This method is open to the same objections as the above and, furthermore, $Ni(OH)_2$ is not so easily filtered and washed as $Ni(OH)_3$.

These two methods are more tedious to carry out and the results are not as accurate as in the case of the first two methods described and will probably not be used much in the future.

Besides the methods described, it has been proposed to precipitate nickel as the sulfide, and weigh it as the oxide by ignition in air. † The method is good but hardly comparable with the dimethyl glyoxime method, the electrolytic method, or the volumetric titration with potassium cyanide.

COBALT, Co. At. Wt. 58.97

Forms: Co, $CoSO_4$

1. Determination as Metal

(*a*) By Electrolysis

The most accurate method for the estimation of cobalt is by electrolysis and the details of the process are precisely the same as have

* Cf. A. Windelschmidt, *Dissertation*, Münster, 1907, and W. D. Treadwell, *Dissertation*, Zurich, 1909.

† H. Cormimboef, *Ann. chim. appl.*, II, 6 (1906). Cf. A. Windelschmidt, *loc. cit.*

been given under nickel, *i.e.*, from a strongly ammoniacal solution containing ammonium salts and the sulfate or chloride (preferably the former) of cobalt. It is customary to use a little more ammonia than in the determination of nickel, because cobalt has a greater tendency to deposit as black $Co(OH)_3$ at the anode. The duration of the electrolysis is the same as with nickel, rather than somewhat longer. At the end of the determination, after the electrodes have been removed, test the entire solution for cobalt by adding ammonium sulfide or potassium thiocarbonate.

(*b*) By Reduction of the Oxide in a Stream of Hydrogen

Heat the cobalt solution to boiling in a porcelain evaporating-dish, and precipitate the cobalt as black cobaltic hydroxide by the addition of caustic potash and bromine water. Filter off the precipitate,* dry and ignite. Then cool and treat the oxides with water to remove the small quantity of alkali which is always present. Filter, ignite in a stream of hydrogen and weigh as metal. After weighing, dissolve the metal in hydrochloric acid, evaporate the solution to dryness, moisten the dry mass with hydrochloric acid, treat with water, and filter off the small residue of silicic acid. Ignite this residue and subtract its weight from that obtained after the ignition in hydrogen. Cobalt may also be precipitated as cobaltous hydroxide by caustic potash alone, but the resulting precipitate is not so easy to filter and wash as the cobaltic hydroxide. Precipitation by means of sodium carbonate is not so satisfactory.

The oxides of cobalt when ignited in air yield a mixture of CoO and Co_3O_4 in varying proportions, so that they are not suited for the quantitative determination of cobalt.

Remark. — The results obtained by this method are usually a little higher than by electrolysis.

2. Determination as Sulfate

The method is the same as was described under Manganese (p. 129).

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* Cobaltic hydroxide, unlike nickelic hydroxide, has the tendency of giving a turbid filtrate on washing. If, however, Schleicher & Schüll's filter-paper No. 589 (blue band) is used, none of the precipitate passes through.

ZINC, Zn. At. Wt. 65.37

Forms: $ZnNH_4PO_4$, $Zn_2P_2O_7$, ZnO, ZnS, Zn

1. Determination as Zinc Ammonium Phosphate or Zinc Pyrophosphate

This excellent method, first recommended by H. Tamm,* has been studied and improved by G. Lösekann and T. Meyer,† M. Austin,‡ and especially H. D. Dakin.§

Procedure. — To the *cold*, acid|| solution of the zinc salt add ammonium hydroxide until the solution is barely acid to methyl orange. Care is necessary at this point, as zinc ammonium phosphate is soluble both in acids and ammonia. Dilute with water to a volume of 150 ml. and heat on the water-bath. To the hot solution, add ten times as much ammonium phosphate as there is zinc present. (If the diammonium phosphate contains some monoammonium phosphate, the salt should be dissolved in cold water and dilute ammonia added until the solution just becomes pink with phenolphthalein.) The precipitate that first forms is amorphous but it soon changes into fine crystals of zinc ammonium phosphate. The transformation takes place more rapidly in proportion to the quantity of ammonium salts present. After the heating has continued for about fifteen minutes, remove the dish from the water-bath and after the precipitate has settled for a short time filter off the precipitate into a Gooch or Munroe crucible, wash with hot, 1 per cent ammonium phosphate solution¶ until free from chloride etc., then twice with cold water, and finally with 50 per cent alcohol. Dry at 100–135° for an hour and weigh as $ZnNH_4PO_4$, which contains 36.64 per cent Zn.

Or, the precipitate may be weighed as the pyrophosphate, $Zn_2P_2O_7$, in which case it is desirable to heat the dried zinc ammonium phosphate very slowly in an electric oven to 900°–1000°. If such an oven is not at hand place the Gooch or Munroe crucible in a larger platinum crucible and heat over the gas flame. Gradually raise the temperature until finally the full heat of the Teclu or Méker burner is reached. Heat to constant weight. $Zn_2P_2O_7$ contains 42.90 per cent Zn.

The determination as pyrophosphate is to be recommended when the zinc solution contains a very large quantity of ammonium salts

* *Chem. News*, **24**, 148.

† *Chem. Ztg.*, **1886**, 729.

‡ *Am. J. Sci.*, **1899**; *Z. anorg. Chem.*, **22**, 212 (1900).

§ *Z. anal. Chem.*, **39**, 273 (1900).

|| If the solution is neutral, add 2 or 3 g. of ammonium chloride and then carry out the analysis.

¶ According to Voigt, *Z. angew. Chem.*, **1909**, 2282, the precipitate can be washed immediately with hot water.

because it requires long washing to remove these and this renders the results a little low. When the precipitate is weighed as pyrophosphate, the ammonium salts are volatilized and it is not necessary to remove them by washing.

Remark. — In some cases, as when magnesium or aluminium is present, the procedure of K. Voigt is followed. To the solution of the zinc salt, containing ammonium salts as well, add an excess of ammonia and the required volume of ammonium phosphate solution. After standing some time, filter off the precipitated magnesium ammonium phosphate and aluminium phosphate; the zinc ammonium phosphate is soluble in ammonia. Heat the filtrate on the water-bath until all the free ammonia has been expelled, whereby zinc ammonium phosphate separates quantitatively in the form of the crystalline precipitate. Treat this precipitate as described above. If some of the precipitate should adhere firmly to the sides of the dish, it may be dissolved in a few drops of hydrochloric acid, the solution immediately neutralized with ammonia, and heated a few minutes on the water-bath before filtering.

2. Determination as Zinc Oxide

The carbonate, nitrate, acetate, and oxalate of zinc are readily and quantitatively changed to zinc oxide by ignition in the air; in the case of the sulfate, when present in relatively large amounts, the transformation into oxide is difficult. Small amounts of the sulfate may be changed to oxide by igniting over the blast-lamp. It is advisable, however, in case the zinc is present as sulfate, to precipitate it from the aqueous solution as sulfide and weigh it as such according to 3; or to dissolve the sulfide on the filter in dilute hydrochloric acid, receiving the solution in a weighed platinum dish, evaporating to dryness on the water-bath, and changing to oxide by the method of Volhard as described below, and weighing as such.

The chloride is readily changed to oxide, according to Volhard, by gentle ignition with pure mercuric oxide. The process is as follows: Treat the neutral solution of the chloride, contained in a platinum dish, with a large excess of pure yellow mercuric oxide,* suspended in water, and evaporate to dryness on the water-bath; mercuric chloride and zinc oxide are formed,

$$ZnCl_2 + HgO = ZnO + HgCl_2,$$

both of which are white substances. Enough mercuric oxide should be used so that the residue obtained after the evaporation is noticeably yellow.

* The mercuric oxide is prepared by precipitating a solution of mercuric chloride with pure caustic potash. Allow the precipitate to settle, wash by decantation with water until free from chloride, and keep suspended in water in a bottle with a wide neck. A considerable amount of the mercuric oxide, say 5–10 g., should leave no weighable residue after ignition.

Ignite the dry mass under a hood with a good draft (on account of the mercury vapors being poisonous), at first gently and finally strongly, and weigh the residue of zinc oxide; both mercuric chloride and oxide are volatile. The results are excellent.

If the solution contains, besides zinc, also alkalies, the zinc can be precipitated as basic carbonate and changed to oxide upon ignition. The precipitation of the zinc carbonate should take place in a porcelain dish and the sodium carbonate solution should be added drop by drop to the cold, barely acid solution free from ammonium salts. Add the sodium carbonate solution until the zinc solution becomes turbid, then heat to boiling; the greater part of the zinc is precipitated as granular zinc carbonate. Add two drops of phenolphthalein indicator solution and enough sodium carbonate solution to impart a distinct pink color. In this way a precipitate of zinc carbonate is obtained free from alkali, which is not the case if the hot solution is at once precipitated by the addition of an excess of sodium carbonate.* Filter the precipitate from the *hot* solution and wash with hot water until 20 drops of the filtrate leave no residue on evaporation. Dry the precipitate, transfer the greater part to a weighed porcelain crucible, burn the filter by itself in a platinum spiral, and add the ash to the main part of the precipitate in the crucible. Ignite at first gently and finally strongly, over a Teclu or Méker burner and weigh† after cooling in a desiccator.

If the zinc solution contains ammonium salts, it is possible to remove them by boiling with an excess of sodium carbonate solution.

3. Determination as Sulfide

This determination is chosen when the zinc is present in a solution containing ammonium salts, or when it is necessary to separate zinc from alkaline earths, alkalies or metals of this group. Zinc sulfide may be precipitated from ammoniacal solutions. or from solutions containing free acetic, formic, citric, or thiocyanic acids in the presence of ammonium salts.

(*a*) *Precipitation of ZnS from Ammoniacal Solutions*

Place the slightly acid solution in an Erlenmeyer flask and treat with sodium carbonate solution until a permanent precipitate is obtained.

* In case considerable amounts of ammonium salts are present there may be no precipitation. Sodium carbonate should then be added until the solution is slightly alkaline and the solution boiled until all the ammonia is expelled.

† If the solution contains sulfate, the precipitate produced by sodium carbonate always contains more or less basic zinc sulphate, which may easily lead to high results. In the presence of sulfates, therefore, it is advisable to precipitate the zinc as sulfide and determine it as such according to 3.

Dissolve this by the addition of a few drops of ammonia and then, for every 100 ml. of the solution, add 5 g. of ammonium acetate (or, better, ammonium thiocyanate), followed by a slight execss of freshly-prepared ammonium sulfide. Nearly fill the flask with boiled water, stopper and allow to stand twelve to twenty-four hours. Without disturbing the precipitate, pour the clear supernatant liquid through a Schleicher & Schüll's filter No. 590. Cover the precipitate with a 5 per cent solution of ammonium acetate (or ammonium thiocyanate) containing 2 ml. of ammonium sulfide solution. Shake, allow to settle, and pour the turbid solution through the filter, taking care to receive the filtrate in a fresh beaker; in case it comes through turbid pour it through the filter again. Repeat the decantation three times, after which transfer the precipitate to the filter and wash completely with the above wash-liquid, taking pains to keep the filter full during the entire operation, finally washing with water containing ammonium sulfide only. Dry the precipitate, transfer as completely as possible to a weighed Rose crucible, burn the filter by itself and add the ash to the main portion of the precipitate. Mix the precipitate with one-third as much pure sulfur, cover with a layer of sulfur and heat, as described under Manganese (p. 132) in a current of hydrogen. Finally allow the crucible to cool in the stream of hydrogen and weigh the zinc sulfide.

(*b*) *Precipitation of ZnS from Acid Solutions*

To the solution, which has been nearly neutralized with ammonia, add ammonium chloride or sulfate as in the previous method and a little ammonium or sodium acetate; then saturate with hydrogen sulfide. After the precipitate has settled completely, pour the supernatant solution through a filter, and wash the precipitate with 2 to 4 per cent acetic acid which has been saturated with hydrogen sulfide. When thoroughly washed, treat as described above. It is to be noted that the zinc sulfide shows less tendency to form colloidal solutions when it is thrown down from a slightly acid solution than when it is precipitated from alkaline solutions.

The Use of Membrane Filters

Zinc sulfide is characterized by the difficulty in filtering it from solutions in which it has been precipitated. Substances of this type tend to form *colloidal solutions.* According to Wolfgang Ostwald there is no sharp dividing line between a true solution and a colloidal solution on the one hand and between a colloidal solution and a suspension on the other. Arbitrary lines may be drawn on the bases of the average

size of the particles. Individual particles cannot be seen under the microscope when the diameter of the particle is less than half a wave length of light. By working with ultra-violet light of short wave length, particles about one ten-thousandth of a millimeter, or 0.1 μ can be seen. This value Ostwald takes to define the boundary between coarse suspensions and colloidal solutions. The pores of a good hardened filter are about 1.0 μ in diameter: those of clay and porcelain filters are about 0.2–0.4 μ. Colloidal solutions pass unchanged through paper filters and even through most of the very fine porcelain or clay filters. Suspensions do not as a rule pass through paper filters, after the pores have become clogged a little.

Typical molecules have a diameter of one ten-millionth to one millionth of a millimeter, *i.e.*, from 0.1 to 1.0 $\mu\mu$. A large molecule like that of starch has a diameter of about 5 $\mu\mu$.

Substances mixed with water, therefore, may be said to be in a state of molecular dispersion, or in true solution, when the diameters of the individual particles are less than 1.0 $\mu\mu$ and in colloidal solution when the diameters of the smallest particles lie between 1.0 $\mu\mu$ and 0.1 μ.

Zsigmondy* and his co-workers have developed the so-called *membrane filters* of which the pores are fine enough to separate the finer suspensions and the coarser colloids from the menstruum in which they are suspended. The filters themselves are prepared by drying a mixture of colloids. They have somewhat the appearance of parchment or of white glove leather. They can be purchased† in several grades, according to the size of the pores, and will perfectly filter colloidal solutions which will pass unchanged through an ordinary filter. Membrane filters have been recommended especially for the filtering of zinc sulfide.

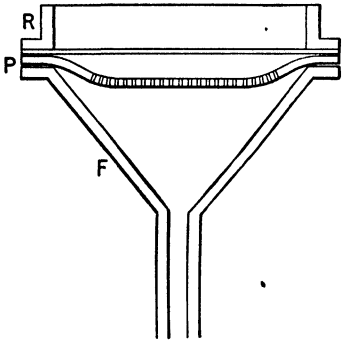


FIG. 41.

These membrane filters can be used with suction in a special filtering funnel such as that shown in Fig. 41. It consists of three parts: a funnel *F*, a perforated filter plate and a rim *R* to prevent the liquid running over. It is well to have rubber rings as gaskets between the

* Zsigmondy and Bachmann, *Z. anorg. Chem.*, **103**, 121 (1918); Zsigmondy and Jander, *Z. anal. Chem.*, **58**, 241 (1919).

† Warmbrunn, Quilitz & Co., of Berlin, Germany and E. de Haën of Selze near Hannover, Germany, were among the first to handle Zsigmondy's filters and filtering apparatus.

different parts. To prepare the filter, place the filter plate, *P*, on top of the funnel and over the perforations of the filter plate place a paper filter. If this paper is not used, only the parts of the membrane filter that lie directly over the holes in the filter plate are used in the filtration. On top of *P* place a membrane filter and on this the rim, *R*, with rubber rings between each part. By means of three or four clamps fasten the parts in place lightly, apply suction until the membrane filter is drawn down onto the filter plate and then tighten the clamps so that there is no chance for leakage. The whole apparatus is very similar to a porcelain Büchner funnel, except that the parts are separate.

In using these filters the liquid should not be poured up to the top of the rim and the filter should not be allowed to drain dry and form cracks.

Precipitates like silver chloride, which have to be heated and allowed to stand before filtering can be filtered immediately with a membrane filter. Precipitates of zinc sulfide which required 6 hours to filter and wash with a paper filter have been filtered and washed in 25 minutes with a membrane filter. On the other hand, time is lost if the precipitate is coarsely crystalline and filters rapidly with paper.

After filtering with a membrane filter it is usually possible to remove the precipitate completely and ignite it in a crucible by itself. The filter can be used for another filtration. Sometimes it is best to dry the precipitate before removing it and sometimes it can best be removed moist.

4. Electrolytic Determination of Zinc

It is possible to deposit zinc electrolytically with a current of 0.2–0.3 ampere from a neutral solution to which sodium acetate and a few drops of acetic acid have been added. From the solution of potassium or sodium zincate, or from the complex alkali zinc cyanides, it is easier to deposit the zinc quantitatively.

(*a*) Method of F. Spitzer*

To the solution of zinc sulfate (chlorides and nitrates should be absent) add a drop of phenolphthalein and sodium hydroxide solution until a permanent coloration is obtained. Then add 20–25 ml. of 4 *N* sodium hydroxide solution, dilute to 150–200 ml. and electrolyze with a current of 0.8–1 ampere and 3–4 volts electrode potential using a platinum gauze cathode. At the end of three hours the electrolysis is finished, provided not more than 0.5 g. of zinc was present. Without breaking the current, raise the electrodes nearly out of the bath, wash the upper portions quickly with water, then remove the electrodes

* *Z. Elektrochem.*, **11**, 401 (1905).

entirely from the solution and rinse with water. Turn off the current, wash the cathode with alcohol, dry over a flame, cool in a desiccator, and weigh. Under these conditions, zinc forms a bluish-gray deposit that adheres firmly to the electrode. To make sure that all the zinc was deposited, clean the electrodes and electrolyze the solution for thirty minutes longer. A slight increase in weight will be obtained in every case because the anode is attacked slightly by the alkaline solution so that the cathode slowly continues to gain in weight from deposited platinum. If at the end of half an hour the gain in weight is not over 0.3 mg. then the deposition of the zinc was complete the first time, as can be shown by testing with hydrogen sulfide. The results are always a little high.*

To clean the electrodes, boil them with 4 *N* hydrochloric acid, wash well with distilled water, and heat over a flame. It is not necessary to cover the platinum gauze with a thin coating of copper or of silver, as has been recommended when a platinum dish is used as the cathode.

Remark. — If too little caustic soda is present, a spongy deposit of zinc is obtained which does not adhere well to the electrode. For this reason the above directions should be followed closely.

In the presence of ammonia the determination is not successful. If, therefore, it is desired to analyze a solution containing an ammonium salt, it must be boiled with caustic soda until all the ammonia has been expelled. If, moreover, chlorides or nitrates are present they must be removed by evaporation with sulfuric acid. Evaporate the solution on the water-bath and finally heat over the free flame until dense vapors of sulfuric acid are expelled. Dilute the solution and electrolyze as described.

(*b*) The Potassium Cyanide Method†

Add a drop of phenolphthalein indicator solution to the solution of zinc sulfate, caustic soda solution until a permanent pink coloration is obtained, and then potassium cyanide solution until a clear solution results. Dilute to a volume of 150–200 ml. and electrolyze with a current of 0.2–0.3 ampere. At first the electrode potential is about 5.8 volts, but it falls during the analysis on account of the current heating the solution. The electrolysis is finished in two or three hours.

Other methods for the electrolytic estimation of zinc are given in Classen-Hall's *Quantitative Analysis by Electrolysis.*

* Ellwood B. Spear, *J. Am. Chem. Soc.*, **32**, 530 (1910). The experiments have been repeated in the author's laboratory by Janini, who obtained as an average from fourteen determinations with 50 ml. of a zinc sulfate solution, the value 0.1014 g. Zn instead of 0.1008 g. Zn, a difference of about 0.6 per cent.

† Luckow, *Z. anal. Chem.*, **19**, 1 (1880); Beilstein and Jawein, *Ber.*, **12**, 446 (1879); Milot, *Bull. soc. chim.*, **37**, 339 (1882); W. D. Treadwell, *Electroanalyt. Methoden.*

SEPARATION OF MANGANESE, NICKEL, COBALT, AND ZINC FROM THE ALKALINE EARTHS

The separation depends upon the insolubility of the sulfides of the metals of this group and the solubility of the sulfides of the alkaline earths.

Procedure. — Treat the neutral solution of the chlorides in an Erlenmeyer flask with ammonium chloride (in case it is not already present) and freshly-prepared colorless ammonium sulfide solution, added drop by drop until no further precipitation takes place and the liquid has a distinct odor of ammonium sulfide. Nearly fill the flask with boiled water, stopper, and allow to stand twelve hours. Filter off the precipitate and wash as described in the Determination of Zinc (p. 144).

If only a small quantity of alkaline-earth metals is present and the ammonium sulfide solution is entirely free from ammonium carbonate, the separation is usually complete after one precipitation; in the presence of considerable calcium, strontium, barium, or magnesium the sulfide precipitate will always be more or less contaminated with these substances, so that the precipitation must be repeated. For this purpose transfer the washed precipitate as completely as possible to a porcelain crucible, burn the filter-paper in a platinum spiral and add the ash to the main part of the precipitate. Cover the crucible with a watch-glass, add 2 *N* hydrochloric acid, and heat gently after the evolution of hydrogen sulfide has ceased, to remove all dissolved gas. Now add a little concentrated nitric acid and heat the mixture until the precipitate is completely dissolved and the solution is evaporated to dryness, add a little concentrated hydrochloric acid and again evaporate to make sure that no nitrate remains. Moisten the dry mass with a few drops of concentrated hydrochloric acid, dissolve in hot water, and filter off the slight residue of sulfur, which, in case barium is present, always contains a small amount of barium sulfate. Wash the residue with hot water, dry, ignite in a porcelain crucible, and weigh. Treat the filtrate exactly as before with ammonium sulfide.

In case nickel is present, an excess of ammonium sulfide must be carefully avoided, as otherwise the nickel sulfide will pass through the filter (cf. Vol. I). In all cases, however, the filtrate should be tested for nickel by acidifying with acetic acid, heating to boiling, and passing hydrogen sulfide into the solution. If a slight black precipitate is produced by this treatment, filter it off and combine with the main precipitate (cf. p. 161 *et seq.*). Free the filtrate, containing the alkaline-earth cations, from ammonium salts by evaporating to dryness and

heating the residue, dissolve this in hydrochloric acid, and examine as described on p. 86 *et seq.*

Remark. — The ammonium sulfide solution used in the above separation must be free from ammonium carbonate. As, however, all commercial ammonia contains this salt, it must be freed from carbonate before being used for the preparation of ammonium sulfide solution.

Preparation of Ammonia Free from Carbonate and Silicate

Add 10 g. of freshly-slaked lime to 500 ml. of concentrated ammonia contained in a liter flask that is connected with a condenser. Close the condenser by means of a tube containing soda-lime, and allow the contents of the flask to stand for a day with frequent shaking. Then place 300–400 ml. of water in a flask and boil, meanwhile passing through the water a current of air that has been freed from all traces of carbon dioxide by passing through concentrated caustic potash solution and then through a tower filled with soda-lime. Allow this water to cool in this air-stream. Place the flask containing the ammonia on the water-bath in such a position that the condenser-tube is inclined slightly upward, and connect this with the delivery-tube, through which the air previously passed into the flask of boiling water. By heating the water-bath, distil the ammonia over into the flask containing the boiled water, by which it is completely absorbed. By saturating a part of this ammonia with hydrogen sulfide, a solution of ammonium sulfide is prepared suitable for the above-described separation.

Separation of the Bivalent from the other Metals of the Ammonium Sulphide Group

This separation is often designated as that of the *protoxides* from the *sesquioxides;* this designation is not applicable in the case of titanium and uranyl derivatives.

Insoluble hydroxides or basic salts of tervalent iron, chromium and aluminum and of quadrivalent titanium and zirconium precipitate when the acidity of the solution lies between 10^{-6} and $10^{-7.5}$ moles of hydrogen ions per liter. Bivalent uranyl ions usually precipitate also at this acidity.

It is quite common to express the acidity of a solution in terms of the so-called *hydrogen exponent,* p_H, which is the value log $1/c$ when c is the concentration of H^+ in moles per liter or exponent. Thus a concentration of 10^{-6} mole of hydrogen ions per liter is expressed briefly by saying $p_H = 6$. Since the logarithm to the base 10 of 1 is 0 and the logarithm of a fraction is the logarithm of the numerator minus the

logarithm of the denominator, it is evident that *log* $1/c = 6$ when $c = 10^{-6}$.

It is easy to tell when the hydrogen ion concentration corresponds approximately to $p_H = 5$ because methyl red indicator in dilute solution changes from red to yellow at this point. Most methods for separating ions of iron, chromium and aluminium from the bivalent ions of the third group depend upon the neutralization of an acid solution. This may be accomplished by the careful addition of ammonia, by adding a salt of a weak acid, or by adding an insoluble carbonate or oxide. Theoretically, the separation could be accomplished by the addition of caustic alkali or alkali carbonate provided the solution was never allowed to become more alkaline than corresponds to $p_H =$ about 5 but it is practically impossible, because some portion of the solution is likely to contain a slightly lower acidity, even although it is well stirred, and the excess of this causes the precipitation of insoluble hydroxides of bivalent metals. It is difficult to make the separation with ammonium hydroxide, for this same reason, but when ammonium hydroxide is added to a solution containing an ammonium salt, its ionization is repressed so that it amounts to less than one hundredth as much as that of a caustic alkali solution of the same normal concentration. Moreover, in ammonium hydroxide solution, the greater part of the reagent consists merely of dissolved NH_3 and this forms complex ions with many bivalent ions, particularly copper, cadmium, nickel, cobalt and zinc ions, and the formation of these complexes prevents precipitation of hydroxides.

Chemists have known for a long time that a rough separation of the tervalent and bivalent ions can be accomplished by means of ammonia and ammonium chloride but the practice has been discouraged because of the danger of adding too much ammonia to some part of the solution before all of the solution has been sufficiently neutralized.

The Barium Carbonate Method

This method depends upon the fact that ferric, aluminium and chromic ions (as well as titanic, zirconic and uranyl ions) are precipitated in the cold by barium carbonate, while the bivalent manganese, nickel, cobalt, zinc, and ferrous ions are not. Salts of the tervalent metals undergo hydrolysis when in dilute aqueous solution:

$$Fe^{+++} + HOH \rightleftarrows Fe(OH)^{++} + H^+.$$

Free acid and a basic salt are formed by this hydrolysis, the composition of the latter depending upon the quantity of the water and the temperature. If the free acid is removed by the addition of barium carbonate, the equilibrium is disturbed and the hydrolysis goes further until finally the insoluble hydroxide is formed:

$$Fe(OH)^{++} + 2\,HOH \rightarrow \mathbf{Fe(OH)_3} + 2\,H^+.$$

The barium carbonate, then, serves only to neutralize the acid set free by the hydrolysis, and the total reaction is expressed by the following equation:

$$2\ Fe^{+++} + 3\ HOH + 3\ BaCO_3 \rightarrow 3\ Ba^{++} + 2\ Fe(OH)_3 + 3\ CO_2 \uparrow.$$

The salts of the bivalent metals are not subject to this hydrolysis *in the cold*, consequently they are not precipitated by the addition of barium carbonate. On warming, however, they are hydrolyzed to an appreciable extent and are then precipitated by barium carbonate.

Procedure. — Add sodium carbonate solution, drop by drop, to the slightly acid solution of the chlorides or nitrates, but not the sulfates* of the metals, in an Erlenmeyer flask until a slight, permanent turbidity is produced; redissolve this by the addition of a few drops of dilute hydrochloric acid. Dilute the solution and add pure barium carbonate† (suspended in water) until, after thoroughly shaking, an excess of the latter remains on the bottom of the flask. Stopper the flask and allow to stand for several hours with frequent shaking. Then decant off the clear liquid through a filter, treat the residue with cold water and again decant. Wash the precipitate three times in this way, transfer the precipitate to the filter and wash thoroughly on the filter with cold water. The precipitate contains all of the iron, aluminium, chromium, titanium, and uranium in the presence of the excess of barium carbonate. The filtrate contains the bivalent metals and barium chloride.

Dissolve the precipitate in normal hydrochloric acid solution, boil to remove carbon dioxide, and separate the iron, aluminium, chromium (titanium and uranium) from the barium‡ by double precipitation with ammonium sulfide as described on p. 149. Separate the iron, aluminium, chromium (titanium, zirconium and uranium) from one another as described on pp. 108–128.

In the filtrate from the barium carbonate precipitation remove barium by the addition of sulfuric acid§ to the boiling solution after it has been made acid with hydrochloric acid. Filter off the barium sulfate and separate the bivalent cations from one another as described on pp. 161–171.

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* Barium carbonate will precipitate the bivalent metals when sulfates are present, *e.g.*:

$$ZnSO_4 + BaCO_3 = ZnCO_3 + BaSO_4.$$

† The barium carbonate must be free from alkali carbonate.

‡ Most authorities recommend precipitating the barium first with sulfuric acid and then separating the iron, aluminium, etc. The precipitate of barium sulfate always contains small amounts of the heavy metals, so that the author prefers the above procedure.

§ Or, better, by double precipitation of the other metals with ammonium sulfide.

Remark. — The above separation of the sesquioxides from the protoxides is not absolutely certain in the presence of nickel and cobalt. In this case, particularly when considerable iron is present, the precipitate produced by barium carbonate contains a little nickel and cobalt. This difficulty can be overcome, however, by adding ammonium chloride to the solution (3–5 g. for each 100 ml. of solution) before precipitating with barium carbonate; the separation is then satisfactory.

SEPARATION OF IRON, ALUMINIUM, AND TITANIUM (BUT NOT CHROMIUM AND URANIUM) FROM MANGANESE, NICKEL, COBALT, AND ZINC

Basic Acetate Method

This classic method depends upon the fact that ferric, aluminium and titanium acetates are hydrolyzed in hot, dilute solutions much more readily than the acetates of the bivalent metals. From the equation

$$Fe(C_2H_3O_2)_3 + 2\ HOH \rightleftarrows 2\ HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2,$$

it is evident that acid is set free which tends to stop the reaction, due to the solvent action of hydrogen ions. The concentration of free hydrogen ions, however, is kept low by the addition of sodium acetate. Then, as a rule, some manganese is likely to be precipitated, so that it is advisable to dissolve the precipitate and repeat the precipitation. Hydrated manganese dioxide $MnO_2.H_2O$ or manganic hydroxide, $Mn(OH)_3$, is more insoluble than manganous hydroxide, $Mn(OH)_2$, and hence long boiling in the air tends to increase the quantity of manganese precipitated. The method is somewhat tedious, but gives excellent results.

Procedure. — To the slightly acid solution of the *chlorides*, contained in a small beaker, add sodium carbonate solution in the cold until a slight permanent opalescence is obtained; redissolve the precipitate by the addition of a few drops of dilute hydrochloric acid. Meanwhile prepare a boiling, dilute solution of sodium or ammonium acetate in a large round-bottomed flask, containing for each 0.1–0.2 g. of iron or aluminium, 1.5–2 g. of acetate and 300–400 ml. of water. When the iron solution is ready, take away the burner from beneath the flask, add the solution of iron, aluminium, etc., replace the burner and continue the boiling for one minute. Then remove the flame (the precipitate becomes slimy on long boiling), allow the precipitate to settle and filter while the liquid is hot, through a fluted filter, washing three times by decantation with boiling water containing ammonium or sodium acetate. Spread the filter together with the precipitate upon a glass plate, rinse the bulk of the precipitate into a porcelain dish, and dissolve the precipitate remaining on the filter by alternately treating with hot 3 *N* hydrochloric acid and with hot water. Evaporate the resulting solution nearly to dryness on the water-bath and repeat the basic acetate precipitation exactly as before. Dissolve the filtered and washed precipitate in hydrochloric acid and separate the iron from

aluminium according to page 108. To the combined filtrates from the basic acetate precipitation, add 10–20 ml. of concentrated hydrochloric acid, to prevent the precipitation of hydrated manganese dioxide, evaporate almost to dryness, dilute with a little water and precipitate manganese, nickel, cobalt and zinc by ammonium sulfide as described on p. 149, and analyze according to p. 161.

Remark. — This procedure requires practice. It is especially suited for the separation of iron and titanium from the protoxides; the separation is usually less satisfactory with aluminium, so that in case considerable amounts of the latter are present, the barium carbonate separation is to be preferred. If it is merely a case of the

Separation of Iron from Manganese,

the following modifications of the basic acetate process give satisfactory separations with only a single precipitation.

(*a*) O. Brunck's Method*

To the acid solution, containing not more than 0.3 g. of iron, add 0.35 g. of potassium chloride or 0.26 g. ammonium chloride for each 0.1 g. of iron present. Evaporate the solution to dryness on the water-bath, break up the residue by pressure with a glass rod, and heat 5 or 10 minutes longer. By this time practically all the mineral acid is expelled. Dissolve the residual salts in 10–20 ml. of water and to the resulting solution add 1.5 g. of sodium acetate for each 0.1 g. of iron present.† Dilute the solution with boiling water to a volume of 400–500 ml. for each 0.2 g. of iron present; heat, with constant stirring, until boiling begins, then remove the flame and allow the precipitate to settle. Decant off the solution through a fluted filter and wash the precipitate with hot water. Dissolve the precipitate in as little hydrochloric acid as possible, precipitate the iron by ammonia, filter, dry, and ignite as described on p. 94. Make the filtrate from the basic acetate precipitation, or better the combined filtrates from both precipitations,‡ acid with hydrochloric acid, evaporate nearly to dryness, dissolve the deposited salts in a little water and precipitate manganese, nickel, cobalt and zinc with ammonium sulfide according to the directions on p. 149, and separate according to p. 161.

* *Chem. Ztg.*, **1904**, I, 513. Cf. W. Funk, *Z. anal. Chem.*, **45**, 181 (1906).

† The sodium acetate crystals often contain a little sodium carbonate; they should be dissolved in a little water and the solution made barely acid before adding it to the iron solution.

‡ To the ammoniacal filtrate from the $Fe(OH)_3$ precipitate, add 5 ml. of concentrated hydrochloric acid before adding the solution to the filtrate from the basic acetate precipitation, otherwise manganese is likely to be precipitated when the two filtrates are mixed.

(*b*) Method of A. Mittasch*

Neutralize the slightly acid solution, containing not more than 0.3 g. of iron and having a volume of not over 100 ml., by adding ammonium carbonate solution (200 g. of the commercial salt in 1 liter of water) from a pipet or buret while stirring constantly. When a precipitate is produced which dissolves very slowly on stirring, finish the neutralization with a more dilute ammonium carbonate solution, prepared by taking 50 ml. of the first solution and diluting to 1 liter. Add the dilute reagent until a slight precipitate is produced which will not dissolve by 1 or 2 minutes of stirring. At this point, add 3 ml. of 2 *N* acetic acid, and stir until the precipitate disappears. Dilute the solution with 400 ml. of hot water and heat until it begins to boil, when the greater part of the iron will have been precipitated. Then add 20 ml. of ammonium acetate solution (60 g. of the commercial salt in 1 liter of water) † and continue boiling for a minute longer. Without waiting for the precipitate to settle, filter and wash with hot water until the precipitate is free from chlorides.

Dissolve the small quantity of precipitate that adheres to the sides of the vessel in which the precipitation took place by adding a few drops of hydrochloric acid, precipitate the iron in the solution by ammonia and filter off the ferric hydroxide through a separate filter. Ignite both precipitates and filters and weigh the iron as Fe_2O_3.

Separation of Iron and Aluminium from Manganese, Nickel, Cobalt, and Zinc

(*a*) Sodium Succinate Method

This method, applicable for the separation of large quantities of iron from small quantities of manganese, nickel, etc., is based upon the fact that ferric iron is precipitated quantitatively from *neutral* solutions as light-brown ferric succinate by the addition of neutral alkali succinate solution, while manganese, nickel, etc., remain in solution.

Procedure. — In case the solution contains free acid and all the iron is in the ferric form, neutralize with ammonia until a reddish-brown coloration is formed, then add sodium or ammonium acetate until the

* *Z. anal. Chem.*, **42**, 508 (1903).

† Commercial ammonium acetate has the symbol $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$. If none of it is on hand, mix 50 ml. 2 *N* ammonium hydroxide with 100 ml. 2 *N* acetic acid; the mixture must be faintly acid. Of this solution use 10 ml. mixed with 5 ml. 2 *N* acetic acid for the precipitation of the iron, and use 10 ml. of 2 *N* acetic acid to dissolve the precipitate produced by ammonium carbonate.

color becomes a deep brown. Dilute the solution to at least 200 ml. for each 0.1 g. of iron present and add 3 g. of sodium succinate dissolved in a little water. Heat nearly to boiling, filter, and wash at first with cold water, then with warm normal ammonium hydroxide solution, until 20 drops of the filtrate leave no residue when evaporated to dryness on platinum. By means of the washing with ammonia, the ferric succinate is changed to ferric hydroxide. Ignite and weigh as ferric oxide in a porcelain crucible. If aluminium is present, analyze the ignited residue as described on p. 110. The bivalent metals in the filtrate are best precipitated by the addition of ammonium sulfide and analyzed as described on p. 161.

(*b*) Separation by Ammonia and Ammonium Chloride*

To the acid solution containing 5 g. of ammonium chloride and not more than 0.2 g. of iron and aluminium cations in 200 ml. of solution, add a few drops of a 0.2 per cent solution of methyl red in alcohol and heat just to boiling. Carefully add normal ammonium hydroxide solution, drop by drop, until the color of the solution changes to a distinct yellow. Boil 2 minutes and filter promptly. Wash with hot 2 per cent ammonium nitrate solution until free from chloride. The precipitate contains $Fe(OH)_3$ and $Al(OH)_3$ and $Ti(OH)_4$ and $Zr(OH)_4$ if the corresponding elements are present.

As good a separation of iron and aluminium from manganese is accomplished in this way as by a single basic acetate precipitation. It is advisable to dissolve the precipitate and repeat the precipitation when the precipitate upon ignition is likely to weigh more than 0.1 g. or when a 9 cm. filter is more than half full of the precipitate.

Remark. — Lundell and Knowles showed that iron and aluminium can be separated from manganese and nickel as satisfactorily by this method of precipitation, which is the same as that recommended by Blum for precipitating aluminium, as by the basic acetate or barium carbonate methods. Phosphoric and vanadic acids follow the iron and aluminium and do not affect the separation if sufficient iron and aluminium is present. If more phosphoric acid or vanadic acid is present than is equivalent to the iron and aluminium, the separation fails as does that of the basic acetate or barium carbonate procedure. Under the above conditions, some cobalt, copper and zinc will precipitate if present but a fair separation is effected then by increasing the ammonium chloride content. An excess of both ammonia and ammonium chloride gives better results in the separation of iron from copper and zinc but the precipitation of the aluminium is then less complete.

* Lundell and Knowles, *J. Am. Chem. Soc.*, **45**, 676 (1923).

The Use of Cupferron in Quantitative Analysis

Cupferron is a short name for the ammonium salt of nitrosophenyl hydroxylamine, $C_6H_5N.NO.ONH_4$. O. Baudisch* first suggested its use as a reagent for the quantitative precipitation of cupric and ferric ions. By means of cupferron, it is possible to precipitate quantitatively copper, iron, titanium, zirconium and thorium from strongly acid solutions and in this way a number of separations may be accomplished which otherwise involve considerable difficulty. The copper salt is gray, the ferric salt red and the titanium salt yellow.

As a precipitant for copper, the reagent apparently offers no special advantages, and when silver, lead, mercury, tin or bismuth are present, these elements contaminate the precipitate to some extent. On the other hand, in the case of iron, titanium and zirconium it is very useful to possess a reagent which will precipitate these elements quantitatively from acid solutions without contamination from aluminium, chromium, manganese, nickel, cobalt, zinc or alkaline earth metal. The advantages of cupferron for effecting separations have been pointed out by a number of chemists.†

Cupferron is readily soluble in water and the ammoniacal solution keeps well. The reagent is not very stable in acid solutions, particularly in hot solution or when an oxidizing agent is present. By oxidation, nitrosobenzene is formed and its presence can be detected by the peculiar, sweetish odor in nearly every precipitation with cupferron. When much nitrosobenzene is formed it separates out in the form of white needles. Precipitation with cupferron is always effected in cold, acid solution and an excess of the reagent must be used. The precipitate is stable as long as an excess of cupferron is present.

When iron and copper are precipitated together by means of cupferron, washing with 6 *N* ammonium hydroxide serves to remove the copper and the excess of cupferron; it also serves to convert the iron precipitate into ferric hydroxide, in which form it is more readily converted into ferric oxide on ignition. In the ammoniacal solution of the copper precipitate, the copper can be precipitated by the addition

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* O. Baudisch, *Chem.-Ztg.*, **33**, 1298 (1909); Baudisch and King, *J. Ind. Eng. Chem.*, **3**, 629 (1911).

† Nissenson, *Z. angew. Chem.*, **23**, 969 (1910); Biltz and Hodtke, *Z. anorg. Chem.*, **66**, 426 (1910); Hanus and Soukup, *ibid.*, **68**, 52 (1910); R. Fresenius, *Z. anal. Chem.*, **50**, 35 (1911); Schroeder, *Z. anorg. Chem.*, **72**, 89 (1911); Bellucci and Grassi, *Gazz. chim. ital.*, **43**, I, 570; Thornton, *Am. J. Sci.*, **37**, 173 and 407 (1914); Lundell and Knowles, *J. Ind. Eng. Chem.*, **12**, 344 (1920).

of acetic acid and by washing with one per cent sodium carbonate solution the cupferron may be removed from the copper.

The manner of preparing the reagent and four methods illustrating its use will be described.

Preparation of Cupferron*

Cupferron is prepared from β-phenylhydroxylamine, ammonia and amyl nitrite.

Preparation of β-Phenylhydroxylamine. — Place 8 liters of water, 500 g. of nitrobenzene and 250 g. of ammonium chloride in a 4-gallon earthenware jar. Stir the mixture rapidly to an emulsion by means of an efficient mechanical stirrer and, while still stirring, sift into the mixture 670 g. of zinc dust (75 to 80 per cent Zn) during the course of fifteen to twenty minutes. To obtain a good product it is advisable to keep the temperature below 20° by the addition of shaved ice.

After the zinc dust has been added, continue stirring for about fifteen minutes when the end of the reaction is indicated by the fact that the temperature of the mixture no longer rises. Continue stirring another five minutes and then filter off the insoluble zinc oxide with the aid of suction and wash with about one liter of water. Saturate the filtrate with sodium chloride and cool to nearly 0°. Filter with the aid of suction and dry between filter papers.

As phenylhydroxylamine solutions are active skin poisons, the hands and face should be washed with water and then with alcohol in case any solution spatters on them.

Preparation of Cupferron. — Weigh the moist crystals obtained by the above process and dissolve them in three liters of ordinary ether. Filter through a dry filter into a 5-liter round-bottomed flask. Weigh the insoluble residue (sodium chloride) to determine the quantity of dissolved β-phenylhydroxylamine. The flask should be fitted with a mechanical stirrer and be immersed in an ice-salt bath. When the temperature has fallen to 0° pass a rapid stream of dry ammonia gas through the solution. After about fifteen minutes add the theoretical quantity of freshly-distilled amyl nitrate (107 g. per 100 g. of β-phenylhydroxylamine) slowly through a dropping funnel. The addition of amyl nitrate usually requires about thirty minutes, during which time the stream of ammonia gas should be continued in order to make sure that an excess of ammonia is always present. If this precaution is not observed, a colored product will result. The tempera-

* Marvel and Kamm, *J. Am. Chem. Soc.*, **41**, 276 (1919); cf. Baudisch, *loc. cit.*

ture of the reaction mixture should be maintained below 10°; this is controlled best by the rate of adding the amyl nitrite.

After all the amyl nitrite has been added, continue stirring about ten minutes longer to insure completion of the reaction. Filter off the cupferron and wash several times with small portions of fresh ether. Spread on sheets of filter paper until all ether is volatilized. Keep a closely-stoppered bottle, containing a small lump of ammonium carbonate placed upon a doubled sheet of filter paper, on top of the cupferron. As reagent use a freshly-prepared 6 per cent aqueous solution.

1. THE DETERMINATION OF IRON IN MANGANESE ORES

Principle. — After effecting the solution of the ore, the iron is precipitated in acid solution by cupferron. The filtrate then contains all the aluminium, chromium, manganese, nickel, cobalt, zinc and alkaline earths. After the removal of any of these elements that may be present, by washing the precipitate with cold water, the organic matter is removed and the iron converted into ferric hydroxide by washing the precipitate with ammonia. The precipitate is ignited and weighed as Fe_2O_3.

Procedure. — Dissolve about 1 g. of the finely pulverized ore in concentrated hydrochloric acid, and evaporate the solution to dryness. Moisten the residue with strong hydrochloric acid, dilute with water, boil and filter. Fuse the residue with sodium carbonate in a covered platinum crucible, and after the fusion, dissolve the melt in water and dilute hydrochloric acid. Evaporate this solution to dryness, and after the removal of the silica in the usual manner, add the filtrate to the main solution. To the cold solution add 50 ml. of cupferron reagent in a fine stream down the sides of the beaker, while stirring vigorously. A brownish red, partly amorphous and partly crystalline precipitate of the ferric salt separates out. As soon as a drop of the reagent causes the formation of a snow-white precipitate of nitrosophenylhydroxylamine, all the iron is precipitated. Add a slight excess of the reagent and allow the solution to stand about 10 minutes. Filter through an ashless paper, using gentle suction. In case the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them and remove the ether by adding a little boiling water. Wash the precipitate with cold water until the washings are no longer acid to litmus and then with 6 *N* ammonia to remove the excess of the reagent and form ferric hydroxide. Finally wash the filter once more with cold water. Ignite the precipitate and weigh as Fe_2O_3.

2. THE DETERMINATION OF MANGANESE IN FERRO-MANGANESE

Dissolve about one gram of the material in strong hydrochloric acid and fuse the residue with sodium carbonate in a platinum crucible.

Heat the melt with water and add alcohol to reduce the manganate to hydrated manganese dioxide. Filter and dissolve the residue in hydrochloric acid; add this solution to that obtained in the first place. Precipitate iron with cupferron, as in the previous method, but do not add the ammonia washings to the solution. In the filtrate determine manganese as described on pp. 130 and 133.

3. THE DETERMINATION OF NICKEL AND COBALT IN ARSENICAL SULFIDE ORES*

Dissolve 1 g. of the ore in 20 ml. of a saturated solution of bromine in concentrated hydrochloric acid, and evaporate the solution somewhat to volatilize arsenious chloride. Add 10 ml. of 18 *N* sulfuric acid and evaporate the solution until dense fumes are evolved. Dilute to 500 ml., heat to boiling, and introduce hydrogen sulfide to precipitate the metals of the copper group and any remaining arsenic. In the filtrate precipitate the iron by cupferron as in Method 1, and after evaporating the filtrate until fumes of sulfuric acid are evolved, determine the nickel and cobalt electrolytically according to pp. 135, 138.

4. THE DETERMINATION OF TITANIUM AND ITS SEPARATION FROM IRON, ALUMINIUM AND PHOSPHORIC ACID†

Principle. — The iron may be reduced completely to ferrous salt by passing hydrogen sulfide into an acid solution, and then, in the presence of tartaric acid which prevents the precipitation of titanium, precipitated as ferrous sulfide in ammoniacal solution. After acidifying and boiling off the hydrogen sulfide, the titanium can be precipitated quantitatively by means of cupferron while the aluminium and phosphoric acid remain in the tartaric acid solution. It is unnecessary to remove the organic matter before igniting the yellow titanium precipitate.

Procedure. — To the solution, which should have a volume not greater than 100 ml., add at least four times as much tartaric acid as corresponds to the weight of the oxides of iron, titanium, aluminium, and phosphorus. Neutralize with ammonia, add 3 ml. of 18 *N* sulfuric acid and introduce hydrogen sulfide until the solution becomes colorless. Unless the iron is all reduced, the subsequent precipitate of iron sulfide will contain some titanium. After the reduction of the iron is complete, add ammonium hydroxide in considerable excess and precipitate the iron as ferrous sulfide by introducing more hydrogen sulfide gas; the solution should remain alkaline to litmus paper. Filter off the ferrous sulfide, and wash with water containing a little colorless ammonium sulfide. To the filtrate, add 40 ml. of 18 *N* H_2SO_4 and expel the liberated

* H. Nissenson, *Z. angew. Chem.*, **23**, 969 (1910).

† W. M. Thornton, Jr., *Am. J. Science*, **37**, 407 (1914).

hydrogen sulfide by boiling. When this is accomplished, cool the solution to room temperature, dilute to 400 ml., and treat with an excess of 6 per cent cupferron solution, added slowly down the sides of the beaker while the solution is being well stirred. After the precipitate has subsided, test the supernatant liquid by adding more of the cupferron solution. A white precipitate of nitrosophenylhydroxylamine indicates that an excess of the reagent is present but a yellow turbidity shows that the precipitation of the titanium is incomplete. It is also well to test the filtrate in the same way. Collect the titanium precipitate on filter-paper, using gentle suction, and wash twenty times with normal hydrochloric acid solution. Ignite very cautiously in a platinum or quartz crucible until the organic matter is all consumed. Finally, heat to constant weight over a Méker burner and weigh as TiO_2.

Other Determinations with Cupferron

Zirconium can be precipitated quantitatively from solutions containing as much as 40 per cent of concentrated sulfuric acid by volume and the presence of tartaric acid has no effect upon the precipitation. The ignited precipitate is ZrO_2. Thorium, on the other hand is not precipitated quantitatively in the presence of sulfuric acid but can be thrown down from acetic acid solutions. Vanadium, in either the quadrivalent or quinquevalent condition, can be determined quantitatively by precipitation in one per cent hydrochloric or sulfuric acid solution provided the precipitate is washed with one per cent acid containing cupferron.

Lead, silver, mercury, tin, bismuth, cerium, tungsten, interfere more or less with cupferron determinations and are likely to precipitate to some extent in most of the methods that have been described.

Separation of the Bivalent Metals of the Ammonium Sulfide Group from One Another

Separation of Zinc from Nickel, Cobalt, and Manganese

Most methods for this separation depend upon the slight solubility of zinc sulfide and the greater solubility of the other sulfides* in their state of formation.

It was shown in Vol. I that the solubility products of ZnS, NiS, CoS, FeS, Fe_2S_3 and MnS are all so small that these substances are

* Nickel and cobalt sulfides when once formed are insoluble in dilute acids. These substances probably exist in two allotropic modifications, of which one is soluble and the other insoluble. The soluble form has never been isolated.

precipitated quantitatively whenever the corresponding cations come in contact with any appreciable concentration of sulfide ions, as by adding a solution of ammonium sulfide. It was also shown in Vol. I that hydrogen sulfide is a weak acid and only slightly ionized. By adding acid, the concentration of the sulfide ion diminishes in proportion to the square of the concentration of hydrogen ions. Thus, if to an aqueous solution of hydrogen sulfide, enough acid is added to increase the hydrogen ion concentration ten fold, the concentration of the sulfide ion is diminished to about one one-hundredth of its former value.

In a liter of water saturated with hydrogen sulfide at 25°, there is present about 0.1 mole of undissociated hydrogen sulfide, 0.9×10^{-4} mole of hydrogen ions and only 1.2×10^{-15} mole of sulfide ion. In the saturated solution the relation $[H^+]^2 \times [S^{--}] = 1.1 \times 10^{-23}$ always holds at 25°, according to theory, and, therefore, it is easy to fix the concentration of the sulfide ion by regulating the concentration of the hydrogen ion.

Thus, to take a concrete case, suppose a solution to contain 0.2 g. of zinc ions and 0.2 g. of ferrous ions in 400 ml. of solution. What concentration of hydrogen ions is necessary to effect a quantitative separation of zinc and iron by hydrogen sulfide? Let us assume that the separation can be called quantitative when all but about 0.5 mg. of zinc is precipitated and not over 0.5 mg. of iron.

The solubility product of zinc sulfide is given in Vol. I as 1.2×10^{-23} and that of ferrous sulfide as 1.5×10^{-19}. Now 0.5 mg. of Zn in 400 ml. $= \frac{0.0005}{65.4} \times \frac{1000}{400} = 1.9 \times 10^{-5}$ mole per liter. To reach the solubility product of ZnS it is necessary to have $\frac{1.2 \times 10^{-23}}{1.9 \times 10^{-5}} = 6.3 \times 10^{-19}$ mole per liter of S^{--} ions.

The ionization of hydrogen sulfide in a saturated solution is repressed to this value when $[H^+]^2 = \frac{1.1 \times 10^{-23}}{6.3 \times 10^{-19}} = 0.17 \times 10^{-4}$ and $[H^+] = 4 \times 10^{-3}$ mole per liter. A similar computation for FeS shows that the concentration of H^+ ions required to prevent the precipitation of 0.2 g. of Fe is about 8×10^{-4} mole per liter. Therefore, to separate 0.2 g. of Fe completely from 0.2 g. of Zn in 400 ml. of solution it is necessary to keep the concentration of the acid between 8×10^{-4} and 4×10^{-3} mole per liter or, in other words, the solution must be kept between 0.0008 and 0.004 normal in hydrogen ions.

The values for the solubility products given in Vol. I are not accurate enough to predict with certainty whether a definite separation will be accomplished satisfactorily but they indicate the possibility of such

separations. The above computation, therefore, suggests the possibility of separating zinc from iron by means of hydrogen sulfide and it has been found possible to accomplish this in the laboratory.

To reach the desired concentration of hydrogen ions it is not permissible merely to add just the right quantity of a mineral acid at the start. During the precipitation of ZnS more hydrogen ions are formed as the following equation shows:

$$Zn^{++} + H_2S = \mathbf{ZnS} + 2\,H^+$$

It is necessary, therefore, to make sure that the acidity is correct when all of the zinc is precipitated. This is more important than the acid concentration at the start, for when hydrogen sulfide is passed into a solution, the least soluble sulfide forms first and if at one part of the solution a more soluble sulfide forms, it will itself precipitate another less soluble sulfide when it meets the other ion in another part of the solution.

Experimentally, it has been found possible to separate zinc as sulfide from very dilute hydrochloric acid solution after the addition of alkali acetate, and also from a solution containing dilute hydrochloric acid and a large quantity of ammonium salt. In the latter case it is probable that the ammonium salt exerts a " salting out effect " and precipitates colloidal zinc sulfide, making the solubility product smaller than it apparently is in pure water.

Method of Smith and Brunner*

Procedure. — Treat the hydrochloric acid solution of the four metals with sodium carbonate until a permanent precipitate is formed, and redissolve by the addition of a few drops of 2 *N* hydrochloric acid. Into this nearly neutral solution introduce hydrogen sulfide for five minutes, then add a few drops of 2 *N* sodium or ammonium acetate solution and saturate with hydrogen sulfide. Allow the mixture to stand over night, filter, and wash with hydrogen sulfide water containing 2 per cent of ammonium salt (either the chloride, sulfate, or thiocyanate). Determine the zinc either as oxide or sulfide according to the methods described on pp. 142–144.

Remark. — Inasmuch as the exact amount of acid to be set free is unknown, it is impossible to tell exactly how much alkali acetate is necessary, and herein lies the chief difficulty. If too much alkali acetate is added, some nickel or cobalt sulfide may be precipitated (shown by the gray color of the zinc precipitate). If not enough alkali acetate is added, the zinc will not be completely precipitated. The following separation is more certain.

* *Chem. Centrabl.*, **1895**, 26.

Method of Cl. Zimmermann*

Procedure. — Treat the slightly acid solution with sodium carbonate solution until a permanent precipitate is formed and redissolve by the addition of a few drops of 2 *N* hydrochloric acid, then for every 80 ml. of the solution add 10, or at the most 15, drops of 2 *N* hydrochloric acid,† and 10 ml. of 20 per cent ammonium thiocyanate solution. Now heat the solution to about 70° C. and saturate with hydrogen sulfide. At first the solution becomes only slightly turbid,‡ but after some time pure white zinc sulfide is thrown down in clouds, constantly becoming denser. After the solution has become saturated with hydrogen sulfide, cover the beaker and allow it to stand in a warm place until the precipitate has settled and the upper liquid is clear. Then filter and wash the precipitate, as described in the method of Smith and Brunner.

From the filtrate nickel, cobalt, and manganese are precipitated by means of ammonium sulfide, filtered and separated according to the following methods.

" Salting-out Method "

Experiments were performed by G. H. Kramers to determine whether the separation of zinc from nickel and cobalt could be accomplished in weakly acid solutions by hydrogen sulfide after the addition of *any* ammonium salt of a strong acid. The results obtained showed this to be possible.

Procedure. — To the neutral solution§ containing nickel and zinc as sulfate or chloride (the sum of the oxides present amounting to about ¼ per cent of the weight of the solution) add 8–10 drops of 2 *N* hydrochloric acid and about 2 per cent of ammonium sulfate (referred to the total amount of liquid). Saturate the solution at 50° C. with hydrogen sulfide. Allow the warm solution to stand until the white precipitate of zinc sulfide has settled out and then treat exactly as described under the Method of Zimmermann.

* *Ann. chem. pharm.*, **199**, p. 3 (1879); **204** (1880), p. 226.

† The addition of hydrochloric acid is in all cases necessary, because otherwise nickel sulfide will be precipitated with the zinc sulfide, especially when considerable nickel and little zinc are present.

‡ There are at the start but few zinc ions in the solution. The four metals are present for the most part in the form of complex thiocyanates of the general formula $[R(CNS)_4](NH_4)_2$. The zinc salt, like carnallite (see Vol. I) is slightly dissociated,

$$[Zn(CNS)_4](NH_4)_2 \rightleftarrows Zn(CNS)_2 + 2\,NH_4CNS,$$

and the zinc thiocyanate is converted into insoluble sulfide by the action of hydrogen sulfide. When the zinc begins to precipitate as sulfide, the equilibrium is disturbed and eventually all the zinc becomes precipitated.

§ If the solution is acid, neutralize with sodium carbonate as described in the preceding methods.

Separation of Manganese from Nickel and Cobalt

Treat the solution of the chlorides or sulfates with an excess of sodium carbonate, add a liberal excess of acetic acid and, for each gram of nickel or cobalt present, introduce 5 g. of ammonium acetate. Dilute the solution to 100–200 ml., heat to 70–80° C., saturate with hydrogen sulfide, filter, and wash with hot water. The manganese is in the filtrate, and the nickel and cobalt are in the precipitate.

Remark. — The filtrate often contains small amounts of nickel and cobalt. In order to remove these metals, the solution should be concentrated and colorless ammonium sulfide should be added. Then make slightly acid with acetic acid, warm, and filter. In case a precipitate of nickel or cobalt sulfides is formed by this treatment, test the filtrate in the same way again and repeat the process until no further precipitation is produced.

Separation of Cobalt from Nickel

(*a*) Method of Tschugaeff-Brunck*

This method is probably the quickest and most accurate for the estimation of nickel in the presence of cobalt. It depends upon the fact that nickel is quantitatively precipitated by means of dimethyl glyoxime, from a barely ammoniacal solution or from a slightly acid solution containing sodium acetate. Cobalt, under these conditions, is not precipitated.

Procedure. — If the quantity of cobalt present does not exceed the quantity of nickel, the procedure is exactly the same as when nickel alone is present; with larger quantities of cobalt add two or three times as much of the dimethyl glyoxime reagent and carry out the precipitation exactly as described on p. 134. For the determination of both nickel and cobalt, divide the original solution into two portions. In one portion determine the nickel as outlined above, and in the other deposit the two elements electrolytically as described on p. 135 or p. 138, and find the cobalt by difference. If only a little of the substance is available, deposit the two metals together by electrolysis, dissolve the weighed deposit in nitric acid (the electrodes must be completely immersed in the acid and the solution boiled for at least 20 minutes), concentrate the resulting solution to a small volume, and determine the nickel as described above. The method can be recommended strongly. Sometimes, when the quantity of cobalt is larger than that of the nickel, it is better to dissolve the first precipitate in nitric acid and repeat the precipitation to get a purer precipitate.

* O. Brunck, *Z. angew. Chem.*, **1907**, 1848.

(*b*) The Potassium Nitrite Method of N. W. Fischer*

Brunck's Modification†

Evaporate the solution containing an excess of acid to dryness in a porcelain dish and treat the residue with one or two drops of 2 *N* hydrochloric acid and 5–10 ml. of water. Add pure caustic potash solution, drop by drop, until the reaction is barely alkaline. Dissolve the resulting precipitate in as little glacial acetic acid as possible, add half of the solution's volume of 50 per cent potassium nitrite solution and 10 drops more of acetic acid. Stir the mixture well and allow it to stand twenty-four hours. At the end of this time the precipitation is almost always complete. This should be proved, however, by removing a little of the undiluted solution with a pipet, adding to it a little more potassium nitrite solution, and allowing to stand a little longer. If at the end of an hour no further precipitation results, then all the cobalt has been precipitated. If a precipitate is formed, add more potassium nitrite to the main solution and again allow to stand. Decant off the clear liquid through a filter, transfer the residue to the filter and wash with a 10 per cent potassium acetate solution until 1 ml. of the filtrate on being acidified with acetic acid and boiled with 1 ml. of a 1 per cent solution of dimethyl glyoxime will show no test for nickel. This is usually the case after washing four times. Transfer as much of the precipitate as possible to a small porcelain dish, cover with a watch-glass, cautiously acidify with sulfuric acid, and heat on the water-bath until no more brown vapors are evolved. Dissolve the small quantity of precipitate remaining on the filter by pouring hot, dilute sulfuric acid through the filter and add this acid to the main solution of the cobalt. After evaporating as far as possible on the water-bath, continue heating on an air-bath until dense vapors of sulfuric acid are evolved. After cooling, dissolve the residue in water and determine the cobalt electrolytically, as described on p. 135. If it is not convenient to carry out an electrolysis, dissolve the nitrite precipitate in hydrochloric acid and determine the cobalt according to p. 141 (*b*).

Remark. — This method gives reliable results provided the solution is free from alkaline earths. In the latter case the nickel and alkaline-earth metals are precipitated with the cobalt. (Cf. Vol. I.)

(*c*) Method of Ilinsky and von Knorre‡

This method depends upon the fact that cobalt can be precipitated as purple red $[C_{10}H_6O(NO)]_3Co$ by treatment with α-nitroso-β-naphthol in hydrochloric acid solution. Nickel is not precipitated under these conditions.

* *Pogg. Ann.*, **71**, 545 (1847).

† *Z. angew. Chem.*, **1907**, 1847.

‡ *Ber.*, **18**, 699 (1885).

Procedure. — To the neutral solution containing not more than 0.2 g. of nickel and 0.1 g. of cobalt, add 10 ml. of 6 *N* hydrochloric acid, dilute to 200 ml., heat to 80° and add a solution of α-nitroso-β-naphthol, in 50 per cent acetic acid, until no further precipitation takes place. Cool and make sure that no more precipitate is formed by adding a little more of the reagent. Filter after 2–3 hours into a Gooch crucible and wash with 12 per cent hydrochloric acid until all of the nickel is removed. Finish washing with hot water. Dry, sprinkle a little pure oxalic acid upon the precipitate, to prevent too sudden combustion during the heating, and heat very slowly to redness in an electric oven. Cool, place the crucible on a larger porcelain crucible with a perforated cover, and heat in a stream of hydrogen until the cobalt oxide is reduced to metal. Cool in hydrogen and weigh as Co. In another sample determine the nickel with dimethylglyoxime (p. 134).

Separation of Nickel from Zinc. Method of Tschugaeff-Brunck*

Treat the solution with ammonium chloride, and add enough ammonia to make slightly ammoniacal; no precipitate will be formed if sufficient ammonium chloride has been added. Make slightly acid with hydrochloric acid, heat to boiling and precipitate the nickel with an alcoholic 1 per cent dimethyl glyoxime solution exactly as outlined on p. 135.

In the filtrate, it is best to precipitate the zinc as sulfide by acidifying with acetic acid and saturating the hot solution with hydrogen sulfide (cf. p. 145).

Remark. — When considerable zinc is present it is necessary to add more dimethyl glyoxime to precipitate the nickel.

Separation of Nickel from Manganese. Method of Tschugaeff-Brunck†

Carry out the analysis exactly as described above with the only difference that the final precipitation should take place in an acetic acid solution. Neutralize the greater part of any mineral acid present with ammonia, treat the barely acid solution with 1 per cent dimethyl glyoxime solution and then, after the precipitate has formed, add sodium acetate and continue the analysis according to p. 135. If the alkali acetate is added before the dimethyl glyoxime, a very voluminous precipitate is formed which, to be sure, can be filtered with suction, but even then the filtration is tedious. Thus, when possible, it is best to

* *Z. angew. Chem.*, **1907**, 1849.

† *Ibid.*

add the sodium acetate *after* the dimethyl glyoxime. If, on the other hand, iron has been removed by a basic acetate separation and nickel and manganese are to be determined in the filtrate, the precipitation must take place in a solution already containing sodium acetate. In the filtrate from the nickel dimethyl glyoxime precipitation, precipitate the manganese with ammonium sulfide and determine as described on p. 130.

Separation of Nickel from Iron

If the iron is present in the ferrous condition, oxidize it by boiling with nitric acid. Then dilute to 300 ml., add 1–3 g. of tartaric acid and make the solution ammoniacal to find out whether enough tartaric acid has been added (the solution must remain perfectly clear). Make slightly acid with hydrochloric acid, precipitate the nickel with dimethyl glyoxime, carefully neutralize the acid with ammonia, and continue the analysis according to p. 135.

Determination of Nickel in Steel*

Dissolve 0.5 g. of steel in 10 ml. of concentrated hydrochloric acid, add 2 ml. of concentrated nitric acid to completely oxidize the iron, and, if there is any separation of silica at this point, add some hydrofluoric acid. Dilute to 100 ml. and add 3 g. of tartaric acid. Test to see whether enough tartaric acid is present to prevent any precipitation of iron when the solution is made alkaline with ammonia, adding more tartaric acid if necessary. Make the solution *slightly* acid, dilute to 300 ml., heat nearly to boiling and treat with 30 ml. of a 1 per cent alcoholic solution of dimethyl glyoxime. Finally make slightly neutral and add just enough ammonia to make the solution barely smell of this reagent. After allowing the solution to stand for a few minutes, add 10 ml. more of dimethyl glyoxime reagent to see if further precipitation takes place and repeat the treatment if necessary. Allow the solution to stand in a warm place for an hour and then cool for about half an hour. Finally filter the solution through a Gooch or Munroe crucible, wash with hot water, dry at 110°–120° for 45 minutes and weigh as $Ni(C_4H_7N_2O_2)_2$.

By this method the nickel in a sample of steel can be determined within about two hours. The results are accurate, but lower than is sometimes obtained in practice, when the cobalt is determined with the nickel.

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* O. Brunck, *Stahl und Eisen*, **28**, 331.

Removal of Ferric Chloride by Ether, Method of Rothe*

The fact that ferric chloride dissolved in hydrochloric acid, *d.* 1.1, is more soluble in ether than in this acid, is often taken advantage of in the determination of metals such as nickel, manganese, cobalt, copper, aluminium, titanium, vanadium and chromium in samples of steel. It has also been used for the determination of sulfur in steel after oxidation to sulfuric acid, which does not dissolve in the ether. The underlying principle is the same as that governing the distribution of iodine between water and carbon disulfide (see Vol. I). An example will be given of such a process in the following method for determining manganese in steel (cf. p. 284). Beryllium chloride as well as molybdic acid follow the ferric chloride and dissolve in the ether.

Determination of Manganese in Iron and Steel

Requirements. — 1. Hydrochloric acid, *d.* 1.10.

2. Ether-hydrochloric acid. To concentrated hydrochloric acid, *d.* 1.19, add ether in small portions until, after shaking, a layer of ether is on top of the acid. One volume of concentrated acid dissolves about 1.5 volumes of ether.

3. Dilute ether-hydrochloric acid. To approximately 6 *N* hydrochloric acid, *d.* 1.10, add ether in the same way. One volume of the acid dissolves about 0.5 volume of ether.

4. A shaking funnel similar to that shown in Fig. 42. The analysis can be made with two ordinary separatory funnels but this funnel recommended by Rothe is well adapted to this work.

Procedure. — If the iron or steel contains less than one per cent manganese, take 10 g. of sample for analysis, otherwise a correspondingly smaller quantity. Dissolve the sample in a 500 ml. beaker with 7.5 *N* nitric acid, using 15 ml. of the acid for each gram of metal. As soon as the violent reaction is over, heat over a wire gauze until all of the iron has gone into solution and no more brown fumes are evolved. Evaporate the solution to dryness and gently bake the residue. Take up in 50 ml. of 6 *N* hydrochloric acid, heating until all of the ferric oxide and basic salt has dissolved. Then dilute to 150 ml. and filter off the silica.

Evaporate the filtrate nearly to dryness; a thick sirupy liquid should remain but there should be no deposition of crystals. Pour this solution into the upper bulb of the funnel shown in Fig. 42, and rinse out the dish with hydrochloric acid, *d.* 1.10, until no yellow coloration is produced on pouring the acid into the dish. Ten or 15 ml. of the acid,

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* *Z. anal. Chem.*, **1901**, 809.

added in 3 ml. portions, should accomplish this rinsing of the dish. Shake the solution to mix it well and cool under the water faucet. Then for each gram of metal taken, add 6 ml. of the concentrated acid that has been saturated with ether. Mix, cool again and nearly fill the upper bulb with pure ether. Close the stop cock and shake well, cooling from time to time under running water. Fasten the shaking funnel to a ring stand in a vertical position and allow the liquid in the bulb to separate into two layers. The upper, ether layer will contain the greater part of the iron and the lower acid will contain all of the manganese.

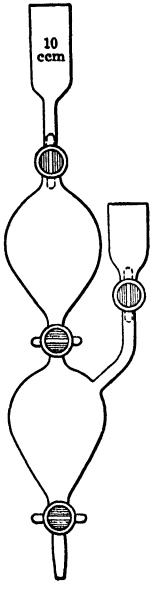


FIG. 42.

Transfer the lower layer to the lower bulb of the shaking funnel without letting any of the upper layer flow into the boring of the stopcock that separates the two bulbs. After a few minutes a little acid will separate out below the ether. Allow this also to run into the lower bulb. To rinse the boring add 3 ml. of the dilute ether-hydrochloric acid mixture and again drain off the lower layer of liquid into the bottom bulb. Now add 10 ml. of the dilute ether-acid mixture to the upper bulb and nearly fill the lower bulb with ether. Shake well. Then draw off the lower layer of the liquid in the lower bulb into a porcelain dish, drain off the lower layer of the upper bulb into the lower bulb and rinse the upper bulb with a little of the dilute ether-acid mixture. Withdraw the lower layer of the upper bulb into the lower bulb and the lower layer of the bottom bulb into the dish. Repeat this washing of the apparatus 3 or 4 times and then it can be assumed that all of the manganese, together with the nickel, cobalt, aluminium, chromium, sulfuric acid and phosphoric acid, is in the dish.

From this solution, evaporate off the ether on a warm water bath, taking care not to boil the solution or to have a lighted flame very near. Finally evaporate to dryness and take up in 5 ml. 6 *N* hydrochloric acid. Dilute to 100 ml. and precipitate the copper with hydrogen sulfide. Filter and wash as described under Copper.

Bauer and Deiss recommend the following treatment to separate the manganese from the remaining elements: — Add a little sulfuric acid to the filtrate from the copper precipitate and evaporate to dryness, finally heating until the excess acid is all expelled. Cover the sulfates in a platinum dish with a solution of 2–5 g. of pure sodium hydroxide dissolved in a little water. Evaporate to dryness and care-

fully heat over a free flame until the sodium salt fuses, keeping the dish in motion. Cool, sprinkle a little sodium peroxide over the mass and again carefully heat until the mass fuses. Avoid injuring the dish by not overheating any part of it. Cool, cover the dish with a watch-glass and digest the fused mass with 60 ml. of hot water. After again cooling, add a little more sodium peroxide to make sure that all of the green sodium manganate is decomposed and hydrated manganese dioxide precipitated. Heat to decompose the excess of sodium peroxide for about an hour on the water bath. Rinse the contents of the dish into a beaker. Dilute to 200 ml. and allow the precipitate to settle; it contains all of the manganese, nickel, cobalt and some iron that was not removed by the ether. If a stain remains on the sides of the platinum dish, dissolve it with a few drops of hydrochloric acid, dilute, add sodium peroxide, heat to decompose the excess and rinse into the beaker.

Filter and wash the precipitate with water containing 2 per cent of dissolved ammonium sulfate. The filtrate will contain all of the chromium as chromate and the aluminium as aluminate besides alkali phosphate and other alkali salts.

Dissolve the moist precipitate in hot 3 *N* hydrochloric acid and precipitate the iron by the basic acetate procedure (p. 154). If a large precipitate is obtained, dissolve it in hydrochloric acid and repeat the basic acetate precipitation.

To remove the nickel and cobalt from the filtrate, add a drop of 6 *N* acetic acid and saturate the solution with hydrogen sulfide. Heat to boiling and after the precipitate has settled, filter off the nickel and cobalt sulfides. Evaporate the filtrate to a small volume and precipitate the manganese by bromine, as described on p. 131 and determine as Mn_3O_4 or as $MnSO_4$.

This method is described in detail because it is capable of giving excellent results. It is well to have accurate gravimetric methods for the determination of constituents which are usually determined by the more rapid and far simpler volumetric methods. In this way a check is obtained upon the accuracy of the volumetric methods.

METALS OF GROUP II

MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN (PLATINUM, GOLD, SELENIUM, TELLURIUM, MOLYBDENUM, GERMANIUM, TUNGSTEN, AND VANADIUM)

A. SULFO-BASES

MERCURY, LEAD, BISMUTH, COPPER, CADMIUM

MERCURY, Hg. At. Wt. 200.6

Forms: HgS, Hg_2Cl_2, and Hg

Determination as Sulfide

(a) Precipitation with Hydrogen Sulfide

The solution should contain not over 0.1 g. of mercury as *mercuric* salt in a volume of 100 ml. and should contain no oxidizing substances ($FeCl_3$, Cl, much HNO_3, etc). Saturate with hydrogen sulfide in the cold, allow the precipitate to settle, filter through a Gooch crucible, wash with cold water, dry at 105°–110° C. and weigh as HgS.

Remark. — This method affords excellent results and should be used whenever possible. Unfortunately, however, it is not always applicable, for in most cases the solution to be analyzed contains strong nitric acid (obtained by the solution of impure mercuric sulfide in aqua regia, by the decomposition of organic mercury compounds by the method of Carius. or by the oxidation of mercurous salts). It is not possible to expel the excess of nitric acid by evaporating the solution with hydrochloric acid, because considerable amounts of mercuric chloride are volatilized with the escaping steam. In such a case the following procedure suggested by Volhard should be used:

(b) Precipitation with Ammonium Sulfide

Nearly neutralize the acid solution of the mercuric salt with pure sodium carbonate and treat with a slight excess of freshly-prepared ammonium sulfide. Add pure sodium hydroxide solution (free from Ag, Al_2O_3, and SiO_2) while rotating the solution, until the dark liquid begins to lighten; then heat to boiling and add more sodium hydroxide until the liquid is perfectly clear. The solution now contains the mercury as sulfo-salt, $Hg\langle^{SNa}_{SNa}$. Add ammonium nitrate (5 g. for each 100 ml.), boil the solution until the ammonia is almost entirely expelled and allow the precipitate to settle. By means of the

boiling with ammonium nitrate, the sulfo-salt is decomposed according to the equation:

$$Hg(SNa)_2 + 2\,NH_4NO_3 = 2\,NaNO_3 + (NH_4)_2S + HgS.$$

Decant the clear liquid through a Gooch crucible, and wash the precipitate by decantation with hot water until the wash water no longer reacts with silver nitrate solution. Transfer the precipitate to the crucible, dry at 110° C., and weigh. In case the precipitate contains free sulfur, boil it with a little sodium sulfite before filtering.*

A still better way of removing free sulfur from the precipitate consists of extracting with carbon bisulfide. In this case filter off the mercuric sulfide, together with the sulfur, through a Gooch crucible, wash thoroughly with water and then three times with alcohol. Now place the crucible upon a glass tripod in a beaker containing some carbon bisulfide (Fig. 43).† Support the beaker over a vessel filled with hot water and cover it with a round-bottomed flask containing cold water to serve as a condenser. After about an hour the sulfur will be completely extracted. Remove the carbon bisulfide from the precipitate by washing once with alcohol and once with ether. Drive off the ether by gently warming, dry the precipitate at 110° C. and weigh as HgS.

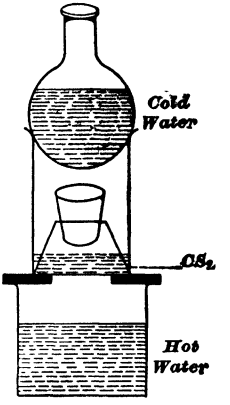


FIG. 43.

Determination of Mercury in Non-Electrolytes

If it is desired to determine mercury in an organic non-electrolyte, decompose the compound by the method of Carius (see Elementary Analysis) by heating in a closed tube with concentrated nitric acid, and precipitate the mercury as sulfide by the method of Volhard; or to the acid solution add pure sodium hydroxide solution to alkaline reaction and then enough pure potassium cyanide to dissolve the mercuric oxide. Now saturate the solution with hydrogen sulfide, add ammonium acetate, boil the solution until the ammonia is almost entirely expelled, allow the precipitate to settle, filter, and wash first with hot water,

* By boiling with sodium sulfite, the sulfur is changed to sodium thiosulfate, $Na_2SO_3 + S = Na_2S_2O_3$.

† G. Vortmann, *Uebungsbeispiele aus der quantitativen chemischen Analyse*, p. 28, Vienna, 1899.

then with hot dilute hydrochloric acid, and finally with water. After drying at 110° C. weigh the precipitate of mercuric sulfide.

Determination as Mercurous Chloride

For the analysis of a solution containing a mercurous salt, treat the solution, at a volume of 100 ml. for each 0.1 g. of mercury, with a slight excess of sodium chloride solution. After standing twelve hours filter through a Gooch crucible, dry at 105° C., and weigh as Hg_2Cl_2. If the solution contains a mercuric salt, first reduce it by the method of H. Rose, using phosphorous acid in the presence of hydrochloric acid.

Procedure. — To the mercury solution (which almost always contains nitric acid) add some hydrochloric acid, enough water to make the volume at least 100 ml. for each 0.1 g. of mercury and an excess of phosphorous acid. After standing for twelve hours filter off the precipitate through a Gooch crucible, dry at 105°, and weigh.

Remark. — The results obtained by this method are always about 0.4 per cent too low, but in spite of this fact the method is to be recommended.

The phosphorous acid necessary for this method can be obtained by the oxidation of phosphorus in moist air or by the decomposition of phosphorus trichloride with water, evaporating the solution to remove the hydrochloric acid and dissolving the residue in water.

Determination as Metal

Nearly all mercury compounds except the iodide are decomposed quantitatively by heating with lime:

$$2\,HgX + 2\,CaO = 2\,CaX + 2\,Hg + O_2.$$

To carry out this determination,* take a glass tube 50 cm. long and 1.5 cm. wide, open at both ends, and near one end place an asbestos plug, follow this with an 8 cm. layer of pure lime, then an intimate mixture of a weighed amount of substance with lime, and finally a layer of lime 30 cm. long. At the other end of the tube insert another asbestos plug. After the tube has been filled, draw out the tube at the end nearest this second asbestos plug until it is only 4 cm. wide. Connect this end of the tube by means of rubber tubing with the empty, narrower arm of a very small Péligot tube. Loosely fill the other and wider end of the Péligot tube with pure gold-leaf. Place the glass tube in a combustion-furnace and pass illuminating-gas (carbon dioxide is less suited) through it for half an hour. Then heat the tube, at first where the 30 cm. layer of lime is, then light the other burners one after another until finally the entire contents of the tube is subjected

* First proposed by Erdmann and Marchand, *J. prakt. Chem.*, **31**, 385.

to gentle ignition. During the whole of the operation pass illuminating-gas through the apparatus at the rate of about three bubbles a second. The greater part of the mercury collects in the lower empty end of the Péligot tube and the mercury vapors, that are carried further, amalgamate with the gold. A small amount of the mercury condenses in the drawn-out tube. After cooling the apparatus (in a current of illuminating-gas) cut off the narrow part of the tube both sides of the condensed mercury and weigh. Then heat gently, while passing air through the tube to volatilize the mercury and again weigh. The difference in weight gives the amount of mercury condensed in the combustion tube. The Péligot tube is usually moist; pass dry air through it for some time, and finally weigh it. The gain in weight represents the weight of mercury that amalgamated with the gold.

Although it is easy to obtain good results by this method, it is slower than the sulfide method and is no more accurate.

If it is desired to determine the amount of mercury vapor present in a given space, it is only necessary to aspirate the gas through a calcium-chloride tube filled with gold-leaf. The gain in weight of the latter shows the amount of mercury present in the gas.

Electrolytic Determination of Mercury*

Mercury can be determined satisfactorily by the electrolysis of acid, neutral, or alkaline solutions. The metal is deposited in the form of little drops, which, when the quantity is small, adhere to the electrode, or, when larger amounts are present, the mercury may collect at the bottom of the platinum dish used as cathode.

The electrolysis takes place to advantage in solutions slightly acid with nitric acid.

Procedure. — To 150 ml. of the neutral or slightly acid solution of the mercurous or mercuric salt in a beaker, add 2 or 3 ml. of concentrated nitric acid, and electrolyze with a platinum gauze electrode at the ordinary temperature with a current of 0.05–0.10 ampere. The voltage should be between 3.5 and 5 volts. If the electrolysis is started at night, it will be finished next morning, provided the amount of mercury does not exceed 1 g. By using a current of 0.6–1 ampere the electrolysis is finished at the end of two or three hours. At the end of the electrolysis, wash the metal with water without interrupting the current, then with alcohol† and dry by touching it with filter-paper. Finally

* Luckow, *Z. anal. Chem.*, **19**, 15 (1880); Smith and Knerr, *Am. Chem. J.*, **8**, 206; F. W. Clarke, *Ber.*, **11**, 1409 (1878); Rüdorff, Z. *angew. Chem.*, **1894**, 388; Classen and Ludwig, *Ber.*, **19**, 324 (1886); G. Vortmann, *Ber.*, **24**, 2750 (1891).

† It is usually stated that alcohol is not to be used, but with gauze electrodes it does no harm.

keep it in a desiccator* over fused potassium hydroxide and a small dish of mercury for several hours. In this way correct results are obtained. Drying at 100° and then over sulfuric acid in a desiccator gives rise to low results because the acid absorbs considerable mercury vapor.

During the electrolysis of mercuric chloride† the solution often becomes turbid in consequence of the formation of insoluble mercurous chloride; this does no harm, however, as the metal is subsequently deposited on the cathode.

Mercury can also be electrolyzed from a solution in potassium cyanide in the presence of some caustic alkali, and similarly from a solution formed by dissolving mercuric sulfide in 50–60 ml. of concentrated sodium sulfide solution.

The great advantage of the electrolytic determination of mercury lies in the fact that good deposits are obtained irrespective of the nature of the acid radical, or element, which is combined with mercury.

LEAD, Pb. At. Wt. 207.1

Forms: PbO, $PbSO_4$, PbO_2, and in rare cases $PbCl_2$‡

1. Determination as Lead Oxide, PbO

If the lead is present as carbonate, nitrate, or peroxide, it is only necessary to ignite a weighed portion in a porcelain crucible over a small flame and weigh the residue. The treatment of the nitrate requires care, because on rapid ignition the mass decrepitates.

2. Determination as Lead Sulfate, $PbSO_4$

If the lead is present in solution in the form of its chloride or nitrate, add an excess of dilute sulfuric acid§ and evaporate the mixture on the water-bath as far as possible, then over a free flame until dense white

* Private communication from A. Miolati, cf. Borelli, Revisto tecnica, V, Part 7 (1905). Even at 20° the tension of mercury vapor is considerable. It amounts to 0.00133 mm.

† In the electrolysis of the chloride, it is better to use a platinum dish with dull, unpolished inner surface (Classen) because then any mercurous chloride will certainly be reduced to metal, which is not always the case with gauze electrodes. When a dish is used as cathode, wash the electrode with water, without breaking the current, by pouring water into it from a wash-bottle while the solution is being siphoned off. As soon as the ammeter (or voltmeter used as an ammeter) reaches the zero mark, the washing is finished. Turn off the current, pour off the solution carefully, dry the electrode as above and weigh.

‡ See *Analysis of Vanadinite.*

§ The solution at the time of filtering should contain about 5 per cent of free sulfuric acid.

fumes of sulfuric acid are evolved. Cool, dilute with 15 volumes of water, stir, allow to stand some hours, and filter through a Gooch crucible. Wash at first with 8 per cent sulfuric acid (by weight), then with alcohol, and dry at 100°. Place the dried precipitate in a larger porcelain crucible, provided with an asbestos ring, and ignite over the full flame of a Teclu or Tirrell burner.

If it is desired to use an ordinary filter, finally wash the precipitate with alcohol until the wash liquid no longer gives the sulfuric acid reaction, dry, transfer as much of it as possible to a weighed porcelain crucible, ignite the filter in a platinum spiral (p. 33), and add the ash to the contents of the crucible. By means of the reducing action of the burning filter, some of the lead sulfate adhering to it is always reduced to lead, which must be changed back to sulfate before weighing. For this purpose, moisten the precipitate in the crucible with dilute nitric acid, evaporate on the water-bath to dryness, add a few drops of concentrated sulfuric acid and heat the crucible over a free flame until no more fumes are evolved. Then ignite gently and weigh.

In case the lead is originally present as acetate, treat the solution with an excess of dilute sulfuric acid and twice its volume of alcohol, filter after standing some hours, and treat the precipitate of lead sulfate exactly as described above.

To determine the lead present in organic compounds, place the substance in a large porcelain crucible, treat with an excess of concentrated sulfuric acid, and very cautiously heat in the covered crucible over a free flame until the sulfuric acid is completely expelled. Then gently ignite the crucible and if the residue is white, it is ready to be weighed. Otherwise add more sulfuric acid and repeat the process until finally a white residue is obtained.

In case the organic lead compound is soluble in water, it is preferable first to precipitate the lead by means of hydrogen sulfide and then transform the precipitate into sulfate. For this purpose, place as much as possible of the washed and dried lead sulfide precipitate upon a watch-glass, heat the filter and remainder of the precipitate in a large porcelain crucible, which is supported in an inclined position. Heat carefully over a small flame until the filter-paper is completely consumed. Add the main part of the precipitate to the crucible, cover with a watch-glass and treat with concentrated nitric acid at the temperature of the water-bath. When the main reaction is over, repeat the treatment with strong nitric acid until the contents of the crucible are pure white in color. Then remove the watch-glass, add 5 or 10 drops of dilute sulfuric acid, and evaporate the liquid as far as possible on the water-bath. Remove the excess of sulfuric acid by heating on the air-bath

(cf. Fig. 14, p. 38) and weigh the lead sulfate. Should the precipitate be dark colored after the ignition, moisten it with concentrated sulfuric acid and again expel the excess of acid.

If the lead is present in an organic compound which is not capable of dissociation, the compound should be decomposed in a closed tube with strong nitric acid according to the method of Carius (see p. 292), finally washing out the contents of the tube, adding sulfuric acid, and treating the precipitate as above described.

Separation of Lead Sulfate from Barium Sulfate and Silicic Acid

In the analysis of sulfide ores containing lead, it is customary to dissolve the finely powdered ore in nitric acid, or aqua regia, and to remove the volatile acids by evaporation with sulfuric acid, eventually heating over the free flame until fumes of sulfuric acid come off thickly. The sulfuric acid should be diluted with an equal volume of water before adding it to the original solution; usually 10 ml. of the diluted acid is sufficient. After the evaporation, allow the moist residue to cool, add 100 ml. of water and filter off the precipitate, washing it with 5 per cent sulfuric acid. The precipitate contains all the lead as sulfate but often contains silica and barium sulfate (also strontium sulfate and sometimes calcium sulfate). To purify it, redissolve the lead sulfate in hot ammonium acetate solution (made by neutralizing 6 *N* acetic acid with 6 *N* ammonia, and leaving the mixture barely ammoniacal). When the precipitate is large in amount it is best to wash it into a beaker or flask and heat it with about 20 ml. of 2 normal ammonium acetate solution (or enough to dissolve all the lead sulfate), then filter through the original filter and wash with hot ammonium acetate solution, and finally with hot water until the filtrate gives no blackening with ammonium sulfide. Small precipitates of lead sulfate can be dissolved on the filter. The silica and barium sulfate will all remain behind.

To obtain lead from the acetate solution, precipitate it as sulfide by hydrogen sulfide, and transform, after drying, into sulfate as described on p. 177. Or, add 10 ml. of 18 *N* sulfuric acid to 100 ml. of the ammonium acetate solution, remove the acetic acid by evaporation, allow the residue to cool, dilute with water to 100 ml. and filter the lead sulfate into a Gooch crucible. Wash the precipitate with cold 5 per cent sulfuric acid, heat in an air bath and weigh.

If the amount of ammonium acetate solution used is not too large, the lead may be precipitated by adding enough sulfuric acid to the acetate solution to make the solution contain from 5–10 per cent sul-

furic acid by weight. Sometimes the precipitate is not pure lead sulfate, in which case it should be redissolved in ammonium acetate and the precipitation as sulfate repeated.

3. Electrolytic Determination of Lead as Peroxide (PbO_2)

Lead can be deposited as metal upon the cathode by the electrolysis of solutions containing the complex oxalate, the acetate, the hydroxide dissolved in caustic alkali or the phosphate dissolved either in caustic alkali or in phosphoric acid, *d.* 1.7. The deposit is easily oxidized and there is always danger of some lead peroxide being formed on the anode. No method for the electrolytic determination of lead is as satisfactory as that depending upon the deposition of all the lead, as PbO_2, on the anode by the electrolysis of a nitric acid solution. The concentration of the nitric acid may be such that no copper will be deposited on the cathode or more dilute nitric acid may be used and the copper determined simultaneously.

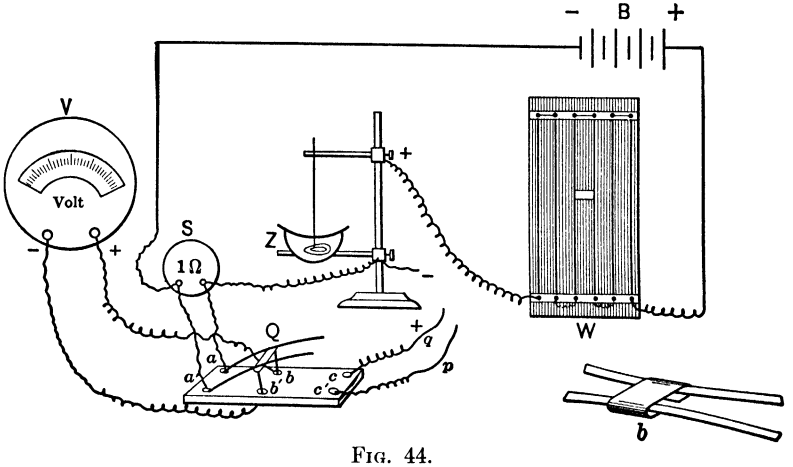


FIG. 44.

Procedure. — Transfer the neutral solution of lead nitrate, containing not more than 0.5 g. lead, to a platinum dish whose inner surface is unpolished (as recommended by Classen), add 20–30 ml. of 15 *N* pure nitric acid, dilute to 150–200 ml. and electrolyze in the cold with a current of about 0.5–1 ampere at 2–2.5 volts. When the electrolysis is carried out in the cold, all the lead will be deposited as the peroxide at the end of two hours and a half or three hours. Only an hour or an hour and a half is required if the temperature of the cell is kept at 50°–60°. If it is desired to let the electrolysis run over night, a current of 0.05 ampere is sufficient.

A suitable arrangement of the electrolytic apparatus is shown in Fig. 44, but the dish should in this case serve as anode and the platinum spiral as cathode, although the drawing is marked otherwise. The

resistance W is made by taking about 10 m. of nickel wire of about 0.5 mm. diameter, fastening it to a board as shown in the drawing and connecting the wires in pairs by means of a brass hook, of which only one is shown in the sketch. By suitably moving these hooks it is possible to vary the resistance at will. Instead of this arrangement, that shown in Fig. 37, p. 136, may be used; such an apparatus is more convenient but also more expensive. At the end of the electrolysis, which is shown by the fact that dilution with a little water so as to expose a fresh surface of platinum causes no yellowish-brown coating to appear at the end of half an hour, wash the dish without breaking the current. This is accomplished by introducing distilled water while the solution is being siphoned off. It is important in this operation to keep the deposit of lead peroxide completely covered with liquid. When the solution that is being siphoned off no longer reacts acid, or at least only barely acid, the washing is complete and the circuit can be broken. Finally wash the dish once more with distilled water, dry at 180°, and weigh. The results obtained are usually slightly high on account of the lead peroxide not being completely anhydrous when dried at this temperature. It is well, therefore, to heat the dish gently over the free flame before weighing, thereby readily converting the peroxide into lead oxide, PbO.*

Remark. — By employing a stronger current and keeping the solution warm during the electrolysis, the deposition is complete in much less time, but according to the author's experience the results obtained are not as satisfactory. By rotating one of the electrodes and using a stronger current, the deposition can be made to take place in a short time. The use of a gauze anode is not advisable with quantities of lead exceeding 0.1 g. because the deposit does not adhere well and is likely to fall off on washing and on drying. When the gauze electrode is used, place the electrode in a small beaker so that any deposit that falls off during drying will be saved. If a little lead deposits on the cathode, this is remedied by stopping the current for a short time, toward the end of the electrolysis. To cleanse the electrode use a mixture of dilute nitric acid and some sodium nitrite.

Besides the above-mentioned forms, lead is also determined as the chromate and as the chloride (Cf. p. 234).

BISMUTH, Bi. At. Wt. 209.0

Forms: Bi_2O_3, Bi_2S_3, Bi

1. Determination as Bismuth Oxide, Bi_2O_3

Solid bismuth nitrate or carbonate is readily changed to the oxide by gentle ignition. When bismuth, however, is present *in solution* as the nitrate, it should be first precipitated as the basic carbonate and this changed by ignition to the oxide.

* Cf. W. C. May, *Z. analyt. Chem.*, **14**, 347 (1875).

Procedure. — Dilute the solution with water (if a turbidity ensues it makes no difference) so that not more than 0.1 g. of metal is present in 150 ml., add a slight excess of ammonium carbonate solution, heat to boiling and allow the precipitate to settle. Filter, wash the precipitate with hot water, dry, ignite,* and weigh as Bi_2O_3. If the solution from which the bismuth is to be precipitated contains besides nitric acid other acids (HCl, H_2SO_4, etc.), the precipitate produced by ammonium carbonate always contains basic salts which cannot be converted to the oxide by ignition. In this case, which is most frequent in analysis, the bismuth should be determined according to one of the following methods.

2. Determination as Sulfide, Bi_2S_3

Dilute the solution until it contains not more than 0.1 g. of bismuth in 100 ml. and is 0.3 *N* in acid, saturate with hydrogen sulfide, heat to coagulate the precipitate and filter through a Gooch crucible. Wash the precipitate with hydrogen sulfide water, then with alcohol to remove the water, and afterwards with freshly-distilled carbon bisulfide to remove any sulfur that may be mixed with the precipitate.

Continue washing with carbon bisulfide until a few drops of the filtrate leave no residue on being evaporated to dryness on a watch-glass. Then wash the precipitate with alcohol to remove the carbon bisulfide and finally with ether, dry at 100°, and weigh as Bi_2S_3.

The removal of the sulfur with carbon bisulfide can be accomplished advantageously by the apparatus shown in Fig. 43, and described on p. 173. Care should be taken during this operation that there is no lighted gas-burner in the immediate vicinity, for otherwise there is danger of the vapors of carbon bisulfide taking fire.

3. Determination as Metal. Method of H. Rose†

First precipitate the bismuth as basic carbonate as described under 1, and place the dried precipitate, together with the ash of the filter, in a porcelain crucible and ignite. Add five times as much of 98 per cent potassium cyanide and fuse the mixture, whereby the oxide and basic salt are changed to metallic bismuth:

$$Bi_2O_3 + 3\,KCN = 3\,KCNO + 2\,Bi$$

$$2\,BiOCl + 4\,KCN = 2\,KCNO + 2\,KCl + (CN)_2 + 2\,Bi.$$

* If the precipitate is large in amount, place the greater part on a watch-glass and dissolve the remainder that adheres to the filter in hot, dilute nitric acid. Evaporate the solution to dryness in a weighed platinum dish and add the main portion of the precipitate. Heat the dish and its contents at first gently but finally over the full flame of a Bunsen burner.

† *Pogg. Ann.*, **110**, p. 425.

Since bismuth melts at 268°, but boils at 1600°, it is possible to perform this operation with a Bunsen flame of about half the usual height without running any risk of losing some of the bismuth by volatilization. The reduction is usually complete at the end of twenty minutes. After cooling, treat the melt with water, which dissolves the salts and leaves the metallic bismuth behind in the form of a fused metallic globule. Frequently, however, the fusion will have loosened some of the glaze of the porcelain crucible, which will remain behind with the bismuth after the treatment with water. Filter off the metallic residue using a paper filter that has been dried at 100° and weighed with the empty crucible. After washing first with water, then with absolute alcohol and ether and drying at 100° C., again place the filter in the crucible and weigh. The gain in weight represents the amount of metallic bismuth.

Bismuth sulfide can also be reduced by potassium cyanide, but in this case a longer and stronger heating is necessary.

4. Determination as Metal. Method of Vanino and Treubert*

In this method the bismuth is precipitated as metal by means of formaldehyde in alkaline solution. Treat the slightly acid bismuth solution, containing not more than 0.1 g. of bismuth in 100 ml., with formaldehyde and a considerable excess of pure 10 per cent caustic soda solution. Heat on the water-bath until the liquid above the precipitate has become perfectly clear; then add more formaldehyde and caustic soda solution and heat the mixture over a free flame.† Decant off the solution through a Gooch crucible and wash the precipitate repeatedly by decantation with water containing a little aldehyde, boiling each time and pressing with a glass rod the partly spongy, partly pulverulent precipitate to make it collect together. Finally, transfer the metal to the crucible, wash with absolute alcohol, dry at 105° and weigh as Bi.

Remark. — The results by this method are usually a little high owing to the difficulty in removing the last traces of alkali. Absolutely accurate results may be obtained by dissolving the precipitated bismuth in nitric acid, precipitating by ammonia and ammonium carbonate and weighing as the oxide according to (1). Naturally this roundabout process would only be chosen when the bismuth solution contained other acids (HCl, H_2SO_4, or H_3PO_4); the necessity of fusing with potassium cyanide would then be avoided.

* *Ber.*, **31** (1898, 1303).

† Frequently, particularly on long boiling, the liquid becomes colored yellow or brown. This has no influence upon the results.

5. Electrolytic Determination of Bismuth *

Dilute the solution of the nitrate to about 100 ml. Too much acid should not be present but just enough to prevent the formation of insoluble basic salt; not more than 2 ml. of concentrated acid should be used. Heat to boiling and electrolyze with a gauze cathode and with the electrodes connected directly to the two poles of a 2-volt storage cell. The electrolysis requires 2–3 hours with 0.3 g. of metal. Wash the electrode with water without interrupting the current, then remove it from the bath, wash with alcohol, dry by holding high above a flame, cool in a desiccator and weigh.

COPPER, Cu. At. Wt. 63.57

Forms: CuO, Cu_2S, Cu, $Cu_2(CNS)_2$

1. Determination as Copper Oxide, CuO

The copper solution must be free from organic substances and ammonium salts. Heat it to boiling in a porcelain dish and add pure potassium hydroxide solution, drop by drop, until the precipitate becomes dark brown and is permanent, and the solution itself shows an alkaline reaction towards litmus-paper. After the precipitate has settled, carefully pour off the upper liquid through a filter and wash the precipitate by decantation with hot water until the wash water no longer shows an alkaline reaction. Transfer the precipitate to the filter and continue washing with hot water. Usually a small amount of copper oxide adheres to the porcelain dish so firmly that it can be removed only by vigorous rubbing with a glass rod covered at the end with a piece of rubber tubing, and finally when the precipitate is removed from the dish some will then remain on the rubber. Consequently it is better to proceed as follows: Remove as much of the precipitate as possible by a stream of water from the wash-bottle, then add 2 drops of 6 *N* acid, and, by inclining the dish and rubbing with the glass rod, moisten with the acid all of the precipitate remaining on the dish. Two drops of the acid are sufficient, with correct manipulation, to dissolve all of the copper oxide. Prepare a small fresh filter and holding the dish in an inclined position, so that the liquid remains near its lip, wash the sides once with hot water and heat the contents of the dish (which is continually maintained in this inclined position) to boiling over a small flame; add dilute potassium hydroxide solution drop by drop until the copper is again precipitated. Avoid a large excess of alkali hydroxide on account of its solvent action upon the

* O. Brunck, *Ber.*, **35**, 1871 (1912).

precipitate.* Quickly pour the contents of the dish through the small filter and immediately wash the dish once with water. The copper oxide is now all on the filter. Wash the precipitate with hot water, dry both filters, and transfer most of the precipitate to a porcelain crucible. Ignite the filters in a platinum spiral, and add the ash to the contents of the crucible. Cover the crucible, ignite at first gently, and finally with the full heat of the Bunsen burner; weigh as CuO. If the process is carried out carefully, the results obtained are almost the theoretical values but as a rule they are a trifle high.

Remark. — According to A. Bayer† copper can be determined in the presence of all other metals of the hydrogen sulfide group in the following manner; — Add caustic soda solution to the copper solution until the copper is all precipitated as hydroxide and then add enough Rochelle salt (sodium-potassium tartrate) to dissolve the precipitate. Heat to boiling in a porcelain dish and to the boiling solution add 2 ml. of 5 per cent hydroxylamine hydrochloride. By boiling one minute all the copper (not more than 0.2 g. should be present) is precipitated as cuprous oxide.

$$4\,Cu\begin{matrix}/\,O.CH.CO_2Na\\ \backslash\,O.CH.CO_2K\end{matrix} + 2\,NH_2OH + H_2O \rightarrow 2\,Cu_2O + 4\,KNaC_4H_4O_6 + N_2O$$

Filter off the cuprous oxide into a Gooch crucible, wash with hot water, dry, ignite in the air and weigh as CuO.

2. Determination as Cuprous Sulfide, Cu_2S

The copper solution may contain enough acid to make it 1.8 normal with sulfuric acid but need not contain more than enough acid to make it 0.3 *N* to prevent the precipitation of metals of the ammonium sulfide group. Heat the solution to boiling and introduce hydrogen sulfide until it becomes cold. If considerable acid was present, the precipitate settles quickly in large flocks and the upper liquid appears perfectly colorless. Before filtering, prepare the wash liquid by passing hydrogen sulfide through the long tube of a wash-bottle for one minute, then close the short tube with a piece of rubber tubing and shake vigorously. As soon as no more bubbles pass through the liquid, the water is saturated; this takes about a minute at the most.

Place a paper filter in a funnel containing a platinum cone or a small hardened filter and fit the funnel to a suction-bottle. Start filtering without using suction, taking care that the filter is constantly kept full. When all the precipitate is on the filter, wash the precipitate with hydrogen sulfide water containing 4 per cent of acetic acid, and, at this point also, the filter must be kept full of liquid. Continue washing until 1

* Cf. Vol. I.

† *Z. anal. Chem.*, **1912**, 729.

ml. of the filtrate shows no test for mineral acid.* Now for the first time allow the filter to drain completely, with the aid of gentle suction. Dry completely by heating in the drying closet at 90°–100° for at least an hour.

Transfer as much of the precipitate as possible to a weighed Rose crucible (of unglazed porcelain),† burn the filter in a platinum spiral and allow the ash to fall at first upon an unglazed crucible cover, where it should be heated gently till it glows, in order to make sure that it contains no unburned carbonaceous matter. Then add the ash to the main portion of the precipitate in the crucible. Also add a little sulfur, that has been recrystallized from carbon bisulfide. Place the perforated cover on the crucible (Fig. 45), pass a stream of hydrogen through it (the wash-bottle shown contains concentrated sulfuric acid‡), and heat the crucible at first over a small flame and finally so that the bottom of the crucible glows faintly. At this temperature the cupric sulfide is changed to cuprous sulfide, $2\,CuS = Cu_2S + S$.

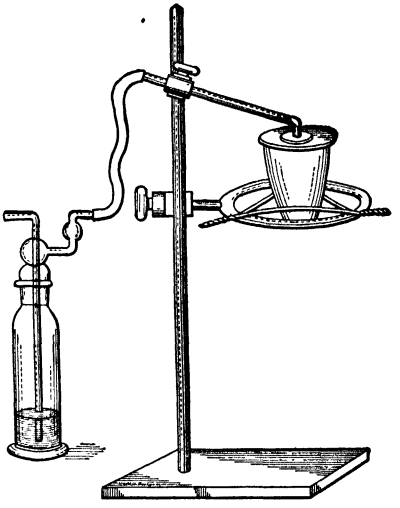


FIG. 45.

Too strong heating is inadvisable according to Hampe.§

When the excess of sulfur has been driven off (which can be readily ascertained by removing the cover of the crucible and finding no blue flame and no odor of burning sulfur), increase the current of hydrogen so that eight bubbles per second pass through the wash-bottle (at first, not more than four bubbles per second should have been the rate), and remove the flame. Allow the crucible to cool in the current of hydrogen and weigh after remaining in the desiccator for fifteen minutes. The cuprous sulfide should be brownish black or black, and should

* Test for sulfuric acid with barium chloride. To test for hydrochloric acid, boil the solution until the hydrogen sulfide is expelled and then treat with silver nitrate.

† A quartz crucible is more desirable, as the transformation of CuS into Cu_2S can then be watched.

‡ If the hydrogen is prepared from zinc and hydrochloric acid, the gas should be passed first through water and then through a wash-bottle containing concentrated sulfuric acid.

§ *Z. anal. Chem.*, **38**, 465 (1894).

show no reddish-brown stains (due to Cu or Cu_2O); this is the case if the current of hydrogen was too slow during the cooling. To remedy this defect, add a little sulfur to the precipitate and repeat the heating in hydrogen.

Remark. — It is evident that the sulfur used for this experiment should leave on ignition no weighable residue. This is why the sulfur used should be recrystallized from carbon bisulfide.

The reason why it is necessary to keep the funnel filled with liquid during the filtration and washing of the cupric sulfide is this: If moist copper sulfide is exposed to the air it is quickly oxidized and the hydrogen sulfide wash water acts upon the salt formed by the oxidation ($CuS_2O_3.CuSO_4$), and transforms it into colloidal cupric sulfide, which passes through the filter, and on coming in contact with the acid filtrate is coagulated. If, however, the precipitate is not exposed to the air during the filtration there is no oxidation and the filtrate remains clear.

Instead of changing the cupric sulfide into cuprous sulfide, it has been proposed to convert it to oxide by ignition in the air and weigh the copper in this form. If, however, the highest degree of accuracy is desired, this should not be done, for the ignited product always contains some sulfate. When this method is chosen, the cupric sulfide should be heated in a glazed porcelain crucible, at first over a small flame, so that the mass does not melt, and the heat gradually increased until finally a blast-lamp is used and the copper weighed as CuO. The results are about 0.1 per cent too high when not more than 0.2 g. of precipitate is present. Holthof* states that copper oxide absolutely free from sulfate can be obtained if the precipitate is ignited wet in an inclined porcelain crucible.

3. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$. Method of Rivot†

The solution should be slightly acid with sulfuric or hydrochloric acid and contain 0.2 g. or less of copper in 100 ml. Oxidizing agents must be absent. To the solution add an excess of sulfurous acid,‡ and normal ammonium thiocyanate solution, drop by drop with constant stirring, whereby at first a greenish mixture of cupric and cuprous salts is precipitated, which after stirring becomes pure white cuprous thiocyanate. Allow the precipitate to settle completely (this requires several hours). Then filter and wash with cold water until the filtrate shows only a slight reddish coloration when ferric chloride is added. Finally wash several times with 20 per cent alcohol, dry at 110–120°, and weigh as $Cu_2(SCN)_2$. The cuprous thiocyanate can be dried at a temperature as high as 160°, but at 180° it begins to decom-

* *Z. anal. Chem.*, **28**, 680 (1889).

† *Compt. rend.*, **38**, 868; see also R. G. van Name, *Z. anorg. Chem.*, **26**, 230, and Busse, *Z. anal. Chem.*, **17**, 53, and **30**, 122.

‡ Instead of sulfurous acid, ammonium bisulfite may be used. The latter is prepared by saturating aqueous ammonia with SO_2.

pose. The Munroe crucible can be used to advantage in this determination. The precipitate permits rapid filtration, and a turbid filtrate is never obtained. After the determination is finished, the greater part of the precipitate can be shaken out of the crucible, and the remainder dissolved in hot nitric acid.

4. Electrolytic Determination of Copper

This most accurate and most convenient of all methods for the determination of copper was first proposed by W. Gibbs in 1864.* Copper may be deposited by means of the electric current from acid, alkaline, and neutral solutions, but for analytical purposes only the use of acid solutions is of importance.

Procedure. — The safest way, according to F. Förster,† is to deposit the copper from a sulfuric acid solution. To the neutral solution containing the copper in the form of sulfate, add 10 ml. of 2 *N* sulfuric acid, dilute the solution to a volume of 100 ml. and electrolyze with exactly two volts potential at the electrodes by simply connecting the electrodes with the poles of a single storage cell. The electrolysis requires at least eight hours if done at the ordinary temperature, but by keeping the solution at 70°–80°, 0.2 g. of copper is deposited in 60–80 minutes. If, therefore, it is desired to carry on the electrolysis over night, it is done in the cold. It is very easy to decide when the electrolysis is finished by adding a little water and noticing whether there is any more copper deposited upon the freshly exposed electrode surface. Wash the cathode with water, without breaking the circuit, exactly as was described under the electrolytic determination of nickel (p. 139). Finally, rinse with alcohol, dry by holding it high above a flame, cool in a desiccator, and weigh.

If these directions are followed closely, the copper is never deposited in a spongy condition. The presence of Ni, Co, Fe, Zn and Cd does not influence the analysis and the copper may be separated from these elements by means of such an electrolysis.

If the solution to be analyzed contains nitric acid and some of the above-mentioned metals, evaporate to dryness, heat with a little sulfuric acid until dense fumes are evolved, cool, add 10 ml. of 2 *N* sulfuric acid, dilute to 100 ml. and electrolyze as described above.

If, however, only copper is present in the solution, it may be deposited satisfactorily in the following manner: To 100 ml. of the neutral solution add 4–5 ml. of concentrated nitric acid. If, originally, it contained more nitric acid than this, either evaporate to dryness or neutralize

* *Z. anal. Chem.*, **3**, 334 (1874).

† *Z. angew. Chem.*, **1906**, 1842, 1849; **1907**, 812, *Ber.* **1906**, 1890.

with ammonia, and then add the required quantity of nitric acid. Boil gently to remove nitrous fumes. Rinse off the cover glass and wash down the sides of the beaker. Add 0.1 g. of solid urea, to react with any remaining nitrous acid, and electrolyze at 50°–60° with a current of 1 ampere and electrode potential of 2–2.5 volts, using a gauze cathode. The electrolysis is over at the end of two hours, when not more than 0.3 g. of copper is present. Finish the analysis as above but there is more danger of traces of copper being dissolved while the electrodes are being removed. If the electrolysis is continued too long, some nitrous acid is formed and the deposit begins to dissolve. To remedy this, add a little more urea and electrolyze a little longer.

The best way to test the solution to see if all copper is removed, is to clean the electrodes and see if any gain in weight is experienced by further electrolysis with the cleaned electrodes.

Remark. — The copper may be deposited electrolytically much more rapidly by the use of a rotating electrode, or any stirring arrangement and a stronger current. The use of a gauze cathode also permits a higher amperage. The solution should not be diluted too much, as spongy deposits are obtained from very dilute solutions unless a very weak current is used. As a general rule, the more concentrated the copper solution, the stronger the current that can be used.

CADMIUM, Cd. At. Wt. 112.4

Forms: Cd, $CdSO_4$, CdO and $Cd_2P_2O_7$

1. Electrolytic Determination of Cadmium

Of all the methods for the determination of cadmium the electrolytic method is not only the most convenient, but by far the most accurate, and of the many methods proposed that of Beilstein and Jawein* can be recommended. From the experience obtained in the author's laboratory the best procedure is as follows: To the solution of the sulfate, add a drop of phenolphthalein indicator solution, and then pure sodium hydroxide solution until a permanent red color is obtained. Now add 10 per cent pure potassium cyanide solution with constant stirring, until the precipitate of cadmium hydroxide produced by the caustic soda has completely dissolved; an excess of potassium cyanide should be scrupulously avoided. Dilute the solution with water to 100–150 ml. and electrolyze in the cold, using a gauze cathode. From 5–6 hours are required with a current of 0.5–0.7 ampere and an electromotive force of 4.8–5 volts; at the end of this time increase the current to from 1–1.2 amperes and electrolyze the solution for one hour more.

* *Ber.*, **12**, 446.

If these directions are followed, all of the cadmium (if not more than 0.5 g. is present) will be deposited as a firmly-adhering, dull deposit of nearly silver-white metal. Stop the current, quickly pour off the liquid and wash the deposited metal first with water, then with alcohol and finally with ether. Dry in the usual way and weigh.

After the electrolysis is finished, the solution should always be tested for cadmium. For this purpose, saturate it with hydrogen sulfide. If much cadmium is present, a yellow precipitate is obtained, but if very little, a yellow coloration results. The latter is due to the formation of colloidal cadmium sulfide, and the color is so intense that R. Philipp estimates the quantity of cadmium not precipitated, by comparing the shade with that produced in a solution containing a known quantity of cadmium and the same amounts of pótassium cyanide and caustic potash as in the solution tested.

Remark. — If for the electrolysis a current of 0.5 ampere is used, the cadmium will not be all deposited at the end of 12 hours; if, however, the current is increased at the end, as above stated, to 1 ampere, the electrolysis will be surely finished in 6 or 7 hours. To work with the stronger current from the beginning is not to be recommended unless a gauze cathode is used, or one of the electrodes is rotated, for otherwise the metal is deposited in a spongy form and on washing some of it is likely to be lost.

A solution containing 0.4568 g. Cd., 3 g. KCN, 1 g. NaOH, and diluted to 125 ml. with water, can be electrolyzed in fifteen minutes with a current of 5 amperes and 5.5 volts if one of the electrodes is rotated.

From neutral and weakly acid solutions, cadmium can be deposited electrolytically, but not from strongly acid solutions.

2. Determination as Cadmium Sulfate, $CdSO_4$

Next to the electrolytic method, the determination of cadmium as sulfate is the best. If the cadmium is combined with a volatile acid, treat the compound in a weighed porcelain crucible with a slight excess of dilute sulfuric acid, evaporate the solution on the water-bath as far as possible, and finally remove the excess of sulfuric acid by heating in an air-bath (see Fig. 14, p. 38). Apply the heat at first slowly, and raise the temperature gradually until finally no more fumes of sulfuric acid are evolved. The outer crucible can even be heated with the full flame of a Teclu burner without running any risk of decomposing the cadmium sulfate; it is, however, not necessary to heat it so strongly. As soon as the fumes of sulfuric acid cease to come off, stop heating and weigh the crucible and its contents after cooling in a desiccator. The cadmium sulfate should be pure white and should dissolve in water to form an absolutely clear solution.

If the cadmium has been precipitated from a solution as the sulfide, place the greater part of the precipitate in a large porcelain crucible, cover with a watch-glass, and treat with 3 *N* hydrochloric acid on the water-bath. After the precipitate has dissolved and the evolution of hydrogen sulfide has ceased, wash the lower side of the watch-glass, place the crucible under the funnel, and dissolve the precipitate which adhered to the filter-paper by dropping hot, 3 *N* hydrochloric acid upon it. Finally wash the filter with hot water and evaporate the solution upon the water-bath, continuing as described above.

The Precipitation of Cadmium as Sulfide

The frequently-recommended determination of cadmium as the sulfide must be rejected; it is useless. It is not possible to precipitate pure cadmium sulfide from acid solutions by means of hydrogen sulfide; the precipitate is always contaminated with a basic salt (Cd_2Cl_2S — Cd_2SO_4S, etc.) whether the precipitation takes place in cold or hot solutions, whether under atmospheric pressure or under increased pressure (in a pressure-flask), and in fact the amount of basic salt formed increases with the amount of free acid present. Results are obtained as much as 5 per cent too high. Follenius* attempted to make the method possible by igniting an aliquot part of the dried and weighed precipitate in a stream of hydrogen sulfide. If the sulfide was contaminated with sulfate, he succeeded in changing it all to sulfide and obtained results that were acceptable. If, however, choride was present, a considerable part was lost by sublimation, so that the results obtained were too low. It is, furthermore, not possible to ignite the cadmium sulfide with sulfur in a current of hydrogen, as was described under Zinc and Copper, for cadmium sulfide is so volatile that some of it is lost.

On the other hand, the method of precipitating the cadmium as sulfide from solutions containing 2 ml. of concentrated sulfuric acid in 100 ml. is to be recommended, for by this means a precipitate is obtained which can be readily filtered and which by solution in hot 6 *N* hydrochloric acid and evaporation with sulfuric acid can be changed without loss to the sulfate and weighed as such.

3. Determination as Cadmium Oxide, CdO

Cadmium carbonate and cadmium nitrate can be changed to the oxide by strong ignition.

* *Z. anal. Chem.*, **13**, 422

To the dilute, boiling cadmium solution add a slight excess of potassium carbonate, and after the precipitate has completely settled after standing for some time on the water-bath, filter it off, wash with hot water, and dry. Transfer as much of the dried precipitate as possible to a watch-glass and set aside for the time being. Wash the filter with hot 2 *N* nitric acid to dissolve the precipitate which still adheres to it and receive the solution in a weighed porcelain crucible. Evaporate to dryness, add the main portion of the precipitate, and heat the crucible at first very gently until the whole mass has become a uniform brown. Now gradually raise the temperature until finally the full heat of the burner is reached. It is important during this operation to take care that the inner flame mantle does not touch the crucible, for otherwise reducing gases may enter and reduce a part of the oxide to metallic cadmium, which is volatile at this temperature.* The cadmium oxide is obtained as a brown powder which is infusible, insoluble in water, but readily soluble in dilute acids.†

Remark. — It is not advisable to precipitate the cadmium by means of *sodium* carbonate solution, for in that case it is difficult to wash the precipitate free from alkali.

4. Determination of Cadmium as Cadmium Pyrophosphate‡

The cadmium solution used for this method of analysis should not contain ammonium salt other than the reagent and should be faintly acid. If considerable acid is present, neutralize with sodium carbonate solution.

To the cold, faintly acid solution containing not over 0.2 g. of cadmium in 100 ml., add a concentrated aqueous solution of $(NH_4)_2HPO_4$ until the weight of added salt is 10–15 times as great as that of the cadmium present. Allow to stand for 12 hours to allow the amorphous precipitate to become crystalline. Filter through a Gooch or Munroe crucible, wash with cold 1 per cent ammonium phosphate solution and finally with 60 per cent alcohol. Dry in an electric oven at 800–900° and weigh as $Cd_2P_2O_7$.

SEPARATION OF THE SULFO-BASES FROM THE METALS OF THE PRECEDING GROUPS

Hydrogen sulfide added to a solution which is 0.3 *N* in acid precipitates only the metals of the "hydrogen sulfide group." It is to be

* If the cadmium carbonate is filtered into a Munroe crucible, and ignited in an electric oven, the transformation takes place readily without danger of any volatilization.

† The oxide after ignition is a black, crystalline powder.

‡ Miller and Page, *Z. anorg. Chem.*, **28**, 233 (1901).

noted that zinc precipitates with this group if the solution is not acid enough, while if the solution is too acid lead and cadmium are often incompletely precipitated.

EXAMPLE

Analysis of Brass (Alloy of Copper and Zinc sometimes containing Small Amounts of Tin, Lead, Iron, and Nickel)

Weigh out 0.4–0.5 g. of the alloy into a 200 ml. casserole* and dissolve in 20 ml. of 6 *N* nitric acid. Cover the casserole with a watch-glass to prevent loss by spattering. After the reaction begins to slacken, heat on the water-bath until the metal is all dissolved. Evaporate the solution to complete dryness, moisten the residue with a little nitric acid, dissolve in about 50 ml. of hot water, and if any metastannic acid settles out on standing filter it off, wash with hot water, dry, and determine the tin according to p. 215. To the cold filtrate add 3 ml. of pure, concentrated sulfuric acid, evaporate the solution on the water-bath as far as possible, and then heat cautiously over a free flame until dense white fumes of sulfuric acid are evolved. Cool, treat the residue with 50 ml. of water and 15 ml. of alcohol, stir well, filter, wash, and determine the lead sulfate according to p. 177. Evaporate the filtrate until the alcohol is completely removed, dilute with 100 ml. of water, heat the solution to boiling, and conduct hydrogen sulfide into it until it becomes cold. Then filter off the copper sulfide, wash first with hydrogen sulfide water containing in every 100 ml. 20 ml. of 2 *N* sulfuric acid and at the end with 5 per cent acetic acid, also saturated with hydrogen sulfide, until the filtrate gives no precipitate on being treated with barium chloride. Determine the copper, according to p. 184, as Cu_2S.

Evaporate the filtrate from the copper sulfide to a small volume in order to remove the excess of hydrogen sulfide, oxidize the iron by the addition of bromine water, precipitate by ammonia, and filter. To make sure that the precipitate of ferric hydroxide contains no zinc, redissolve it in a little hydrochloric acid and repeat the precipitation with ammonia. Filter, wash, ignite and weigh as ferric oxide (cf. p. 94).

Make the combined filtrates from the ferric hydroxide acid with a little sulfuric acid, heat to about 50° C., and determine the zinc as zinc sulfide according to the "salting-out" method described on p. 164. For the determination of nickel, boil the filtrate from the zinc sulfide to expel the hydrogen sulfide and precipitate the nickel as the salt of dimethyl glyoxime according to p. 135.

* The borings are often somewhat oily. They should then be washed with ether before weighing. Cf. p. 221, footnote.

The best brass alloys contain very little tin, lead, iron or nickel. In commercial laboratories, often the copper and lead content is determined electrolytically and the zinc determined *by difference, i.e.*, by subtracting the percentages of copper and lead from 100 per cent.

The following method of analysis, however, provides for the determination of copper, lead, tin, iron and zinc and is capable of giving accurate results.

Weigh 1 g. or less of the alloy into a slender beaker of about 125 ml. capacity. Add 8 ml. of 6 *N* nitric acid, cover the beaker and heat gently till all the brass is dissolved. If a clear solution is obtained, no tin is present and the solution after dilution is ready for electrolysis.

If a white precipitate of metastannic acid forms, evaporate the solution just to dryness but do not bake the residue. Add 2 ml. of 6 *N* nitric acid, dilute with 25 ml. of water and boil gently to dissolve the nitrates of copper and zinc. Filter off the metastannic acid, wash it with hot water, ignite in a porcelain crucible and weigh as SnO_2.

Dilute the clear solution of the nitrates to 75 ml. and boil gently for one minute to remove any nitrous oxides. Wash down the sides of the beaker and the cover-glass and electrolyze with a current of about 3 amperes using a gauze cathode and a rotating anode. After the solution has become colorless, continue the electrolysis ten minutes longer, adding 1 g. of urea and washing down the sides of the beaker.

Wash the electrodes as much as possible before removing entirely from the solution. If the beaker is supported above the working bench, this is easily accomplished by holding the beaker in the left hand, removing the support and washing both electrodes while the beaker is gradually lowered.

Finally wash the electrodes and weigh the copper on the cathode and the lead dioxide on the anode after the usual drying.

To make sure that all the copper has been deposited, add a slight excess of ammonia to the entire solution. If a blue color is noticeable,* make acid with dilute sulfuric acid and electrolyze with clean electrodes until all the copper is removed.

To the filtrate add a little bromine water, to make sure that any iron is in the ferric condition, and enough ammonia to dissolve the zinc hydroxide precipitate that may form at the neutral point. If any precipitate of ferric or aluminium hydroxide forms, filter it off. To make sure that no zinc hydroxide is in the precipitate, redissolve the precipi-

* A blue color may indicate the presence of nickel but usually is caused in brass analysis by some copper that escaped deposition. If there is any doubt, test a little of the solution with potassium ferrocyanide and acetic acid; a red precipitate proves copper to be present.

tate in a little hot 2 *N* hydrochloric acid, dilute to 50 ml. and precipitate again by adding ammonia. Ignite and weigh the precipitate as Fe_2O_3. If there is any likelihood of aluminium being present, examine the ignited oxides as described on p. 112.

To the ammoniacal solution containing the zinc, add methyl orange indicator and enough hydrochloric acid to make the solution barely acid. Precipitate the zinc as phosphate and finish the analysis as described on p. 142.

Method for Copper in Irons and Steels

Dissolve 10 g. of sample in 200 ml. of 10 per cent sulfuric acid and when the metal is dissolved dilute to at least 500 ml. with water. Heat to boiling and saturate with hydrogen sulfide. Filter on paper or paper pulp and wash a few times with a 1 per cent sulfuric acid solution saturated with hydrogen sulfide. Ignite the residue and paper in a porcelain crucible and fuse with a small amount of alkali pyrosulfate. Dissolve the cooled melt in the crucible in 1 to 2 ml. of hydrochloric acid and a few ml. of water, add 5 per cent sodium hydroxide (free from organic matter) in slight excess, boil, digest, and filter. Dissolve the precipitate in hot dilute nitric acid, add 5 ml. of sulfuric acid, evaporate to fumes of sulfuric acid, cool, dilute to 40 ml. and add 10 ml. of concentrated ammonium hydroxide (*d.* 0.90). Heat the still acid solution to boiling and saturate with hydrogen sulfide. Filter, wash thoroughly with slightly acidified hydrogen sulfide water, ignite and weigh as cupric oxide.

Remark: This separates Cu from Mo and As, the only other members of the hydrogen sulfide group likely to be present.

SEPARATION OF THE SULFO-BASES FROM ONE ANOTHER

1. Separation of Mercury from Lead, Bismuth, Copper, and Cadmium

Method of Gerhard v. Rath

Principle. — This separation is based upon the insolubility of mercuric sulfide in boiling, dilute nitric acid (*d.* 1.2–1.3) and the solubility of the remaining sulfides in this acid.

Procedure. — The solution must contain the mercury entirely in the mercuric form and should be 0.3 *N* in hydrochloric or sulfuric acid. Into the hot, fairly dilute solution introduce hydrogen sulfide in excess. Filter off the precipitate, wash it with hydrogen sulfide water, transfer to a porcelain dish and boil for a considerable length of time with nitric acid of the above concentration. Then dilute with a little water and wash

with water containing nitric acid. The residue of mercuric sulfide thus obtained always contains sulfur, and in case considerable lead was present it will also contain lead sulfate. Dissolve it, therefore, in a little aqua regia, dilute with water, filter from the separated sulfur and lead sulfate and precipitate the mercury with ammonium sulfide (cf. p. 172) according to the method of Volhard. If some of the lead sulfate should go into solution with the mercury on treating with aqua regia, it will be converted by the ammonium sulfide and potassium hydroxide into insoluble lead sulfide, while the mercury will be in the form of its soluble sulfo-salt. In this case filter off the lead sulfide, wash with dilute potassium hydroxide solution, and precipitate the mercury as sulfide, as described on p. 172.

2. Separation of Bismuth from Lead

(*a*) *Method of Löwe**

Principle. — Bismuth nitrate is changed by the action of water into an insoluble basic salt, but lead nitrate undergoes no such transformation.

Procedure. — Evaporate the nitric acid solution of these two metals on the water-bath until it reaches a sirupy consistency. Add water, and after thorough stirring with a glass rod repeat the evaporation and continue this treatment until the addition of the water fails to produce any further turbidity, a sign that the bismuth has been completely converted into the basic salt $Bi_2O_2NO_3OH$. Add 100 ml. of a cold, 2 per cent ammonium nitrate solution, and after standing some time, with frequent stirring, to make sure that the lead nitrate is completely dissolved, filter the solution. Wash the precipitate with the dilute ammonium nitrate solution and dry. Transfer as much of it as possible to a weighed porcelain crucible, burn the filter and add the ash to the crucible and ignite to a constant weight of Bi_2O_3.

From the filtrate precipitate the lead as sulfate, according to p. 176, and weigh as such. It is less satisfactory to precipitate the lead as sulfide and weigh it in this form after gentle heating with sulfur in a Rose crucible.

(*b*) *Method of Jannasch*†

Principle. — The separation depends upon the different volatility of the two bromides. Bismuth bromide is fairly readily volatile; lead bromide is only difficultly so.

Procedure. — Evaporate the solution of the nitrates to dryness, to the residue add 100 ml. of water, sufficient hydrochloric acid to afford a

* *J. pr. Chem.*, **74**, 345 (1858). Cf. Little and Cahen, *The Analyst*, **35**, 301.

† Praktischer Leitfaden der Gewichtsanalyse.

clear solution, and a few drops of fuming nitric acid.* Introduce hydrogen sulfide and promptly filter off the precipitated sulfides. Dry the precipitate at 100°, in a stream of carbon dioxide. Transfer as much of the precipitate as possible to an agate mortar and add the ash of the filter to it. Grind up the whole of the precipitate and transfer the powder without loss to a weighed porcelain boat, and introduce it into the decomposition tube *R*† (Fig. 46), made of difficultly-fusible glass. At first, pass a stream of dry carbon dioxide through the apparatus and gently heat the substance by means of a small flame, to dry it. Drive over the water that condenses in the front part of the tube into *E* by careful heating.

Connect the bottle *A*, containing bromine,‡ with the apparatus and pass the stream of carbon dioxide through it; lead the gas, carrying bromine vapors with it, through the vertical calcium chloride tube filled with pieces of calcite, then through the concentrated sulfuric acid contained in *B*, next through the tube *C* containing glass beads moistened

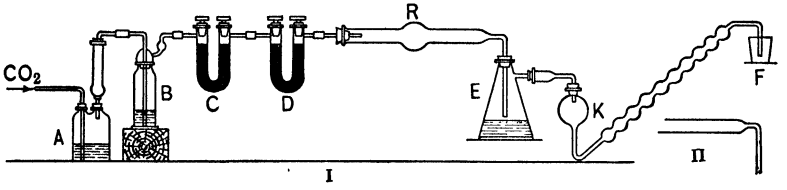


FIG. 46.

with sulfuric acid, and finally through the tube *D* filled with glass wool; from this the dry bromine vapors reach the substance. Heat the latter over a small flame (kept in constant motion) and distil off the yellow bismuth bromide which condenses partly in the narrow part of the tube and partly in the receiver *E*, containing 5 *N* nitric acid (1 HNO_3 : 2 H_2O). Heat the tube hotter, whereby more bismuth bromide is volatilized, and again distil this as completely as possible into the receiver. Finally,

* By the addition of the fuming nitric acid the precipitated sulfide is contaminated with considerable sulfur; such a precipitate is more readily decomposed by the action of bromine.

† In this determination, the bulb of the tube is unnecessary; it should be replaced by one such as is shown in Fig. 46, *II*. For other analyses it is better to have the bulb.

‡ For this experiment the bromine used must be absolutely free from chlorine and can be prepared as follows: treat 50–60 ml. of commercial bromine in a tightly stoppered separatory funnel, with a 10 per cent potassium bromide solution. Shake the funnel vigorously, and separate the bromine from the aqueous alkali solution. After washing two or three times with water it is ready for use.

heat even more strongly still, until the lead bromide begins to melt. When no more of the yellow sublimate is formed, the decomposition is shown to be complete; allow the lead bromide to cool in a stream of carbon dioxide. Pass the bromine that escapes from the tube *K* into alcohol contained in the beaker *F*. When the apparatus has become cold, remove the bromine bottle, and expel all the bromine from the apparatus by passing carbon dioxide through it for some time. Weigh the boat filled with lead bromide and from the weight of the $PbBr_2$ compute that of the lead. To check this, dissolve the lead bromide in freshly-prepared chlorine water, add an excess of dilute sulfuric acid, and evaporate the solution to remove the hydrochloric acid, at first on the water-bath and finally over a free flame until dense fumes of sulfuric acid are evolved.

After cooling, add water and alcohol, filter off the precipitate and determine the weight of the lead sulfate as described on p. 177. For the bismuth determination, pour the nitric acid solution contained in *E* and *K* into a beaker, filter if necessary from any sulfur, evaporate to a small volume, and precipitate the bismuth as basic carbonate by the addition of ammonium carbonate and determine as metal as described on p. 181.

There have been many other methods proposed for the separation of lead and bismuth,* all of which are less satisfactory than the two methods just described, so that they will not be discussed in this book.

3. Separation of Bismuth from Copper

To the dilute solution add an excess of ammonium carbonate solution, heat gently, and filter. The precipitate of basic bismuth carbonate almost always contains small quantities of copper; redissolve it in nitric acid and repeat the separation by means of ammonium carbonate. Fuse the basic bismuth salt with potassium cyanide and weigh the bismuth according to p. 181.

For the copper determination, combine the two filtrates, evaporate to remove the excess of ammonium carbonate, make acid with sulfuric acid, and precipitate the copper by means of hydrogen sulfide. Weigh the copper as cuprous sulfide according to p. 184, or electrolyze the sulfuric acid solution as described on p. 187.

According to Fresenius and Haidlin, bismuth can be separated from copper very satisfactorily by means of potassium cyanide. For this purpose, treat the acid solution with a slight excess of sodium carbonate, add potassium cyanide, heat the solution and filter. All of the copper is

* Cf. O. Steen, *Z. angew. Chem.*, **1895**, 530.

found in the filtrate, while the precipitate contains bismuth oxide contaminated with alkali. Dissolve the residue, therefore, in nitric acid, precipitate the bismuth by means of ammonium carbonate and determine as metal according to p. 181. Evaporate the filtrate containing the copper with nitric acid, to destroy the cyanide, and determine copper electrolytically according to p. 187.

4. Separation of Lead from Copper by Means of Electrolysis

This separation depends upon the fact that the electric current deposits lead quantitatively as PbO_2 upon the anode from solutions containing considerable nitric acid, while the copper is either not deposited at all under these conditions or is found upon the cathode to some extent. After the lead is completely deposited, the copper solution is poured into a second weighed platinum dish, the excess of the acid is neutralized with ammonia, and the solution again electrolyzed. The copper will now deposit quantitatively upon the cathode.

Procedure. — Transfer the solution of the two nitrates to a platinum dish of the form recommended by Classen with the inner surface unpolished. Add 15 ml. of 15 *N* nitric acid to 150 ml. and electrolyze at 50°–60° C. with a current of 1–1.5 amperes and an electrode potential of 1.4 volts. After 1–1.5 hours practically all the lead will be deposited upon the anode (dish) in the form of a firmly adhering, brown coating of lead peroxide, PbO_2. At the cathode (a plate electrode) a considerable part of the copper will be deposited, but the remainder will still be in solution. Break the circuit and pour the solution as quickly as possible into a second weighed platinum dish, and add the washings to this dish. After washing the electrodes with water, dry the first dish with the PbO_2 deposit at 180° and weigh. The solution in the second dish contains a little lead and some copper. Make it slightly ammoniacal, add 4 ml. of 15 *N* nitric acid, and electrolyze the solution at 60°. The platinum dish now serves as the cathode, while the plate electrode* serves as the anode; in case traces of lead remain in solution after the first electrolysis, it will now be deposited. After an hour or two with a current of one ampere all the remaining copper and lead will be deposited. When the electrolysis is complete wash the electrodes without breaking the circuit and determine the weight of the copper and PbO_2.

If only small amounts of lead and copper are present it is better to carry out the electrolysis as described on p. 187.

* The plate electrode with copper upon it was weighed, cleaned, and then weighed again.

5. Separation of Lead from Copper and Cadmium

(From Bismuth less satisfactorily)

To the solution of the nitrates or chlorides add an excess of sulfuric acid, evaporate to remove the nitric or hydrochloric acid, and determine the lead as sulfate as described on p. 177.

6. Separation of Copper from Cadmium

(a) By Electrolysis

The solution should contain not more than 0.2 g. of cadmium. To the neutral solution add 10 ml. of 6 *N* nitric acid, dilute to 150 ml. in a platinum dish and electrolyze with the dish as cathode. Adjust the anode, a disk electrode, so that it only dips into the liquid a short way. Under these conditions, 0.2 g. of copper is deposited, perfectly free from cadmium, within 12–14 hours by a current of 0.2–0.3 ampere and a voltage of 1.9–2.3 volts. With a current of 1–1.5 amperes and 2.5–2.6 volts electrode potential, the copper is deposited in about five hours. When the deposition is complete, siphon off the solution while pouring pure water into the dish without breaking the current. Finally rinse the dish with alcohol, dry and weigh with the deposited copper. Add a little sulfuric acid to the solution, evaporate to expel the nitric acid, cool, dilute and electrolyze the cadmium from cyanide solution as described on p. 188.

Remark. — If considerably more than 0.2 g. Cd is present in 150 ml. of the solution, there is danger of small amounts of cadmium separating out upon the copper during the washing of the deposit, especially when the anode extends well into the solution. This is because the concentration of the acid becomes less during the washing. In analyzing a solution containing a large amount of cadmium and small amount of copper, therefore, it is best to wash at first with 2 per cent nitric acid rather than with distilled water.

The separation requires but a few minutes with a rotating anode or cathode, and a stronger current.

F. Foerster recommends the following conditions for an electrolytic separation of copper and cadmium: — Electrolyte; 100 ml. of 2 *N* sulfuric acid. Electrodes; a large platinum gauze electrode as cathode and a smaller one as anode. Connect the electrodes directly with the terminals of a single storage cell so that the voltage is kept constant throughout the electrolysis. After 60–90 minutes 0.2 g. of copper will be deposited completely. Remove the cathode in the usual way (p. 139), neutralize the solution with potassium hydroxide solution, add potassium cyanide and electrolyze for cadmium according to directions on p. 188.

(b) Method of Rivot-Rose

Precipitate the copper as thiocyanate according to p. 186, and in the filtrate precipitate cadmium as sulfide and determine as sulfate according to p. 189. The results are good.

B. DIVISION OF THE SULFO-ACIDS

Arsenic, Antimony, Tin

(SELENIUM, TELLURIUM, GOLD, PLATINUM, TUNGSTEN, MOLYBDENUM, VANADIUM)

ARSENIC, As. At. Wt. 74.96

Forms: As_2S_3, As_2S_5, $Mg_2As_2O_7$

1. Determination as Arsenic Trisulfide, As_2S_3

For the determination of arsenic in this form, it must be present in its tervalent state, *i.e.*, as arsenious acid or as arsenite.

Make the solution strongly acid with hydrochloric acid and precipitate the arsenic in the cold with hydrogen sulfide. Remove the excess of the latter by a stream of carbon dioxide, and filter through a Gooch crucible that has been previously dried at 105°. Wash the precipitate with hot water, dry at 105° to constant weight, and weigh as As_2S_3.

2. Determination as Arsenic Pentasulfide, As_2S_5, according to Bunsen*

Modified by Fr. Neher†

To the solution, which must contain all of the arsenic as arsenic acid, add 12 *N* hydrochloric acid little by little (it is best to keep the solution cooled by surrounding the flask with ice) until the solution is at least 4 *N* in hydrochloric acid. Conduct a very rapid stream of hydrogen sulfide into this solution (contained in a large Erlenmeyer flask) until it is saturated with the gas. Then stopper the flask and allow to stand two hours. Filter off the arsenic pentasulfide through a Gooch crucible which has been dried at 105°, and wash the precipitate thoroughly with water, then with hot alcohol (to hasten the subsequent drying). After drying at 105° weigh the precipitate as As_2S_5. It is not necessary to wash it with carbon bisulfide.

Remark. — If the above directions are followed exactly, this method gives faultless results. If, on the other hand, the directions are deviated from in the slightest respect, the precipitate is likely to contain some arsenic trisulfide, whereby low results will be obtained. If the solution is not kept cool and the hydrochloric acid is added too rapidly, the heat of the reaction suffices to change a part of the arsenic

* *Ann. chem. pharm.*, **192**, 305.

† *Z. anal. Chem.*, **32**, 45; see also Brunner and Tomicek, *Monatshefte*, **8**, 607; McCay, *Z. anal. Chem.*, **27**, 682, and J. Thiele, *Ann. Chem. Pharm.*, **265**, 65.

chloride (this compound probably exists in solution) to arsenious chloride and chlorine, so that on passing hydrogen sulfide into the solution a mixture of arsenic trisulfide and arsenic pentasulfide will be obtained.

3. Determination of Arsenic as Magnesium Pyroarsenate, according to Levol

The solution must contain all of the arsenic as arsenate, and have a volume of not over 100 ml. per 0.1 g. arsenic. Add 5 ml. of 12 *N* hydrochloric acid drop by drop, with constant stirring, and then, for each 0.1 g. of arsenic, add 7–10 ml. of magnesia mixture* and a drop of phenolphthalein indicator solution. Now, with constant stirring, add 6 *N* ammonia from a buret until the phenolphthalein imparts a permanent red color to the solution, and then add enough more ammonia to make one third the volume of the neutralized solution. After standing twelve hours filter the liquid through a Gooch or Munroe crucible. Transfer the precipitate in the beaker to the crucible by some of the original solution blown from a small wash bottle. Wash the precipitate with 1.5 *N* ammonia solution containing 2–3 per cent of ammonium nitrate until free from chloride. Drain the crucible as completely as possible by suction, dry at 100° and heat in an electric oven quite gradually to a temperature of 400° to 500°, until there is no more ammonia evolved. Then raise the temperature to 800°–900° and keep there for about 10 minutes. Cool the crucible in a desiccator and weigh as $Mg_2As_2O_7$.

If an electric oven is not available, place the crucible with the precipitate in an air-bath (cf. Fig. 14, p. 36), having the bottom of the outer Gooch crucible come within about 2–3 mm. of the bottom of the crucible. Sprinkle a thin layer of powdered ammonium nitrate† upon the precipitate, and heat, gently at first, gradually increasing the temperature until the outer crucible is light red. Cool in a desiccator and weigh as $Mg_2As_2O_7$. The results obtained are excellent.

Remark. — The precipitate produced by the magnesia mixture has the formula $MgNH_4AsO_4 + 6\ H_2O$ and loses $5\frac{1}{2}$ molecules of water at 102°; it has, therefore, been proposed to weigh the precipitate after drying at this temperature, but it is impossible to obtain a constant weight.

Remark. — According to Levol, 600 ml. of pure water dissolve 1 g. of magnesium ammonium arsenate but J. F. Virgili,‡ found that it required 25 liters of 1.5 *N* ammonia to dissolve 1 g. of the precipitate.

* Dissolve 55 g. crystallized magnesium chloride and 70 g. ammonium chloride in 650 ml. water and dilute to a volume of one liter with ammonia water, *d.* 0.96.

† Instead of using ammonium nitrate, the crucible may be provided with a perforated cover and heated in a current of oxygen.

‡ *Z. anal. Chem.*, **44**, 504 (1905).

Colorimetric Determination of Arsenic

Small quantities of arsenic, such as are present in wall papers, may be estimated very accurately by means of the Marsh apparatus, comparing the mirror with a series of standards formed with known quantities of arsenic.* It is just as accurate, however, to use the much simpler apparatus recommended for the Gutzeit test. Treadwell and Comment† allow the arsine to react with disks containing silver nitrate and compare the resulting color with a standard which, unfortunately, must be produced freshly with each analysis, as it does not keep very well. Almost equally accurate, and much more convenient is the method of F. Hefti‡ and that of C. R. Sanger and O. F. Black§ in which the arsine is made to react with mercuric chloride paper.

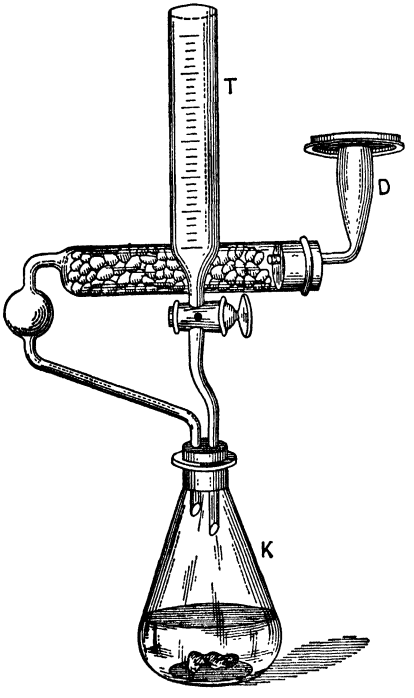


FIG. 47.

(*a*) Method of Hefti

First destroy all organic matter by heating the sample in a tube (see Vol. I), with fuming sulfuric and nitric acids, both of which must be free from arsenic. Evaporate the resulting liquid with sulfurous acid on the water-bath to reduce the arsenic acid to arsenious acid.|| When all the excess of SO_2 has been expelled, pour the solution into the graduated tube *T* of the apparatus shown in Fig. 47. In the 100–150 ml. flask *K*, place 6–8 g. of granulated zinc coated with copper|| and about 20 ml. of 4.5 *N* sulfuric acid free from arsenic. At the end of ten minutes all the air should be expelled from the apparatus by the evolved

* C. R. Sanger, *Am. Chem. J.*, **13**, 431 (1891); *Z. anal. Chem.*, **38**, 137 and 377; G. Lockemann, *Z. angew. Chem.*, **1905**, 429 and 491.

† This method was given in the early editions of this book.

‡ *Inaug. Dissert.* Zürich, 1907.

§ *Proc. Am. Acad. Arts and Sci.*, No. 8, 1907; *J. Soc. Chem. Ind.*, **26**, 1115 (1907).

|| Cf. Vol. I.

hydrogen. Now cover the outlet D* with a piece of mercuric chloride paper and weight it down with a small piece of ground glass. According to the quantity of arsenic present, allow all or a part of the solution in T to flow into the flask K. After twenty minutes remove the test-paper and compare the color of the spot produced with spots similarly obtained with known quantities of arsenic.

Prepare the discs of mercuric paper by dipping pieces of pure filter paper into a saturated solution of mercuric chloride and drying in an oven at 60°–70°.

Prepare the standards by a series of experiments with known quantities of arsenic. The spots thus obtained soon lose their color when exposed to moist air, but when dry can be kept in the dark for several days. An older standard is not reliable, but can be used to estimate the approximate quantity of arsenic and then, by making two or three standards with known quantities, the exact amount of arsenic can be determined. A convenient standard solution of arsenious acid used in preparing the scale contains 20 mg. of As_2O_3 in a liter. For less than 0.02 mg. of As_2O_3 (= 1 ml. of the standard solution) dilute the solution tenfold.

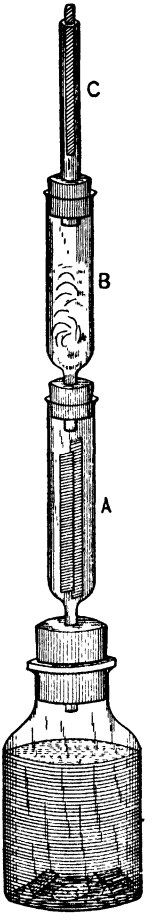


FIG. 48.

(*b*) Method of Sanger-Black

Place 10 g. of chemically pure stick zinc, a few stannous chloride crystals and a piece of platinum foil with several perforations in the 30 ml. evolution bottle (Fig. 48). Add a measured volume of the arsenic solution, nearly fill the flask with 7 N sulfuric acid and insert the stopper carrying the tubes A, B and C as shown in the drawing. The tube A is 7 cm. long and 1 cm. wide and contains a few strips of filter paper that have been moistened with 5 per cent lead acetate solution, to remove traces of hydrogen sulfide that may be formed from sulfur in the zinc. The tube B is a little shorter than A and contains a wad of cotton moistened with 1 per cent lead acetate solution. The tube C contains a dry strip of mercuric chloride paper prepared by allowing strips of thick drawing paper to remain for an hour in 5 per cent alcoholic mercuric chloride solution, hanging the strips on glass rods and allow-

* For quantities of arsenic under 0.02 mg., the upper diameter of the tube D should be 8 mm. and for larger quantities it should be 16 mm. The upper edge of the tube is ground perfectly flat.

ing them to dry in the air. After a few minutes the mercuric chloride paper begins to darken and after 45 minutes a maximum depth of color

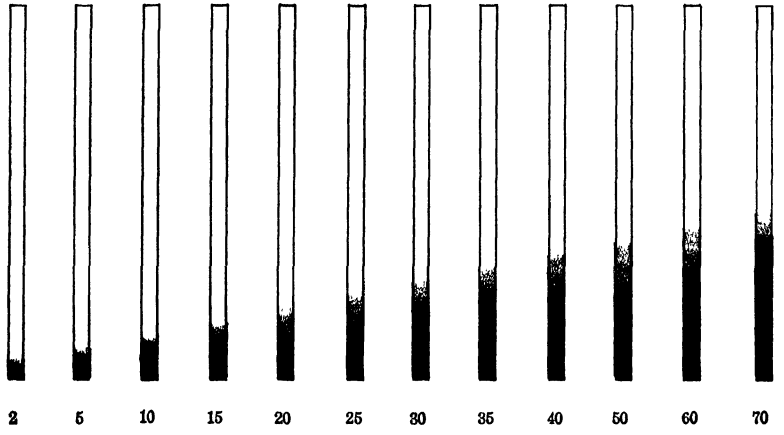


FIG. 49.

is obtained. Compare the color with that produced similarly by known quantities of arsenic produced in the same way with the same apparatus. Fig. 49 shows the way the standard strips should look.

(*c*) Electrolytic Determination of Arsenic*

Instead of producing the arsine by the action of zinc and acid, it may be formed by cathodic reduction, $AsO_2^- + 6\ominus + 7\ H^+ \rightarrow AsH_3\uparrow + 2\ H_2O$. Thorpe passes the arsine through a heated tube and produces an arsenic mirror, but Hefti† allows the gas to react with mercuric chloride paper. In both cases the apparatus devised by Thorpe (Fig. 50) can be used.

As cathode a perforated cone of thin lead foil, *K*, is recommended. Hang this upon the platinum wire that has been fused into the ground-glass stopper of the cathode compartment. As anode use platinum foil, two or three centimeters wide wrapped around the porous cell, *D*.

Procedure. — Pour pure, 4.5 *N* sulfuric acid into the porous cell *D*, and into the glass outer vessel, *E*. The level of the acid should be about 2 or 3 cm. from the bottom in the former, and about 0.5 cm. higher in the latter. For the colorimetric determination, pour the arsenic solution directly into the acid of the inner cell. It must be present as arsenious acid, cf. p. 202. For the production of mirrors, the air must all be expelled by hydrogen before the arsenic solution is added. The tube *C* should contain crystallized calcium chloride. Cover the outlet at *D* with

* Cf. Bloxam., *Z. anal. Chem.*, **1**, 483 (1862); T. E. Thorpe, *Proc. Chem. Soc.*, **19**, 183 (1903); W. Thomson, *Manch. Memoirs*, **48**, No. 17 (1904); S. R. Tootmann, *Chem. Zentr.*, **1904**, I, 1295; H. J. S. Sand and E. Hackford, *Chem. Zentr.*, **1904**, II, 259.

† *Inaug. Dissert.*, Zürich, 1907.

a disk of mercuric chloride paper (see Method *a*) and electrolyze with a current of 2–3 amperes at about 7 volts. The analysis is finished at the end of twenty minutes. Estimate the quantity of arsenic by comparing the spot with a standard scale. (See Method *a*.) If the apparatus is connected with a horizontal delivery tube, Sanger's method can be used. (See Method *b*.)

Remark. — As cathode Thorpe recommends bright platinum foil and Hefti uses lead. Polished platinum does not hold arsenic back, but platinum with a rough surface does, and since bright platinum becomes dull with use, it is easily possible for low results to be obtained. Experiments performed by Hefti in the author's laboratory showed that zinc alloyed with a trace of copper or platinum, bright platinum foil and lead did not hold back arsenic when used as the cathode; on the other hand, zinc in the presence of chloroplatinic acid and platinum foil with spongy platinum held back a considerable quantity of arsenic.

To determine arsenic in a mineral water, evaporate 100 ml. to a small volume in a porcelain dish. Add a little sulfuric acid, reduce with sulfurous acid, expel the excess of the latter, and analyze by one of the above three methods.

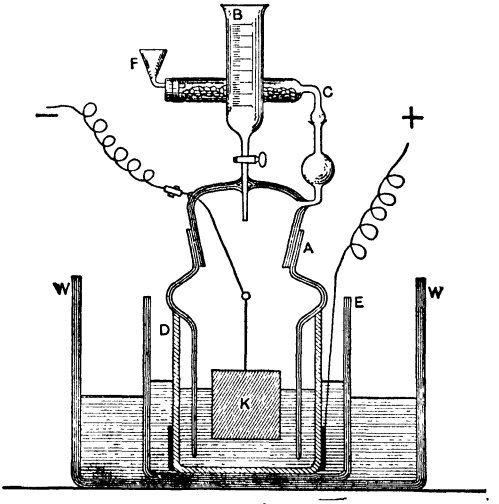


FIG. 50.

Determination of Larger Quantities of Arsenic as Arsine. Method of F. Hefti

In the electrolysis of larger quantities of arsenic it was not possible, in the past, to recover all the arsenic as arsine; some arsenic was deposited upon the cathode in the form of the element arsenic and was not transformed into arsine by the further action of the electric current. The quantity of arsenic deposited as metal depends upon the potential of the electric current at the electrodes, the temperature, and the concentration of the arsenic solution. At high potentials, low temperature, and low concentration of the solution, the quantity of arsenic deposited becomes zero and the yield of arsine is then quantitative. The estimation of the latter is best accomplished iodimetrically. If arsine is passed through a solution of iodine in potassium iodide, it is immediately oxidized to arsenic acid in the cold.

$$AsH_3 + 10\,NaHCO_3 + 4\,I_2 = Na_2HAsO_4 + 8\,NaI + 10\,CO_2 + 6\,H_2O$$

If the excess of iodine is titrated with sodium thiosulfate (see Iodimetric Methods) it is possible to determine the quantity of iodine that has reacted with the arsine. If T ml. of 0.1 N iodine were used at the start, and t ml. of 0.1 N thiosulfate solution were used for the titration, then the quantity of arsenic or arsenic trioxide, present is

$(T - t) \times 0.000937$ g. arsenic,
$(T - t) \times 0.001237$ g. As_2O_3.

The apparatus necessary is shown in Fig. 51. The decomposition cell is also shown in Fig. 52 and consists of a wide U-tube capable of holding 120 ml. of solution. The tube is made in two halves, the edges of the bottom being ground so that they fit tightly together. Between these edges place a piece of thin parchment paper,

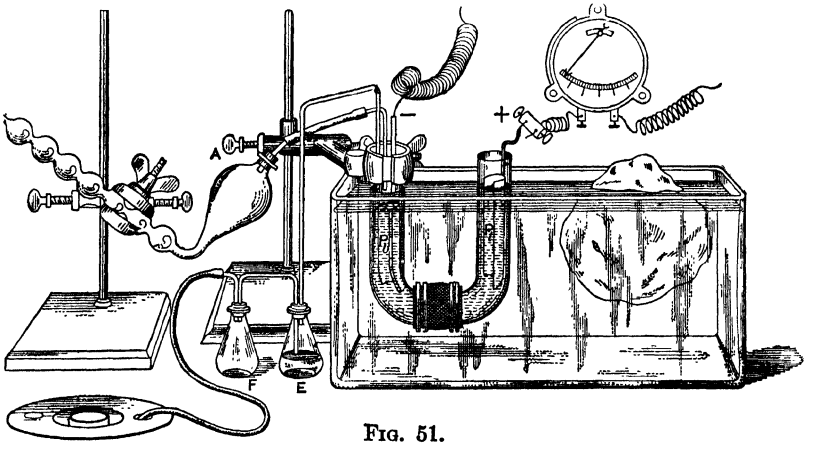


FIG. 51.

and fold the extending edges over one side of the tube. Bind the two halves of the U-tube together by a piece of rubber tubing which also holds the parchment paper in place. Wire this tubing tightly in place, taking care that the edges of the parchment paper are also covered by the wire. In one arm of the tube (the anode compartment) which remains open during the whole experiment, suspend a platinum plate electrode as anode, and tightly stopper the other arm (the cathode compartment) with a three-holed rubber stopper. Through one hole insert a glass tube containing mercury, and with a platinum wire sealed into the bottom; from this suspend a plate electrode of lead foil to serve as cathode. Make the wire from the negative pole of the battery dip into the mercury. Through the second hole in the stopper insert a gas delivery tube leading to the absorption vessel *A*. The third hole in the stopper carries a tube that leads to the Erlenmeyer flask *E* containing a little water, which, in turn, is connected with the empty flask *F*, and the latter with the rubber tubing shown in Fig. 51. This tubing leads to the hood. Such an arrangement provides for the regulation of the pressure in the cathode space. If the pressure there exceeds that of the anode space, a part of the arsenic solution will pass into the anode compartment and will be lost in the analysis. By applying suction at the extreme end of the absorption apparatus so that bubble after bubble of air passes through the Erlenmeyer, it is easy to overcome the pressure in the absorption vessel without having diminished the pressure in the cathode compartment enough to tear the parchment membrane.

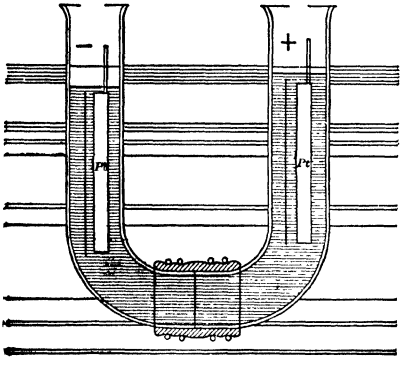


FIG. 52.

Procedure. — The arsenic solution to be tested must contain all the arsenic in the tervalent condition. First of all, fill the anode compartment to within 3 cm. of the top with 2 *N* sulfuric acid, pour the arsenite solution into the cathode compartment and fill this to within 3.5 cm. of the top, leaving the level of the liquid about 0.5 cm. lower than on the other side of the U-tube; the concentration of the arsenic solution in the U-tube, after this dilution with acid, should not exceed 80 mg. As_2O_3 in 50 ml. of solution. Place the U-tube in ice-water and connect the gas delivery tube with two ten-bulb absorption tubes, of which only one is shown in the drawing. Into the first absorption tube place an accurately-measured volume of tenth-normal iodine solution, and into the second tube, which is not shown in the drawing, 10 ml. of standard 0.1 *N* sodium thiosulfate solution diluted with 40 ml. of water. The purpose of the sodium thiosulfate solution is to catch any iodine that may escape from the first absorption tube. While the absorption vessels are being filled, the arsenic solution should be in the ice-water, and its temperature should be about 0° when the analysis is ready to begin. Apply gentle suction at the end of the second absorption tube, close the electric circuit, using 2–3 amperes as in the preceding method of analysis, and regulate the suction so that bubble after bubble of air slowly streams through the pressure regulator and into the cathode compartment throughout the duration of the electrolysis. Moreover, take care that sufficient ice remains in the cooling bath. When all the conditions are maintained satisfactorily, the liquid in the cell should remain perfectly clear, or at the worst be colored only by a slight brownish turbidity, which eventually disappears. If a black turbidity is formed that settles to the bottom of the U-tube, something has gone wrong and it is useless to continue the experiment. In a normal experiment, the evolution of the arsine is finished in an hour, if not more than 50 mg. of As_2O_3 are present. Then turn off the current and pour the contents of the two absorption tubes (first the iodine and then the thiosulfate solution) into a beaker containing 5 ml. of a saturated solution of pure $NaHCO_3$. Titrate the excess of iodine with 0.1 *N* sodium thiosulfate solution using starch solution as indicator. If on mixing the contents of the two absorption bulbs the solution is decolorized, finish the titration with 0.1 *N* iodine.

This method can be carried out very easily and gives accurate results in the presence of iron, so that it is suitable for a rapid determination of the arsenic present in iron minerals.

W. D. Treadwell* recommends a simpler apparatus, shown in Fig. 53. The glass beaker is about 14 cm. tall. The cathode compartment,

* *Elektroanalytische Methoden* (1915).

from which the arsine is evolved, consists of a glass tube about 12 cm. tall and 2.5 cm. wide, fastened at the bottom, by means of the short piece of rubber tubing, G, to the porous diaphragm T of the same outside diameter. This bottom part is made by sawing off the bottom of an ordinary porous cell, leaving an edge of only about 1 cm. The glass tubing is shown separated from the diaphragm in the drawing merely to indicate that the two tubes are joined at this place. As cathode, use a piece of lead wire wound into a spiral as shown by K in the drawing. Thicken the lead wire at the top so that it fits tightly into the glass tubing of H, thus preventing loss of arsine through this tubing. Outside of this cathode compartment place an ordinary platinum gauze electrode to serve as anode. Pour 4 N sulfuric acid into the beaker and cover the anode with this electrolyte. Pour the solution to be tested for arsenic into the cathode compartment and have the level of the sulfuric acid in the beaker about 2 cm. higher than that of the solution around the cathode. Close the cathode compartment with a stopper carrying the cathode and the gas delivery tubing. Place the beaker in ice water to keep the temperature below 10° and electrolyze as described above. The absorption flask J should contain 25 ml. of 0.1 N iodine solution and it should be connected with a similar absorption flask containing 25 ml. of 0.1 N thiosulfate. Both solutions must be measured carefully from a pipet or buret.

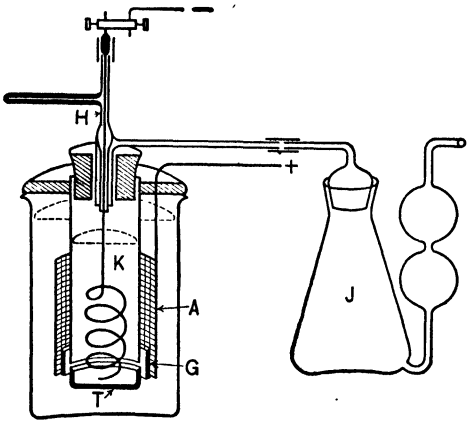


FIG. 53.

Determination of Arsenic in Mispickel

Fuse 1 g. of the finely-powdered mineral in a nickel crucible with 6 g. of sodium carbonate and 1 g. of potassium nitrate. Extract the resulting melt with hot water and wash the residue (Fe_2O_3, NiO) with hot sodium carbonate solution. To the filtered solution add 200 ml. of water saturated with SO_2 to reduce the arsenic, boil to expel the excess of SO_2, allow to cool, dilute to 500 ml. with water and sulfuric acid so that the entire solution is about 2 N in H_2SO_4, and determine the arsenic as outlined above, using one-tenth of the solution.

Instead of extracting the melt with water, it may be treated with

dilute sulfuric acid, whereby all the iron goes into solution. After this solution has been reduced with sulfurous acid, the analysis of an aliquot part gives the same result as when the first procedure is followed.

ANTIMONY, Sb. At. Wt. 120.2

Forms: Sb_2S_3, Sb_2O_4, and Sb

1. Determination as Trisulfide, Sb_2S_3

(*a*) Method of F. Henz*

The best method for the determination of antimony is unquestionably the following:

Conduct hydrogen sulfide for twenty minutes into the cold solution of an antimonite or antimonate, then, without stopping the current of hydrogen sulfide, slowly heat the solution to boiling and continue the stream of hydrogen sulfide for fifteen minutes more. Remove the flame, allow the precipitate to settle and filter through a Gooch crucible which has been heated at 280–300° and weighed. Wash the precipitate four or five times by decantation with 50–75 ml. of hot, very dilute acetic acid into which hydrogen sulfide has been passed. Wash on the filter with the same liquid until all chloride is removed. At first the filtrate runs through perfectly clear, but after all the mineral acid has been removed, the filtrate shows a slightly orange tint, owing to an unweighable amount of the antimony sulfide passing through in colloidal solution. As soon as this point is reached, stop the washing.

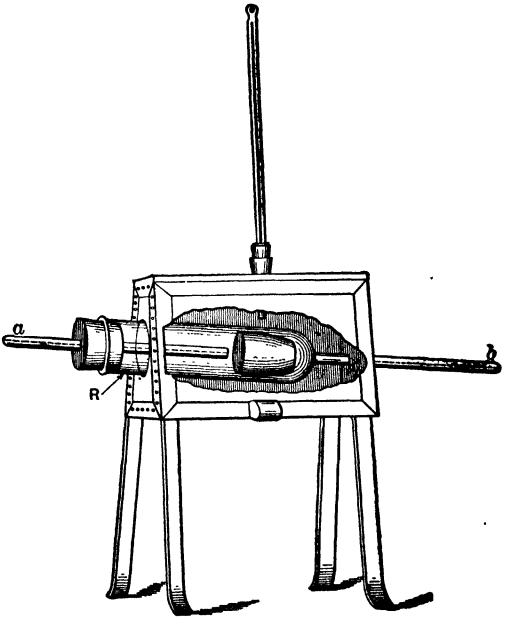


FIG. 54.

Place the crucible, after the precipitate has been dried as much as possible by suction, in the tube *R*, Fig. 54, which is fitted to a drying oven (about 18 cm. long and 10 cm. high and covered with asbestos

* F. Henz, *Z. anorg Chem.*, **37**, 18 (1903).

paper). Close the tube *R* with a rubber stopper that holds a glass delivery tube, and push *R* into the drying closet until the end of the stopper is reached. To protect the rubber stopper during the subsequent heating, fit a Rose crucible cover against it, holding it in place by wrapping the tube *a* with a strip of asbestos paper.

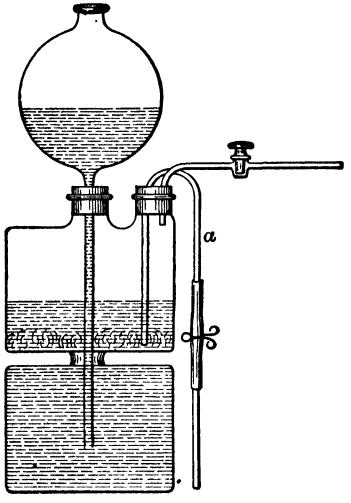


FIG. 55.

Expel all air from the tube by a stream of dry, air-free carbon dioxide* and heat for two hours at 100° to 130°. Inasmuch as the tube *R* extends so far into the drying oven, there is no danger of water condensing in the tube; it is all expelled as vapor at *b*. The precipitate is now dry and the air completely expelled from the heating tube.

Now withdraw the tube *R* a little ways out of the oven, about 5 cm., as shown in the drawing, raise the temperature to 280–300° and keep it there for two hours.

Hereby some sulfur is volatilized and collects in the tube *R* outside the oven. The orange pentasulfide is also completely changed into the black antimony trisulfide by this heating.† Allow the crucible to cool in the stream of carbon dioxide, transfer

* In order to obtain accurate results it is necessary to have the carbon dioxide perfectly free from air. This may be prepared by the use of the Kipp generator as modified by Henz (*Chem. Ztg.*, **1902**, 386) see Fig 55.

This differs from the ordinary form of the Kipp apparatus only as regards the siphon tube *a*; but herein lies a distinct advantage. The apparatus is charged as follows: First of all, place pieces of pure marble in the middle compartment, open the stop-cock, and pour water through the upper compartment, until it begins to run out through the stop-cock, which is then closed. By this means all the air has been expelled from the lower parts of the apparatus and it only remains to introduce the hydrochloric acid. To accomplish this, allow the water to run out through the siphon while pouring 2.5 *N* hydrochloric acid in at the top of the generator. As soon as carbon dioxide begins to be evolved, close the tube *a* and the apparatus is ready for use. When the acid has become too weak, remove it through the siphon, pouring in a fresh supply at the top; there is no need of taking the apparatus apart during this operation. It is obvious that the same apparatus can be employed to advantage for generating hydrogen or hydrogen sulphide.

† According to Paul (*Z. anal. Chem.*, **31**, 540 (1892)), the transformation of antimony pentasulphide can be accomplished at 230° but it is much more rapid at 280–300°. It is more difficult to replace the air completely with carbon dioxide in Paul's drying oven.

to the balance case,* and after standing half an hour is weighed. The black antimony trisulfide is not at all hygroscopic. A further heating in the current of carbon dioxide will rarely show any change in weight.

(*b*) Method of Vortmann and Metzel †

When antimony is precipitated by hydrogen sulfide from a hot solution which is strongly acid with hydrochloric acid, the sulfide eventually becomes grayish black in color, is crystalline, and can be filtered easily and washed with water without the slightest tendency to pass into the hydrosol condition.

To each 100 ml. of neutral solution in an Erlenmeyer flask, add 24 ml. of 12 *N* hydrochloric acid. Heat to boiling, and subject the hot solution to the action of hydrogen sulfide gas. Place the Erlenmeyer flask containing the solution in a dish of boiling water and keep the water in the latter boiling during the precipitation. It is advisable to introduce the hydrogen sulfide gas quite rapidly at first, but towards the end a slow stream is sufficient. The antimony sulfide as it comes down is yellow at first, but as the precipitation proceeds, it becomes redder; gradually it becomes heavier and denser, assumes a crystalline form and becomes darker, and finally black in color. The transformation into the crystalline form is hastened by shaking the flask. At first, while the precipitate is of a yellowish color, there is no need of shaking the flask but later on it is very desirable to do so. The shaking, however, should not be too violent, as otherwise some of the precipitate is likely to adhere to the upper portions of the flask and escape the transformation. The reaction requires 30–35 minutes. Finally a heavy, dense, crystalline precipitate of antimony trisulfide is obtained which settles well and permits a rapid filtration. Dilute the solution with an equal volume of water, allowing it to flow around the walls of the flask in order to wash down any adhering sulfide. The dilution almost always causes the formation of a slight yellow turbidity. The reason for this is that a little of the antimony is held in solution by the strong acid and as the solution is diluted this is caused to precipitate by the dissolved hydrogen sulfide. Once more shake the flask, replace it in the vessel of boiling water and introduce more hydrogen sulfide. In two or three minutes the solution above the precipitate will become clear. Filter through a Gooch crucible, wash with water to remove the acid, then with alcohol, place in the drying oven and heat as described under (*a*).

* Roll up a piece of writing-paper and place it in the tube *R*, so that the crucible does not come in contact with any of the sulfur sublimate, on withdrawing it. Remove the crucible with the paper.

† *Z. anal. Chem.*, **44**, 526 (1905).

2. Determination as Tetroxide, Sb_2O_4 (Bunsen)

This method is based upon the fact that antimony pentoxide, when ignited at a definite temperature, changes into Sb_2O_4. Bunsen,* who first proposed the method, later abandoned it because his assistant succeeded in volatilizing more than 0.1 g. of the precipitate by heating it over the blast lamp.† Brunck,‡ Rössing § and Henz|| have shown, however, that accurate results can be obtained. In 1897, Baubigny¶ discovered that antimony pentoxide is converted quantitatively into the tetroxide at a temperature of 750°–800°. The literature is conflicting with regard to the volatility of Sb_2O_4. This oxide is often regarded as antimonous antimonate with one atom of antimony in the tervalent condition and the other atom in the quinquevalent state. The oxide Sb_2O_4 is very easily reduced and Sb_2O_3 volatilizes quite rapidly at 1000° (0.35 g. in 30 minutes)

Procedure. — In most cases it is desired to determine the amount of antimony present in a mixture of its tri- and pentasulfides, or in a mixture of one or the other of the two compounds with sulfur. It is best to proceed as follows: Precipitate the sulfide of antimony from a hot solution, wash the precipitate first with hot water, then with alcohol, afterwards with a mixture of alcohol and carbon disulfide (in order to remove the sulfur),** again with alcohol and finally with ether. Then dry the precipitate, separate the bulk of the precipitate from the filter and place it upon a watch-glass. Put the filter in a small porcelain dish and boil it with a little freshly-prepared ammonium sulfide solution stirring constantly with a glass rod. Pour the resulting solution through a small filter into a 30 ml. porcelain crucible, and treat the filter repeatedly with ammonium sulfide until it is no longer colored brownish red at the edge of the paper, where it begins to dry; the extraction of the antimony sulfide is then complete. Evaporate the solution in the crucible to dryness and add the main part of the precipitate. To oxidize the antimony sulfide, Beckett places the crucible, with a dish of fuming nitric acid beside it, under a bell-jar and allows it to stand over night. The vapors of fuming acid slowly oxidize the precipitate in the crucible and in the morning it is possible to complete the oxidation by means of nitric acid (*d.* 1.4) without the reaction being too violent. Heat the crucible on the water-bath until the precipitate becomes white and the greater part of the acid is expelled. Add a little water and, with stirring, enough concentrated ammonia to give an

* *Ann. Chem. u. Pharm.*, **106**, 3 (1858).
† *Ibid.*, **192**, 316 (1878).
‡ *Z. anal. Chem.*, **34**, 171 (1895).
§ *Ibid.*, **41**, 9 (1902).
|| *Loc. cit.*
¶ Compt. rend., **124**, 499 (1897).
** Thiele, *Ann. d. Chem. und Pharm.*, **263**, 372.

alkaline reaction. Evaporate the contents of the crucible to dryness on the water-bath, carefully heat in an air-bath (Fig. 14, p. 38) until no more fumes of sulfuric acid are evolved, and then for half an hour at 800° in an electric oven. Cool in a desiccator, transfer the crucible quickly to a glass-stoppered weighing beaker, allow to stand twenty minutes in the balance case, and then weigh. Repeat the ignition and weighing until a constant weight is obtained.

3. Determination of Antimony as Metal

Antimony may be deposited from acid solutions by means of the electric current; the metal, however, does not adhere well to the electrode, so that this method cannot be used for its quantitative determination. On the other hand, the following method is suitable; it was first proposed by Parrodi and Mascazzini,* then modified by Luckow,† and afterwards improved by Classen and Reiss.‡ According to the experience in the author's laboratory, it is not as accurate as the trisulfide method.

If a solution of sodium or ammonium sulfoantimonite, or antimonate, containing not more than 0.2 g. Sb in a volume of about 140 ml. is subjected to electrolysis with a current of 1–1.5 amperes at 65° for 90 minutes, the antimony will be deposited upon a platinum dish, which has been etched by treatment with dilute aqua regia, as steel-gray, metallic antimony, and the deposit adheres so firmly that it can be dried and weighed without loss. The chief condition for the success of this operation is the absence of polysulfides. In case these substances are present the antimony is incompletely deposited and in some cases not at all, or the deposited antimony may pass into solution, on account of being oxidized to sodium antimonite by means of the sodium polysulfide which is formed at the anode during the electrolysis: $2\,Sb + 3\,Na_2S_2 = 2\,Na_3SbS_3$.

It is necessary, therefore, to prevent the formation of polysulfides during the electrolysis. For this reason Lecrenier§ added sodium sulfite to the bath, whereby the polysulfide is transformed into thiosulfate: $Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S$.

Ost and Klapproth|| carry out the electrolysis with the aid of a diaphragm to keep the polysulfide away fron the cathode.

It is better, however, to make use of potassium cyanide for this purpose.¶

$$Na_2S_2 + KCN = Na_2S + KCNS.$$

Procedure. — In most cases the antimony is first isolated as the sulfide, which is either precipitated by hydrogen sulfide from acid solution or obtained by acidifying an alkaline solution of the sulfo-salt. Dissolve the filtered and washed precipitate, corresponding to not over 0.2 g. Sb, on the filter by pouring pure sodium sulfide solution (*d.* 1.14) over it. Catch the solution as it runs through the filter in a weighed platinum

* *Z. anal. Chem.*, **18**, 587 (1879).

† *Ibid.*, **19**, 13 (1880).

‡ *Berichte*, **14**, 1629 (1881); **17**, 2474 (1884); **18**, 408 (1885); **27**, 2074 (1894).

§ A. Lecrenier, *Chem. Ztg.*, **13**, 1219 (1889).

|| *Z. angew. Chem.*, **1900**, 828.

¶ Cf. A. Fischer, *Ber.*, **36**, 2048 (1903); *Z. anorg. Chem.*, **42**, 363 (1904); Hollard, Bull. Soc. Chem., **23** [3] 292 (1900); F. Henz, *Z. anorg. Chem.*, **37**, 31 (1903).

dish with etched inner surface. After washing the filter with the sodium sulfide solution, the total volume of the liquid in the platinum dish should not be over 80 ml.; if less than this, add more sodium sulfide solution. Dilute the solution with 30 ml. of 10 per cent, freshly-prepared, pure potassium cyanide solution and dilute to 125 ml. Heat to 65° (not over 70°) and electrolyze with a current of 1.2–1.3 amperes and electrode potential of 2–3 volts. After 1.5–2 hours all the antimony will be upon the cathode in the form of a firmly-adhering, light-gray deposit.* Now, without breaking the circuit, siphon off the electrolyte, while adding water until the current ceases to pass through the liquid (the voltmeter connected as ammeter points to the zero read ing). Remove the cathode, wash thoroughly with water, then with 95 per cent alcohol, dry at about 80°, cool in a desiccator, and weigh.

Cleaning the Electrodes. Ost† recommends heating with a mixture of equal parts concentrated nitric acid and a saturated solution of tartaric acid. The antimony will also dissolve readily by heating with a solution of alkali polysulfide. The results by this method are usually a little high.

TIN, Sn. At. Wt. 119.0

Forms: SnO_2, Sn

1. Determination as Tin Dioxide, SnO_2

Two cases are to be distinguished:

(*a*) *The Tin is Present as Metal (in an Alloy).*

(*b*) *The Tin is Present in Solution.*

(*a*) The Tin is Present in an Alloy

Method I

In case the tin is present in an alloy it may be treated according to the method of Busse‡ as follows:

Cover 0.5 g. of the alloy, in the form of borings, with 6 ml. of nitric acid (*d.* 1.5) and slowly add 3 ml. of water; quickly cover the beaker with a watch-glass. As the water is mixed with the acid a violent

* To make sure that the deposition is complete, the liquid may be transferred quickly to a second dish and electrolyzed for half an hour longer. It is seldom that there will be any gain in weight shown by this dish.

† *Z. angew. Chem.*, **1901**, 827.

‡ *Z. anal. Chem.*, **17**, 53. The method gives good results with tin alloys but gives low results with alloys containing only a little tin.

reaction takes place. When the evolution of nitric oxide (brown vapors on coming in contact with the air) has ceased, heat the solution to boiling and dilute with 50 ml. of boiling water and allow to stand for 2 hours on the water-bath. Allow the precipitate to settle completely, then filter and wash with hot 1 per cent nitric acid and dry. Ignite, at first gently and finally strongly, over a Méker burner, or a blast-lamp, in an open porcelain crucible and weigh as SnO_2.

The tin dioxide thus obtained is never pure; it always contains small amounts of other oxides and must be purified as follows: After weighing, add to the precipitate six times as much of a mixture consisting of equal parts sodium carbonate and pure sulfur. Heat in a porcelain, covered crucible over a small flame until the excess of sulfur is almost entirely removed. This point is easily recognized by there being no longer any odor of SO_2 and no blue flame of burning sulfur evident between the cover and the crucible. Cool and dissolve the melt in a little hot water; the tin goes into solution* as sodium thiostannate (cf. Vol. I), together with some copper and iron. Treat the deep-brown liquid, therefore, with sodium sulfite† solution until it becomes only slightly yellow in color; any iron or copper, etc., will now be precipitated quantitatively as sulfides. Filter off the latter and wash first with water to which a little sodium sulfide has been added and finally with hydrogen sulfide water. As a rule the amount of insoluble sulfide formed by this treatment is so small that after drying it can be ignited in an open porcelain crucible and changed to oxide without introducing any appreciable error. If this weight is subtracted from the original amount of impure stannic oxide, the weight of pure stannic oxide will be obtained. If, however, the amount of impurity present with the residue of metastannic acid should be large, the different metals must be separated, according to one of the methods for the separation of the sulfo-bases, the weight of each oxide determined separately, and the sum of their weights subtracted from the original weight of the tin dioxide. Instead of determining the amount of impurity present with the tin dioxide, the filtrate from the insoluble sulfides can be acidified with acetic acid and the tin precipitated as yellow stannic sulfide, which, after it has completely settled, can be filtered off changed by careful ignition in an open porcelain crucible, to tin dioxide, as described on p. 218, and weighed as such.

* Frequently a single fusion with sodium carbonate and sulfur is insufficient; this is recognized by obtaining a sandy residue insoluble in water. In this case filter off the residue, wash, dry, and repeat the fusion.

† The sodium sulfite changes the sodium polysulfide to monosulfide, in which copper and iron sulfides are insoluble.

Method II

Dissolve the alloy in nitric acid, filter off the insoluble metastannic acid and wash as in the first method. Instead of igniting the precipitate, however, wash it into a porcelain evaporating dish, evaporate on the water-bath almost to dryness, and then treat with 1 ml. of pure sodium hydroxide solution and 10–15 ml. of saturated sodium sulfide solution. Cover the evaporating dish with a watch-glass, and heat for about 45 minutes on the water-bath, whereby all the tin should pass into solution, and the other metals remain undissolved as sulfides. Filter and wash with very dilute sodium sulfide solution.

The filter, upon which the metastannic acid was filtered, still retains some of the precipitate. Spread it out, therefore, in a second small evaporating dish, cover with about 1 ml. of sodium sulfide solution and heat on the water-bath. After half an hour, the tin should all be dissolved. Pour the solution through a small filter and wash the latter with a little hot water.

Dry the two filters, ignite in a porcelain crucible, treat the ash with a small quantity of strong nitric acid and add the resulting solution to that obtained by dissolving the alloy in nitric acid.

For the determination of the tin, combine the two solutions containing sodium thiostannate, make acid with acetic acid and boil to expel the hydrogen sulfide. Filter off the precipitated stannic sulfide, wash once with water to remove the most of the alkali salts, then transfer back to the original beaker and dissolve in 10 ml. of 50 per cent potassium hydroxide solution, and 1 g. tartaric acid; these quantities suffice for 0.1–0.2 g. of tin. To the solution, add pure 30 per cent hydrogen peroxide (Perhydrol, Merck) until the yellow liquid becomes perfectly colorless, then add 1 ml. in excess. Boil the solution for ten minutes to make sure that the oxidation is complete, and that the excess of peroxide is decomposed. As soon as no more bubbles of oxygen are evolved, allow the solution to cool somewhat and add cautiously 15 g. of oxalic acid dissolved in a little hot water. Electrolyze the hot solution as described on p. 219.

The precipitated stannic sulfide, as obtained above by acidifying the sodium thiostannate solution, may be ignited in a porcelain crucible and weighed as SnO_2. The results are usually a little high and the method is not as accurate as the electrolytic determination. Cf. p. 218; β.

Method III

Many chemists prefer to use a more dilute nitric acid for dissolving the alloy than was recommended by Busse. It is possible to obtain, in this way, residues of metastannic acid which are fully as pure and the work is not as unpleasant as when

the more concentrated acid is employed. This method is recommended for the analysis of phosphor-bronze.

Procedure. — Dissolve 0.5 g. of borings in a small beaker with 15 ml. of 6 *N* nitric acid, 1.2. Evaporate the solution just to dryness on the water-bath, and remove the beaker as soon as this stage is reached. Treat the residue with 20 ml. of 2 *N* nitric acid, heat to boiling and decant off the solution through a hardened filter paper. Repeat this treatment. Complete the washing by boiling and decanting with 1 per cent ammonium nitrate solution. Keep as much of the precipitate as possible in the original beaker, and the total volume of the filtrate under 150 ml. Examine the first portions of the filtrate for metastannic acid, refilter if necessary, and remove each successive portion from below the funnel before adding more wash water.

Treat the residue of slightly impure metastannic acid as described under either of the above methods. In case Method II is chosen, however, it is advisable to treat the filters containing the residue from the sodium sulfide treatment with 15 ml. of hot 3 *N* nitric acid instead of burning and treating with nitric acid as directed above. Filter the resulting solution of the impurities that were originally present in the metastannic acid, add the filtrate to the original nitric acid solution and the ash of the filter to the main SnO_2 precipitate.

Remark. — Sometimes a little metastannic acid is left undissolved by the treatment with alkali sulfide. It is not safe, therefore, to discard the filters. In the analysis of phosphor-bronze, the copper, lead and phosphorus may be determined as described on p. 223.

(b) Tin is Present in Solution

(α) *The Solution Contains Tin only*

If the solution contains only tin in the form of stannic salt (chloride or bromide), add a few drops of methyl orange indicator solution and then ammonia until the pink color of the indicator is changed to yellow. Add 24 g. of ammonium nitrate and dilute the solution to a volume of 300 ml. Heat to boiling, filter after the precipitate has settled, wash with hot 2 per cent ammonium nitrate solution, ignite in an open porcelain crucible, and weigh as SnO_2.

Remark. — If the solution contains non-volatile organic acids, this method cannot be used for the determination of tin. In this case the tin must be first precipitated as sulfide by means of hydrogen sulfide (cf. p. 218). If the tin is not in solution as stannic salt, but as stannous salt, the solution must be first oxidized by the addition of bromine water until a permanent yellow color is obtained, after which the solution can be neutralized with ammonia and treated as above described.

According to J. Löwenthal,* tin can be precipitated from slightly *acid* stannic chloride or bromide solutions by boiling with ammonium nitrate. Add methyl orange to the solution and then ammonia until a yellow solution is obtained;† now add dilute nitric acid, drop by drop, until the solution just becomes pink again, and continue as described above.

(β) *The Solution Contains, besides Tin, Metals of the Ammonium Sulfide Group or Organic Substances*

In this case, independent of whether the tin is present in the form of stannic or stannous salts, conduct hydrogen sulfide into the dilute solution until it is saturated with the gas; allow the solution to stand until the odor of hydrogen sulfide has almost disappeared and then filter. Wash the precipitate with a 2 per cent ammonium nitrate solution, dry, transfer as completely as possible to a porcelain crucible, and add the ash of the filter. Heat the tin sulfide at first gently with the flame well in front of the inclined open crucible to avoid loss by decrepitation, and afterwards with the flame at the base of the crucible until the odor of sulfur dioxide is no longer perceptible. Now raise the temperature gradually until finally the full heat of a good Teclu or Méker burner is obtained. As tin dioxide holds fast to some sulfuric acid with great tenacity, after cooling the crucible somewhat add a piece of ammonium carbonate the size of a pea. Again heat and weigh as SnO_2. Repeat the heating with ammonium carbonate until a constant weight is obtained.

Remark. — F. Henz‡ in testing this method always obtained results which were a little too high. This is due to the fact that it is difficult to wash the stannic sulfide precipitate free from sodium salts. It is best, therefore, to dissolve the well-washed stannic sulfide precipitate in a little sodium sulfide, transform the thiostannate into stannioxalate, and determine the tin by electrolysis, according to p. 219, or as oxide by the method of Löwenthal (see above directions).

2. Determination of Tin as Metal§

The electrolytic deposition of tin from a solution of the ammonium stannioxalate gives excellent results. It is necessary, however, to have free oxalic acid always present while the solution is undergoing electrolysis. During the process, ammonium oxalate is changed by anodic oxidation into ammonium bicarbonate and carbon dioxide,

$$C_2O_4^{--} + 2\,H_2O + 2\,\oplus = 2\,HCO_3^- + 2\,H^+$$
$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2\uparrow.$$

* *J. pr. Chem.*, **56**, 366 (1852).

† The excess of acid cannot be removed by evaporation on account of the volatility of stannic chloride.

‡ *Z. anorg. Chem.*, **37**, 39 (1903).

§ Cf. Classen-Hall, *Quant. Anal. by Electrolysis.*

and the solution will smell of ammonia as a result of the hydrolysis of ammonium carbonate. When this point is reached no more tin is deposited. The ammonia often precipitates some stannic acid, which escapes the electrolysis. It is necessary, therefore, to avoid letting the bath become ammoniacal, and this is best accomplished by adding a little solid oxalic acid from time to time.

In the following method the electrolysis is accomplished in a potassium oxalate solution. Not more than 0.3 g. of tin should be present in the solution analyzed.

Procedure. — In the course of an analysis it is usually necessary to precipitate the tin from a solution of alkali thiostannate. This is best accomplished as follows: Decompose the thio-salt by acidifying with acetic acid, boil to expel hydrogen sulfide and dissolve the sulfide by adding 15 g. of solid potassium hydroxide. Oxidize by adding perhydrol (concentrated H_2O_2) drop by drop. At first the color of the solution deepens but eventually it becomes colorless. Finally boil 10 minutes, add 15 g. of oxalic acid and boil 10 minutes more. Then dilute to about 150 ml., heat to 65° and electrolyze with a current of 1 ampere and 3–4 volts potential at the electrodes; at the end of about six hours all the tin will have been deposited upon a gauze electrode. Wash the deposit with water, exactly as prescribed for nickel on p. 139, then with alcohol, dry by holding above a flame, cool in a desiccator, and weigh. The results are excellent.

Remark. — If ammonium oxalate is used in place of the potassium oxalate, the electrolysis requires more time (eight to ten hours). By the addition of hydroxylamine the duration of the electrolysis is shortened (Engel).

If the solution becomes turbid during the electrolysis, insufficient caustic potash solution was used. Add 2–3 g. of potassium hydroxide to dissolve the turbidity.

Separation of Arsenic, Antimony, and Tin from the Members of the Ammonium Sulfide Group

The separation is effected by passing hydrogen sulfide into the acid solution of the above metals whereby arsenic, antimony, and tin are precipitated as sulfides, while the remaining metals remain in solution.

From an alloy, or the solid sulfo-salts of the above metals, arsenic, antimony, and tin may be readily volatilized by heating in a stream of chlorine; the chlorides of these three metals are readily volatile, while those of the remaining metals are only difficultly so.

Separation of Arsenic, Antimony, and Tin from Mercury, Lead, Copper, Cadmium, and Bismuth

If the metals are all in solution, precipitate them by means of hydrogen sulfide, filter and wash the precipitated sulfides and treat with alkali sulfide solution. If mercury is present, ammonium polysulfide should

be used, but in the absence of this metal sodium polysulfide works better (cf. Vol. I).

If the metals of this group are in the form of an alloy (arsenic and mercury are seldom met with to any extent), the antimony and tin are separated from the remaining metals by treating the alloy with nitric acid. The tin is left behind as metastannic acid, insoluble in dilute nitric acid, and the antimony is precipitated completely if ten times as much tin is present. In the presence of sufficient tin, all phosphorus and arsenic are thrown down in the insoluble residue. The small amount of the latter (and the remaining metals of this group) are precipitated by hydrogen sulfide and separated from the copper group by means of alkaline sulfide solution.

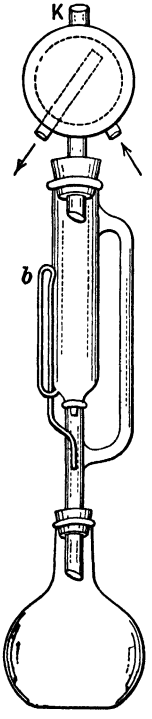


FIG. 56.

The separation of tin from the remaining metals of the group can be illustrated by a practical example.

Analysis of Bronzes

Method I

Bronze is an alloy of tin and copper in varying proportions. It is likely to contain lead, aluminium, iron, manganese, zinc, and phosphorus.

Procedure. — Place 0.5–1 g. of the alloy borings* in a beaker, cover with 6 ml. of nitric acid, *d* 1.5,† add 3 ml. of water, and cover the beaker with a watch-glass. When the reaction begins to diminish, heat the liquid to boiling, until no more brown fumes are evolved, add 50 ml. of boiling water and keep the solution hot for at least 2 hours. Allow the precipitate (containing all the tin, the phosphoric acid, and always small amounts of copper

* The borings are usually somewhat oily, in which case they should be washed with ether that has been distilled over potash, dried at about 80° C., and weighed after cooling in a desiccator. The washing with ether is best accomplished in a Soxhlet's fat-extraction apparatus, as shown in Fig. 56. Place the borings in the extraction-tube, and fill it with ether nearly up to the bend *b* of the siphon-arm. Connect the tube with the condenser *K*. After this add 20 to 30 ml. of ether to the flask and heat gently on the water-bath. The ether vapors pass through the wide side-arm to the condenser *K*, where they are condensed and drop upon the borings. As soon as the ether in the tube has reached the height *b*, it is siphoned back into the flask, where it is again distilled. All the oil will be removed from the borings in from half an hour to an hour.

† See pages 214, 217 and 222.

oxide) to settle. Filter, wash with hot water, ignite in an open porcelain crucible, and weigh. In this way the weight of the $SnO_2 + P_2O_5 +$ foreign oxide is obtained. To obtain the weight of foreign oxide (chiefly copper oxide) fuse the precipitate with a mixture of sodium carbonate and sulfur as described on p. 215. Filter off the sulfides remaining after the solution of the melt in hot water, and convert into oxides by ignition in the air and weigh. By subtracting this weight from that previously obtained, the weight of $SnO_2 + P_2O_5$ is obtained. To obtain the weight of the SnO_2 analyze a separate portion for phosphoric acid (see below), and subtract the weight of phosphoric anhydride from the weight of $SnO_2 + P_2O_5$.

Dissolve the oxides obtained by the ignition of the insoluble sulfides in a little nitric acid (in case Fe_2O_3 is present a little hydrochloric acid is also necessary) and add the solution of the nitrates to the first filtrate from the impure metastannic acid. To this solution add an excess of dilute sulfuric acid and evaporate on the water-bath as far as possible. Then heat over a free flame until dense, white fumes of sulfuric acid are evolved. After cooling, add 50 ml. of water and 20 ml. of alcohol, filter off the precipitate of lead sulfate and determine its weight as described on p. 177. Heat the filtrate from the lead sulfate to remove the alcohol, precipitate copper by means of hydrogen sulfide and weigh as Cu_2S according to p. 184. In the filtrate from the copper sulfide the iron, aluminium, and zinc (also manganese) will be found. Evaporate to a small volume in order to expel the hydrogen sulfide, oxidize by the addition of concentrated nitric acid, and separate the iron and aluminium from zinc by means of a double precipitation with ammonia,* whereby the iron and aluminium are left behind as hydroxides and are analyzed according to p. 109. Precipitate the zinc in the filtrate after acidifying with acetic acid, by passing hydrogen sulfide into the boiling solution. Filter off the precipitated zinc sulfide, dissolve in hydrochloric acid, evaporate to dryness in a weighed platinum dish, and transform to oxide by heating with mercuric oxide by Volhard's method (cf. p. 143).

For the phosphorus determination Oettel† recommends the following procedure: Dissolve 2–5 g. of the substance as before, in nitric acid, filter off the impure metastannic acid with all the phosphorus, dry, and

* If considerable zinc is present, the above separation is inexact. In this case treat the filtrate from the copper sulfide with sodium acetate, heat to 60°, saturate with hydrogen sulfide, and determine iron and aluminium in the filtrate, and zinc in the precipitate. If manganese is present in the alloy, separate it from iron and aluminium as described on pp. 153 to 159.

† *Chem. Zeitung*, **1896**, 19.

transfer as completely as possible to a porcelain crucible. Add the ash of the filter and ignite the contents of the crucible. After cooling, mix the substance with three times as much solid potassium cyanide, cover the crucible, and fuse the contents; the stannic oxide is reduced to metal, $SnO_2 + 2\,KCN = 2\,KCNO + Sn$, while the phosphoric acid is converted into potassium phosphate.

By skilfully rotating the crucible during the fusion, it is possible to unite the small particles of molten tin into a larger button whereby the subsequent filtration is greatly facilitated. After cooling, treat the melt with water and filter. Under a good hood, cautiously add hydrochloric acid to the filtrate and boil to remove the hydrocyanic acid. Then saturate with hydrogen sulfide to remove traces of copper and tin which almost always remain in the solution. Free the filtrate from hydrogen sulfide by boiling, make ammoniacal, and precipitate the phosphoric acid as magnesium ammonium phosphate by the addition of magnesia mixture. After standing for twelve hours, filter off, wash with 1.5 *N* ammonia water, dry, ignite and weigh as $Mg_2P_2O_7$.

Ordinary bronzes may be analyzed satisfactorily in the following manner: Treat the alloy with nitric acid as described above, remove the metastannic acid by filtration and electrolyze the filtrate, using a dull platinum dish as cathode, and a plate as anode, both of which are weighed. Carry out the electrolysis with a current of 1 to 1.2 amperes at about 60°, and at the end of two and one-half to three hours wash the electrodes without breaking the circuit. On the anode will be found all the lead as PbO_2 and on the cathode will be found the copper. The siphoned solution contains the iron, aluminium and zinc, which are determined as above. Determine the phosphorus in another sample.

Remark. — The method just outlined will give exact results only when the metastannic acid is purified and the recovered solution of copper and lead nitrates added to the main solution. In the electrolysis, the chief dangers to be feared are having the solution so acid that the copper is not all precipitated, or so dilute that a spongy deposit is obtained.

Method II

An excellent method for the analysis of phosphor bronze consists in dissolving the alloy as described under Tin, Method III, p. 217, and determining the tin as there described. Determine the copper and lead in the nitric acid solution by electrolysis as described above.

For the phosphorus determination,* weigh out 1 g. of the borings into a small beaker and dissolve in 20 ml. of aqua regia, made by mixing equal volumes of the concentrated acids just previous to use. Cover

* Cf. Dudley and Pease, *Eng. and R. R. Journ.*, March, 1894.

the beaker with a watch-glass, and, after solution is complete, heat nearly to boiling. Cool, add 25 ml. of water and then just sufficient 15 *N* ammonia to redissolve the copper hydroxide * and to produce a deep, blue colored solution; then add 50 ml. of colorless ammonium sulfide solution. This should be enough to precipitate the sulfides, and the supernatant liquid should show no blue color. If it does, more ammonium sulfide must be added. Digest the solution at a temperature near the boiling-point for fifteen minutes, allow the precipitated sulfides of copper and lead to settle, and filter into a 300 ml. Erlenmeyer flask, decanting the clear liquid carefully from the precipitate, and finally throwing the precipitate upon the filter. When the filter has drained, return the filter and precipitate to the beaker; add 50 ml. of ammonium sulfide wash water (one part colorless ammonium sulfide to three parts of water), heat the mixture and stir occasionally for ten minutes. Then pour upon another filter, wash with 50 ml. of ammonium sulfide wash water and allow to drain completely. The total volume of the two filtrates should not exceed 250 ml. To the filtrate add 10 ml. of magnesia mixture and shake the solution. Place the flask in ice water and allow to stand with occasional shaking for two hours. Filter the precipitate of magnesium ammonium phosphate upon a small filter and wash with 1.5 *N* ammonia until nearly free from sulfide. Place 10 ml. of 2 *N* hydrochloric acid in the flask, taking care that all of the precipitate adhering to the walls of the flask is dissolved, and pour the resulting solution through the filter, allowing the filtrate to run into a 100 ml. beaker. Wash the flask and filter with 10 ml. more of the same acid. To the solution add 3 ml. of magnesia mixture, heat to boiling, remove from the flame, and then add 6 *N* ammonium hydroxide solution until the latter is present in large excess. Allow the solution to stand in ice water for two hours, and stir occasionally. Filter and wash the precipitate with 1.5 *N* ammonium hydroxide, until free from chlorides, and ignite with the usual precautions, weighing as $Mg_2P_2O_7$.

Lundell-Hoffman Method for Determining Phosphorus in Bronze†

Weigh out 1–3 g. of sample into a 300 ml. Erlenmeyer flask and dissolve in 20 ml. of aqua regia. When all the metal has dissolved add 10 ml. of water and digest at 90° for 10 minutes. Dilute to 50 ml. and treat with 100 ml. of ammonium molybdate prepared as recommended by Blair (see Index).

* A precipitate of lead or tin hydroxide remains insoluble.

† *Ind. Eng. Chem.*, 15, 172 (1923).

Stopper the flask with a rubber stopper and shake for 10 minutes, occasionally removing the stopper. Allow to stand 4 hours or longer before filtering. Filter, keeping as much as possible of the precipitate in the flask. Wash the precipitate 5 times by decantation with 10 ml. portions of 1 per cent nitric acid.

Dissolve the precipitate on the filter by adding 7.5 *N* ammonium hydroxide to which 2 g. of citric acid have been added. Pour this on the filter in small portions and catch the filtrate in the original flask containing the bulk of the precipitate. Do not use more than 50 ml. of the ammonium hydroxide. Warm the solution slightly to dissolve the precipitate, replace under the funnel and wash the filter with a little hot 5 per cent hydrochloric acid. If the ammoniacal filtrate is not clear at this stage, filter through the same filter and wash the filter with hot water.

Make the solution acid with hydrochloric acid and without regard to a slight precipitate of molybdic acid, which, however, seldom forms in the analysis of alloys with low phosphorus, add 20 ml. of magnesia mixture (p. 201). Heat to boiling and slowly add ammonium hydroxide till a precipitate forms or the solution is ammoniacal. Finally add enough 15 *N* ammonium hydroxide to make the solution 1.5 *N* with ammonia and allow to stand 4 hours. Filter, wash with cold 1.5 *N* ammonium hydroxide, ignite carefully in a porcelain crucible and weigh as $Mg_2P_2O_7$.

SEPARATION OF THE SULFO-ACIDS FROM ONE ANOTHER

1. Arsenic from Antimony

(*a*) *Method of Bunsen**

Principle. — If a slightly acid solution of an alkali arsenate and antimonate is treated with hydrogen sulfide in the cold and the excess of the latter immediately removed by conducting air through the solution, the antimony is quantitatively precipitated as pentasulfide, while the arsenic remains in solution.

Procedure. — The arsenic and antimony are assumed to be present in the tervalent condition. Precipitate both elements by hydrogen sulfide, filter, and wash with water. Transfer the greater part of the precipitate by means of a spatula to a 200-ml. porcelain casserole, and dissolve the precipitate remaining on the filter by dropping hot, dilute potassium hydroxide solution upon it, catching the filtrate in the casserole. 3–5 g. of pure solid caustic alkali should be used.†

Cover the casserole with a perforated watch-glass, place upon the

* *Ann. Chem. Pharm.*, **192**, 305.

† If alkaline earths were the only metals present besides the arsenic and antimony, the first precipitation with hydrogen sulfide can be omitted.

water-bath, and conduct chlorine into the solution until all the hydroxide is decomposed; this takes from one-half to three-quarters of an hour. By this operation the arsenite and antimonite are oxidized to arsenate and antimonate and a small amount of potassium chlorate is formed. Add concentrated hydrochloric acid to the warm solution, drop by drop from a pipet, until all the chlorate is decomposed and no more chlorine is evolved. Remove the watch-glass, evaporate the solution to half its volume, and add then an equal volume of concentrated hydrochloric acid. Again evaporate the solution to half its volume. Transfer the contents of the casserole by means of dilute hydrochloric acid to a large beaker, dilute with water to a volume of 600 ml. and for every decigram or less of the antimony add 100 ml. of freshly-prepared hydrogen sulfide water. An orange precipitate of antimony pentasulfide is formed. Pass a strong current of air (filtered through a wad of cotton) through the solution without delay until the excess of hydrogen sulfide is completely removed; this usually requires about twenty minutes. To avoid loss during this operation a large beaker should be used to contain the solution and it should be covered with a perforated watch glass. The precipitate of antimony pentasulfide is likely to contain traces of arsenic pentasulfide. Dissolve it once more in caustic potash and repeat the above operation. The precipitate now obtained will be pure antimony pentasulfide. Filter into a Gooch crucible, dry at 280° in a stream of carbon dioxide as described under antimony, and weigh as Sb_2S_3.*

For the arsenic determination, concentrate the combined filtrates somewhat by evaporation, add a few drops of chlorine water and pass hydrogen sulfide into the warm solution (kept on the water-bath) for from six to eight hours. Allow the solution to cool in a rapid stream of hydrogen sulfide. After the precipitate has stood for twenty-four hours, filter into a Gooch crucible, wash with water and then with hot alcohol (cf. p. 200). After drying at 110° weigh as As_2S_5.

Remark. — If the solution does not contain a large excess of hydrogen sulfide, the precipitate will always contain trisulfide, so that it is safer to dissolve it in ammoniacal hydrogen peroxide† and then to precipitate the arsenic with magnesia

* Bunsen weighed the antimony as pentasulfide after washing with carbon bisulfide. As, however, antimony pentasulfide is likely to be changed to the trisulfide on treating with carbon bisulfide, the above procedure is better. According to Braun, Sb_2S_3 is reduced to Sb_2S_2 on long-continued treatment with CS_2.

† For this purpose place as much of the precipitate as possible in a beaker, dissolve the precipitate adhering to the filter in hot 2 *N* ammonia catching the filtrate in the same beaker. Heat this until the precipitate dissolves. Then, for every 0.1 g. of As_2S_5, add 30–50 ml. of pure 3 per cent H_2O_2, heat the solution for some time on the water-bath and boil ten minutes.

mixture as magnesium ammonium arsenate, as described on p. 201, weighing it as $Mg_2As_2O_7$.

Remark. — The method gives very accurate results, but consumes considerable time.

(*b*) *Method of Fred Neher**

This excellent method depends upon the fact that quinquevalent arsenic is precipitated from a solution strongly acid with hydrochloric acid by a rapid stream of hydrogen sulfide, while antimony is not.

Procedure. — Starting with a precipitate consisting of the trisulfides of arsenic and antimony, dissolve this in caustic potash solution and oxidize exactly as described under the previous method. When free from chlorate, wash the acid solution into an Erlenmeyer flask and cool by surrounding the flask with ice. In another flask likewise cool some 12 *N* hydrochloric acid. When both solutions are at 0°, dilute the arsenic-antimony solution with twice its volume of the strong hydrochloric acid. Into this cold solution pass a rapid stream of hydrogen sulfide for 90 minutes. Stopper the flask and allow to stand an hour or more before filtering off the As_2S_5 through a Gooch crucible. Wash the precipitate with 4 *N* hydrochloric acid until 1 ml. of the filtrate after being considerably diluted with water and tested with hydrogen sulfide shows no precipitation. Then wash with water, and finally with hot alcohol. After drying at 110° C., weigh the precipitate as As_2S_5.†

Dilute the filtrate from the arsenic sulfide with about four times as much water and saturate with hydrogen sulfide. Filter off the Sb_2S_5 into a Gooch crucible, dry at 280° C. in a current of carbon dioxide and weigh as Sb_2S_3 (p. 209).

(*c*) *The Tartaric Acid Method*

Principle. — The separation is based upon the fact that if magnesia mixture is added to a solution of an alkali arsenate and antimonate containing tartaric acid, only arsenic will be precipitated.

Procedure. — Oxidize the solution obtained by dissolving the sulfides in aqueous caustic potash as described under (*a*). Make acid with hydrochloric acid and add 3 g. of tartaric acid. Add an excess of

* *Z. anal. Chem.*, **32**, 45.

† If the solution was not cold, some arsenic trisulfide will be found in the precipitate. The results are scarcely affected, however, when the precipitate is merely washed with water and alcohol, because the free sulfur is weighed with the sulfide of arsenic. If, however, the precipitate is washed with CS_2, it is evident that the results will be too low. For the highest degree of accuracy, it is advisable to dissolve the precipitated sulfide in ammoniacal hydrogen peroxide, or in fuming nitric acid, and to determine the arsenic as $Mg_2As_2O_7$ as described on page 201.

ammonia; if a precipitate forms, it shows that an insufficient amount of tartaric acid is present. In this case decant off the clear solution, dissolve the precipitate by warming with tartaric acid, and mix the two solutions. To the clear, ammoniacal solution, add magnesia mixture (cf. p. 201, foot-note) slowly with constant stirring. After standing twelve hours, filter off the precipitate of magnesium ammonium arsenate (it usually contains a little basic magnesium tartrate), and wash a few times with 1.5 *N* ammonia. Dissolve the precipitate in hydrochloric acid, heat to boiling and reprecipitate by the addition of an excess of ammonia. After standing for twelve hours more, filter off the precipitate, wash with 1.5 *N* ammonia, and weigh as magnesium pyroarsenate as described on p. 201.

Remark. — Arsenic can also be separated from tin according to the above method, except that more tartaric acid is necessary to prevent the precipitation of the tin than is the case when antimony alone is present (cf. p. 235).

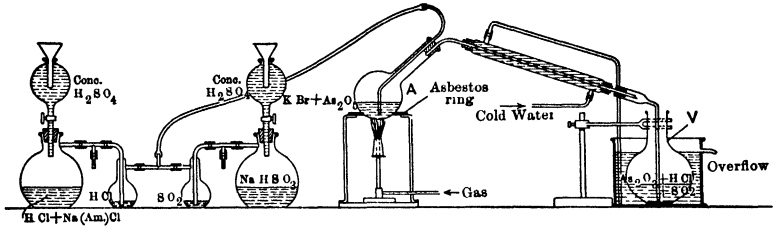


FIG. 57

(*d*) *Method of E. Fischer**

Principle. — This separation depends upon the ready volatility of arsenic trichloride in a current of hot hydrochloric acid gas, under which conditions antimony chloride is not volatile if the temperature is kept below 105°. If the arsenic is present as arsenic acid, which is usually the case, the distillation must take place in the presence of some reducing agent.†

Procedure. — Use the apparatus shown in Fig. 57 for this determination. In the course of analysis, the arsenic and antimony, as a rule, are obtained first as sulfides, and these should be dissolved, as described under (*a*), in caustic potash solution and oxidized by chlorine. Instead of using chlorine, the alkaline solution may be boiled with hydrogen peroxide or potassium percarbonate. If the latter method is used for

* *Z. anal. Chem.*, **21**, 266. The process as described is the modification of M. Rohmer, *Ber.*, **34**, 33 and 1565 (1901).

† Fischer used a ferrous salt, O. Piloty and A. Stock used hydrogen sulfide (*Ber.*, **30**, 1649), and Friedheim and Michaelis used methyl alcohol (*Ber.*, **28**, 1414).

the oxidation, the boiling must be continued until there is no further evolution of oxygen.

Transfer the oxidized solution, by means of a long-stemmed funnel, to the 500-ml. distilling flask, *A*, in which has been placed 1.5 g. of potassium bromide.* Dilute the solution in the flask with 12 *N* hydrochloric acid to a volume of about 200 ml. The receiver, *V*, consists of a large flask of from 1.5–2 liters capacity; keep it cold by circulating a stream of cold water. At the start place 800 ml. of cold water in the beaker and during the analysis keep cold water running through the condenser and have it overflow into the beaker containing the receiving flask. With the apparatus all connected as shown in the drawing, heat the distilling flask and distil in a current of hydrogen chloride,† meanwhile constantly passing a little sulfur dioxide into the flask. At the end of about forty-five minutes, when the volume of liquid in *A* is reduced to about 40 ml., remove the flame and disconnect the T-tube between the two evolution flasks in order to prevent liquid from backing up into the wash bottles. Rinse off the adapter tube which connects the condenser with the receiver and remove the latter.

Place another receiver at the end of the apparatus and make a second distillation to make sure that all of the arsenic has been volatilized.‡ Then, for the determination of the arsenic, dilute the contents of the two receivers with hot water to a volume of about 1250 ml., and remove the excess of sulfurous acid by heating to boiling and passing a stream of carbon dioxide through the liquid as is shown in Fig. 58. When the sulfur dioxide has all been expelled (as can be shown by inserting a stopper with delivery tube into the flask so that the escaping vapors can be led into a dilute sulfuric acid solution of decinormal permanganate which will be decolorized by sulfur dioxide), allow the solution to cool and determine the arsenic as trisulfide according to the directions on p. 200, or titrate the arsenic with iodine.

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* Instead of the potassium bromide, hydrogen bromide may be used which has previously been prepared by treating 1 g. of bromine with sulfurous acid. It is not permissible to introduce the bromine into the flask, *A*, and convert it there to hydrogen bromide by introducing sulfur dioxide gas into the flask, because it is then possible for bromine vapors to get into the receiver by means of the air which is first expelled from the apparatus, and the bromine would oxidize the volatilized $AsCl_3$, and thus interfere with the subsequent determination of the arsenic by precipitation as the trisulfide, or by titration.

† If there is any tendency to suck back, a little more sulfur dioxide should be introduced.

‡ Rohmer found that as much as 0.15 g. arsenic was volatilized completely by one distillation.

To accomplish the titration, add 3 drops of phenolphthalein indicator solution to the solution and add solid potassium hydroxide until a permanent pink color is imparted to the liquid. Then decolorize the solution by a few drops of hydrochloric acid, add 5 g. of sodium bicarbonate, and titrate with decinormal iodine solution as described in Part II.*

Determine the antimony by treating the contents of the distilling flask with 2 or 3 g. of tartaric acid, washing the solution into an Erlenmeyer flask, expelling the sulfur dioxide as above,† and determining the antimony gravimetrically by precipitating as the trisulfide according to the directions on p. 209, or volumetrically by titration with iodine as described in Part II.

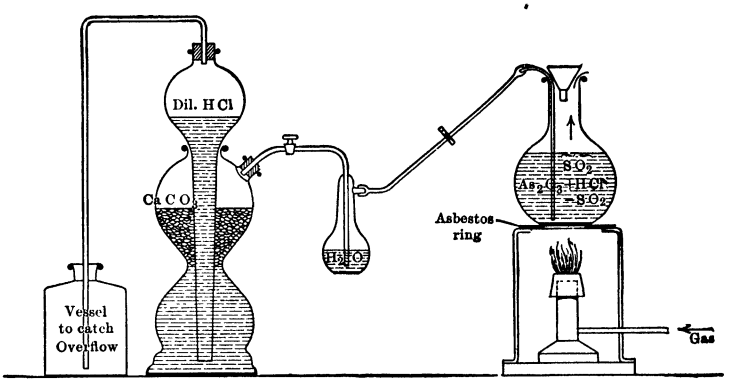


FIG. 58.

Determination of Arsenic in Commercial Sulfuric Acid

To about 30 ml. of concentrated hydrochloric acid and a little potassium bromide, or hydrogen bromide in the distilling flask *A* (Fig. 57), add 50–100 g. of the acid to be tested (determine the weight by weighing a flask before and after adding the acid) through a funnel that is fastened by means of rubber tubing to the upper end of the delivery tube which enters the flask.‡ Rinse out the funnel with concentrated hydrochloric acid, and begin distilling.

* A blank determination should be made with all the reagents that are used, and the iodine solution must be standardized in a solution as dilute as that in which the analysis is made.

† The escaping gas will not decolorize a solution of 2–3 ml. dilute sulfuric acid and one drop of 0.01N. $KMnO_4$, when all the SO_2 is expelled.

‡ When the concentrated sulfuric acid runs into the flask, it often happens that distillation begins to take place and some of the arsenic would be lost if the flask, *A*, were left open.

When the contents of the distilling flask have been concentrated so that only the original volume of the concentrated sulfuric acid remains, keep the acid hot by means of a small flame until all of the arsenic has been expelled. On account of the high temperature, 1 g. of arsenic will be driven over in about fifteen minutes. Finish the analysis as described above.

Separation of Antimony from Tin

(*a*) *F. W. Clarke's Method,* Modified*

Of all the known methods for the separation of antimony from tin, this is probably the most accurate. It depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid, while stannic tin is not. Stannous sulfide, however, is decomposed by oxalic acid, forming an insoluble crystalline stannous oxalate, so that the tin must be in the stannic form.

Procedure. — In most cases it is a question of separating antimony from tin after these metals have been separated from the members of the copper group by means of alkali polysulfide; *i.e.*, the tin and the antimony are in the form of their soluble thio-salts.

To the solution of the thio-salts in a 500-ml. beaker containing not more than 0.3 g. of the two metals, add an aqueous solution of 6 g. of the purest caustic potash (one-third the sum of the weights of tartaric and oxalic acids to be added) and 3 g. of tartaric acid (ten times the maximum weight of the two metals). To this mixture slowly add perhydrol until the yellow solution is completely decolorized; then add 1 ml. in excess and boil the solution for a few minutes to change any thiosulfate to sulfate and to decompose the greater part of the excess peroxide. As soon as the evolution of oxygen ceases, cool the solution somewhat, cover the beaker with a watch-glass, and cautiously add a hot solution of 15 g. pure recrystallized oxalic acid (5 g. for 0.1 g. of the mixed metals). This causes the evolution of considerable gas ($CO_2 + O_2$). Now, in order to remove all of the excess hydrogen peroxide, boil the solution vigorously for ten minutes. The volume of the liquid should amount to from 80–100 ml. After this, introduce a rapid stream of hydrogen sulfide into the boiling solution; for some time there will be no precipitation, but only a white turbidity formed. After five or ten minutes the solution becomes orange-colored and the antimony begins to precipitate; from this point take the time. At the end of fifteen minutes dilute the solution with hot water to a volume of 250 ml., at the end of another fifteen minutes remove the flame, and ten minutes later stop the current of hydrogen sulfide. Filter off the

* *Chem. News*, **21**, 124. Cf. also Rössing, *Z. anal. Chem.*, **41**, 1. F. Henz, *Z. anorg. Chem.*, **37**, 18 (1903). Vortmann and Metzl, *Z. anal. Chem.*, **44**, 525 (1905).

precipitated antimony pentasulfide through a Gooch crucible which, before weighing and after drying, has been heated in a stream of carbon dioxide at 300° for at least one hour. Wash the precipitate twice by decantation with 1 per cent oxalic acid and twice with very dilute acetic acid before bringing it in the crucible. Both of these wash liquids should be boiling hot and saturated with hydrogen sulfide. Weigh the Sb_2S_3 after the treatment described on p. 209.

To determine the tin, evaporate the filtrate to a volume of about 150 ml., nearly neutralize the excess of oxalic acid with potassium hydroxide and deposit the tin electrolytically as described on p. 219.

According to Vortmann and Metzl,* antimony may be separated from tin by passing hydrogen sulfide into a solution containing hydrochloric and phosphoric acids of the proper concentration.

(*b*) *Method of H. Rose*

Principle. — This method is based upon the insolubility of sodium metantimonate and the solubility of sodium stannate in dilute alcohol.

Procedure. — Both metals are assumed to be present in the form of an alloy. Treat the alloy with nitric acid as already described (cf. pp. 214, 217, and 220). Filter off the residue, wash with ammonium nitrate water, dry and transfer as completely as possible to a large silver crucible. Add the ash of the filter, and gently ignite the precipitate. Fuse the oxides with 10–12 times as much solid sodium hydroxide and a little sodium nitrate, or sodium peroxide, placing the silver crucible within a larger porcelain one in order to protect it from the flame. Keep the contents of the crucible liquid for twenty minutes. Cool, place the crucible in a large porcelain dish and treat its contents with hot water until the melt has disintegrated, leaving the insoluble part in the form of a fine meal. Now add one-third of the solution's volume of alcohol (*d.* 0.833) and stir the mixture well. Filter after standing twelve hours. Wash the residue remaining on the sides of the dish onto the filter with dilute alcohol (1 vol. alcohol + 2 vols. water). Wash the sodium metantimonate precipitate with diluted alcohol containing a few drops of sodium carbonate solution as follows: First with a mixture of 1 vol. alcohol + 2 vols. water, then with 1 vol. alcohol + 1 vol. water, and finally with 3 vols. alcohol + 1 vol. water. Continue washing until the filtrate when acidified with hydrochloric acid and tested with hydrogen sulfide no longer gives a yellow coloration (tin sulfide).

If considerable tin and little antimony were originally present, a single fusion of the oxides with caustic soda does not afford a complete

* *Z. anal. Chem.*, **44**, 533 (1905).

separation, as the residue of sodium metantimonate always contains some tin. Dry the precipitate, therefore, separate it from the filter and place in a silver crucible. Treat the filter repeatedly in a *porcelain* crucible with fuming nitric acid until the paper is completely destroyed and then remove the excess of acid by heating in an air-bath. Dissolve the contents of the porcelain crucible in a little caustic soda solution and wash into the silver crucible. Remove the water by heating the silver crucible at first on the water-bath and finally in an air-bath, add 10 g. of solid caustic soda. Fuse the mixture and treat the melt in the same way as before.

The second residue of sodium metantimonate is free from tin. Dissolve it off the filter by a mixture of equal volumes 2.5 *N* hydrochloric and 7.5 per cent tartaric acids, in which it is readily soluble. From this solution precipitate the antimony by hydrogen sulfide and determine as described on p. 209. For the tin determination, gently heat the alcoholic filtrate to remove the alcohol, acidify slightly with hydrochloric acid, and precipitate the tin as sulfide by hydrogen sulfide and determine according to p. 218, β.

Remark. — If the oxide residue which was first fused with sodium hydroxide and nitrate consisted solely of tin and antimony oxides, this method gives very good results. As a rule, however, most antimony and tin alloys contain lead and other metals whose oxides remain to some extent with the tin and antimony on treatment of the alloy with nitric acid, so that the sodium metantimonate is subsequently rendered impure by the presence of these metals. The antimony determination therefore gives too high results. In this case the method of W. Hampe* should be used.

Dissolve the alloy in aqua regia (as described below in the analysis of bearing metal) and separate the tin and antimony from the remaining metals by means of colorless sodium sulfide. From the solution of the thio-salts precipitate the tin and antimony by making barely acid with dilute sulfuric acid. Wash the precipitate and dissolve in a little warm sodium sulfide solution. After cooling, add sodium peroxide in small amounts to the concentrated solution until the liquid becomes colorless, and when treated with more sodium peroxide a distinct evolution of oxygen takes place. By this treatment sodium antimonate is formed; this separates out to some extent, but the tin remains in solution. To completely precipitate the antimony from the solution, add one-third as much alcohol (*d.* 0.833), filter off the precipitate and treat as above described.

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* *Chem. Ztg.*, **18**, 1900.

Analysis of Bearing Metal

This alloy contains tin, antimony, lead, a little copper and usually small amounts of iron, bismuth and zinc.

Treat 1 g. of thin borings in a small beaker with about 15 ml. of 12 *N* hydrochloric acid to which 3 ml. of concentrated nitric acid has been added. Add the acid slowly, a few drops at a time. If the alloy is rich in lead it is necessary to heat on the water-bath for some time, replacing the acid lost by evaporation. When the metal has dissolved, dilute the solution (it should be yellow, or greenish yellow if much copper is present) with 15 times as much alcohol, added in small portions with constant stirring. This stirring is indispensable because lead chloride separates out very slowly from a supersaturated alcoholic solution containing other chlorides. The complete precipitation is best recognized by the fact that no mark is left upon the sides of the beaker when the stirring rod is rubbed against it.

After standing for twelve hours, with frequent stirring, filter off the precipitated lead chloride into a weighed Gooch crucible, wash with absolute alcohol, dry at 150° and weigh. In the filtrate will be found a few milligrams of lead in the presence of antimony, tin, copper, bismuth, iron and zinc.* Pour the alcoholic filtrate into a large, deep porcelain dish† and evaporate off the alcohol at as low a temperature as possible. It is necessary to avoid evaporating the solution to dryness as in that case some $SnCl_4$ will be volatilized. When the alcohol is all gone, add 0.1 g. of potassium chlorate, evaporate the solution to a small volume and add 1 g. of tartaric acid and enough caustic potash to make the solution barely alkaline. Now add, dropwise, as recommended by Finkener, a freshly-prepared hydrogen sulfide water until no further precipitation takes place. In this way all the Cu, Bi, Fe, Zn and the last of the Pb are precipitated as sulfides (precipitate *a*) while all the Sn and Sb remain in solution (solution *b*).‡

Treatment of Precipitate a

Filter off the precipitate, wash with hydrogen sulfide water, dissolve in 6 *N* nitric acid and evaporate with hydrochloric acid to remove

* Alloys low in lead are not treated with alcohol in this way. In such cases it is best to decompose the alloy with chlorine gas, as described in the analysis of tetrahedrite on page 317 or to proceed as in the analysis of bronze, page 223.

† In evaporating off the alcohol there is a tendency for the solution to creep over the edges of the dish so that it is advisable to employ a deep dish and to evaporate the liquid in small portions.

‡ The separation is complete only when all the tin is in the quadrivalent condition. In driving off the alcohol there is always some stannous chloride formed which must be subsequently oxidized by means of $KClO_3$ and HCl.

the nitric acid. Dilute the solution of chlorides until it is only 0.3 *N* in acid. Precipitate the Cu, Pb, and Bi as sulfides by hydrogen sulfide, filter and wash with water containing H_2S. The filtrate contains the iron and zinc (Filtrate *c*).

Dissolve this last precipitate in nitric acid, evaporate with the addition of 4 or 5 drops of concentrated sulfuric acid, and determine the last of the lead as sulfate according to p. 177. From this filtrate precipitate bismuth with an excess of ammonia and determine as Bi_2O_3 according to p. 181.

In the ammoniacal filtrate from the bismuth precipitation, determine the copper electrolytically, after acidifying with sulfuric acid, according to p. 187, or as cuprous sulfide, according to p. 184.

To determine the iron and zinc, oxidize the *Filtrate c* by boiling with a little concentrated HNO_3, precipitate the iron by an excess of ammonia and weigh as Fe_2O_3, p. 94. Determine the zinc in this last filtrate by acidifying with acetic acid, precipitating as sulfide and weighing as such, according to p. 145.

Treatment of Solution b

To determine the antimony and tin, dilute the alkaline solution to exactly 250 ml. in a measuring flask, and after thoroughly mixing, withdraw 100 ml. in a pipet, transfer to a 400-ml. beaker, acidify with acetic acid, and boil to expel the hydrogen sulfide. Then add 3 g. of tartaric acid and 6 g. of purest potassium hydroxide, whereby any precipitated sulfide is redissolved. At this point add perhydrol as described on p. 230 and separate the antimony and tin.

Separation of Arsenic from Tin and Antimony

(*a*) *Method of Fred. Neher**

Dissolve the moist sulfides in freshly-prepared ammonium sulfide, evaporate nearly to dryness in an Erlenmeyer flask and oxidize with hydrochloric acid and potassium chlorate. From this solution precipitate the arsenic as sulfide under the conditions described on p. 200. In the filtrate from the arsenic pentasulfide all of the tin is found and can be precipitated as sulfide after diluting largely with water and passing in hydrogen sulfide. Ignite and change to the oxide as described on p. 218, β.

(*b*) *Method of W. Hampe*†

Dissolve the precipitated sulfides, as soon as possible after filtering and washing, in freshly-prepared ammonium sulfide, evaporate the

* *Z. anal. Chem* (1893), **32**, 45.

† *Chem. Ztg.* (1894), **18**, p. 1900.

solution nearly to dryness and oxidize with hydrochloric acid and potassium chlorate in a flask connected with a return-flow condenser.* Add tartaric acid and ammonia and precipitate the arsenic with magnesia mixture as magnesium ammonium arsenate, according to p. 201. After standing twelve hours, filter off the precipitate, wash with 1.5 *N* ammonia, and, in order to remove a little magnesia, dissolve the precipitate in hydrochloric acid and reprecipitate by the addition of ammonia. After standing another twelve hours, filter off the precipitate and again wash with 1.5 *N* ammonia.

This precipitate can be converted into magnesium pyroarsenate and weighed in this form as described on p. 201. The transformation is somewhat tiresome, however, so that Hampe prefers to dissolve the precipitate in hydrochloric acid once more, to precipitate the arsenic by means of hydrogen sulfide, and then to determine the magnesium in the evaporated filtrate as magnesium pyrophosphate according to p. 78 or p. 79.

(*c*) Method of Plato-Hartmann†

In this interesting method the chlorides of arsenic, antimony and tin, in the lower states of oxidation, are heated with a mixture of phosphoric and hydrochloric acids. Arsenous and antimonous chlorides distil by raising the temperature to 165° but stannous chloride forms a complex with phosphoric acid and remains behind. According to Plato, tartaric acid is added to the first distillate and by a second distillation the arsenous chloride is removed. Hartmann prefers to precipitate the arsenic as trisulfide from a solution quite strongly acid and antimony as trisulfide in the partially neutralized filtrate. After the trichlorides of arsenic and antimony have been distilled from the solution containing hydrochloric and phosphoric acids, the tin is volatilized as stannic chloride by the addition of hydrobromic acid. The latter reacts with the hot, concentrated sulfuric acid and is to some extent oxidized into bromine which in turn oxidizes the tin to volatile stannic chloride.

For the distillations, the apparatus shown in Fig. 59 is suitable. On the extreme right of the drawing is shown a Kipp generator for producing carbon dioxide, connected through the wash bottle and the long glass tube to *B* into which acid can be made to drop from the funnel *T*. The lower part of *B* leads almost to the bottom of the flask *A*. The

* So that no arsenic trichloride will be lost by volatilization.

† Plato, *Z. anorg. Chem.*, **68**, 26 (1911); *Z. anal. Chem.*, **50**, 641 (1911); Hartmann, *Z. anal. Chem.*, **58**, 148 (1919).

stopper of the flask is also fitted with a thermometer and a gas exit tube *D*, leading to the condenser *P*, which in turn is connected with the receiver *E*, in which the subsequent precipitation can also take place. The uncondensed vapors pass through the tube *K*, containing glass beads wetted with water, into the tubing *R*, which is connected with the tower *G* containing pieces of marble. In this way the acid vapors are neutralized so as not to be obnoxious.

It is advisable to wind cord around *D* to prevent the vapors being cooled too much by the air; for the same reason the neck of the flask *A* should be covered with asbestos paper.

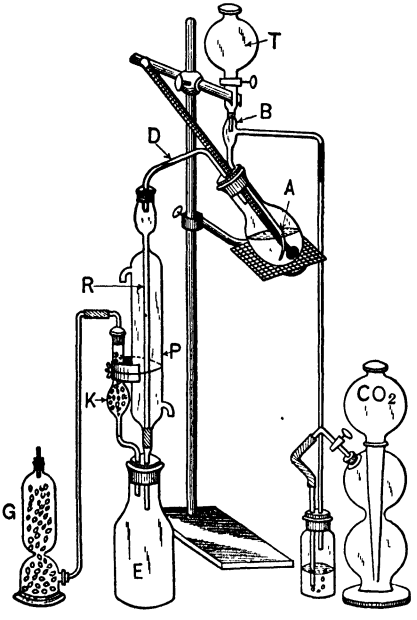


FIG. 59.

Procedure. — In the analysis of an alloy, weigh out 1 g. of the fine borings into the flask *A*, Fig. 59. Add 6 ml. of concentrated sulfuric acid and heat until the alloy is decomposed completely.

To analyze a precipitate of arsenic, antimony and tin sulfides, place the precipitate and filter in the flask and add enough sulfuric acid so that the mass is not quite dry after the carbonization of the filter; continue heating until the sulfuric acid solution is colorless, or a light straw color, and volatilize any sulfur in the neck of the flask by heating carefully with a flame. Evaporate off the excess sulfuric acid, leaving about 6 ml. in the flask. If the carbon of the filter is not oxidized sufficiently, there will be too much foaming during the subsequent distillation.

Cool the contents of the flask and add 7 ml. of aqueous phosphoric acid, *d.* 1.70. Again cool, add 10 ml. of hydrochloric acid, *d.* 1.17 and connect up the apparatus with a little water in the receiver. Start passing a slow stream of carbon dioxide, begin heating the flask, and cause hydrochloric acid, *d.* 1.17 to drop into the flask so that the volume of liquid in the flask does not change much during the distillation. Watch the temperature and keep the thermometer at 155–165°. The arsenic trichloride distils readily but it may take 2 or 3 hours to distil all of the antimony trichloride. To test for antimony, disconnect the

receiver and collect about 20 drops of fresh distillate. To this add a little hydrogen sulfide water and ammonia water to neutralize some of the acid; if no orange precipitate forms, antimony is absent.

When all of the antimony has been volatilized as chloride, stop distilling and disconnect the receiver. Using a fresh receiver, continue the distillation using a mixture of one-fourth pure hydrobromic acid, *d.* 1.40 and three-fourths hydrochloric acid, *d.* 1.17 in the dropping funnel. If bismuth is present, keep the temperature below 145°. Distil until no test for tin is obtained with 1 ml. of distillate. A little sulfur dioxide is always present in the distillate, being formed by the interaction of hydrobromic and sulfuric acids. There is, therefore, always some sulfur precipitated when the H_2S water is added but this milky turbidity can be distinguished from a precipitate of yellow stannic sulfide that forms more quickly. The test is sensitive, but as it takes some time to distil off all of the stannic chloride, the distillation should not be stopped until there is no sign of yellow precipitate in the test.

To determine arsenic in the first distillate, introduce hydrogen sulfide and treat the precipitate of arsenic trisulfide as described on p. 200.

To determine antimony in the filtrate which contains hydrogen sulfide, neutralize with ammonium hydroxide until a permanent precipitate of orange antimony sulfide forms Add a little more ammonium hydroxide, dilute with an equal volume of hot water and saturate with hydrogen sulfide gas. Treat the antimony trisulfide precipitate as directed on p. 209.

To determine tin, take the second distillate, dilute with a little water and add ammonium hydroxide until the stannic hydroxide precipitate does not redissolve well on stirring. Saturate with hydrogen sulfide, allow to stand over night and treat the precipitate as directed on p. 215. It is well to add some filter paper pulp to aid in filtering the stannic sulfide.

Separation of Antimony from Arsenic and Tin

(*a*) *Method of Rose*

Heat the sulfides of arsenic, antimony, and tin with fuming nitric acid in a large covered beaker until the sulfur is completely oxidized, and remove the excess of acid by evaporation on the water-bath. Treat the slightly moist residue with concentrated sodium hydroxide solution and transfer the contents of the dish to a silver crucible. Add a little solid sodium hydroxide and dry the contents of the crucible in an air-bath. Place the silver crucible in a larger porcelain one, heat over a Méker or Teclu burner and keep the contents of the smaller

crucible liquid for about twenty minutes. Cool, extract the melt with water, add one-third as much alcohol (*d.* 0.833) to completely precipitate sodium metantimonate, and after standing twelve hours filter off the precipitate and subject it to the treatment described on p. 232. Make the filtrate containing all the arsenic and tin acid with hydrochloric acid, whereby stannic arsenate is precipitated. Without filtering, conduct hydrogen sulfide into the liquid, filter off the precipitated sulfides of tin and arsenic, oxidize with hydrochloric acid and potassium chlorate, and separate the arsenic from the tin as described on p. 234.

(*b*) *Method of Hampe*

Oxidize the moist sulfides as described on p. 234, *b*, and determine the arsenic in the same way.

In the combined filtrates from the magnesium ammonium arsenate precipitate the antimony and tin by hydrogen sulfide, after making the solution acid. Separate these according to one of the methods already described, cf. p. 230.

SUPPLEMENT TO THE HYDROGEN SULFIDE GROUP

GOLD, PLATINUM, SELENIUM, TELLURIUM, VANADIUM, MOLYBDENUM, TUNGSTEN

GOLD, Au. At. Wt. 197.3

Gold is always determined as the metal itself. There are three cases to distinguish:

1. The gold is present in solution.
2. The gold is alloyed with copper and silver.
3. The gold is present in an ore.

1. Gold is Present in Solution

In most cases gold is deposited as metallic gold from its solutions and weighed after filtering and washing.

For the deposition of gold the following reducing agents can be used; ferrous sulfate, oxalic acid, formaldehyde, and hydrogen peroxide. If the gold is to be precipitated by means of either *ferrous sulfate* or *oxalic acid*, there must be no free nitric acid present in the solution. If some is present, it must be removed by repeated evaporation with concentrated hydrochloric acid and the solution then diluted with water. To this dilute solution add a large excess of clear ferrous sulfate solution, cover the beaker and heat its contents for several hours on the water-bath. Then filter off the precipitate, wash first with water containing hydrochloric acid until the iron is completely removed, and then with pure water. Dry the precipitate, transfer as completely as possible to a porcelain crucible, add the ash of the filter, ignite and weigh the gold. In this way gold can be separated from most metals, even platinum, but not from silver. If silver is present, which is of course never the case in a dilute hydrochloric acid solution, remove it by the addition of hydrochloric acid, filter off the precipitated silver chloride and treat the filtrate as above described.

To precipitate gold by means of *oxalic acid*, dilute the slightly acid solution with water, add an excess of oxalic acid, or ammonium oxalate with a little sulfuric acid, and allow the covered beaker to stand forty-eight hours in a warm place.

Filter off the yellow scales of deposited gold and wash, as above described, with hydrochloric acid and then with water. Ignite and weigh.

Precipitation of Gold by Means of Hydrogen Peroxide
*(L. Vanino and L. Seeman)**

If a gold solution is treated with caustic alkali solution and then with formaldehyde, or, better still, hydrogen peroxide, the gold is soon precipitated quantitatively, even in the cold. By boiling, the finely-divided gold collects together and assumes a reddish-brown color. The reaction takes place according to the following equation:

$$2\,AuCl_3 + 3\,H_2O_2 + 6\,KOH = 6\,KCl + 6\,H_2O + 3\,O_2 + 2\,Au.$$

If the gold is deposited by this method from very dilute solutions it is obtained in such a finely-divided condition that it passes through the filter. If, however, the solution is boiled until the excess of hydrogen peroxide is completely destroyed and it is then acidified with hydrochloric acid, the gold can be readily filtered. Gold can be separated from platinum by this method.

2. The Gold is Alloyed with Silver and some Copper

When gold is present in alloys it is most rapidly and most accurately determined in the dry way. The principle of the method is very simple. Too much copper should not be present as high copper alloys cannot be cupelled.

If a gold-silver alloy is melted in the air with lead upon a " cupel " (a very porous vessel made of bone-ash or magnesia) the lead and copper are oxidized, the oxides fuse and are absorbed by the cupel, while all the gold and silver are left behind in the form of a metallic button, which is weighed. The silver is afterwards separated from the gold by the action of nitric acid which dissolves the silver but leaves the gold behind. If the weight of the gold that is left undissolved is deducted from the weight of the gold-silver button the weight of the silver is obtained.

To obtain accurate results a number of precautions must be taken. By the cupellation of the alloy some noble metal is always lost and the amount lost increases in proportion to the amount of lead used and the higher the temperature. Furthermore, small amounts of the noble metal are absorbed by the cupel and this loss is greater the smaller the quantity of lead used. This second loss amounts to much less than the former one occasioned by the use of too much lead. *Consequently, in every gold cupellation an unnecessary excess of lead must be avoided.*

Experience has shown that the richer a gold-silver alloy is in base metal the more lead is necessary for the cupellation. Furthermore,

* *Ber.*, **32**, p. 1968 (1899).

in the separation or *parting* of gold from silver by means of nitric acid, it is necessary to remember that the separation is only quantitative when the alloy consists of three or more parts of silver to one part of gold. If less than three parts of silver are originally present for one part of gold, it is necessary to add pure silver until this proportion is reached. This operation is known as *quartation* or *inquartation*. If a gold-silver alloy, in the form of foil, consisting of three parts of silver to one of gold, is treated with nitric acid, the latter metal remains behind as a brownish scale; if more silver is present, it is left as a fine powder, unless the acid is extremely dilute.

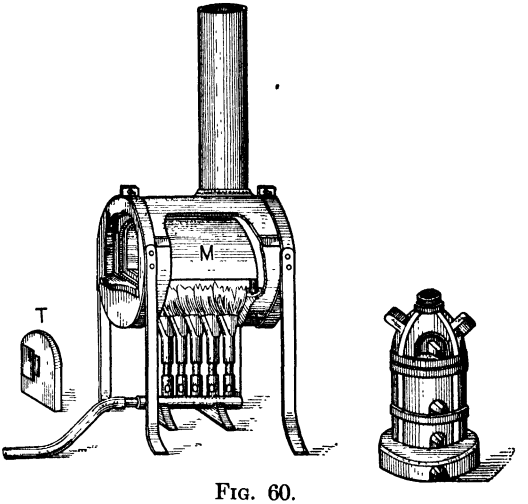


FIG. 60.

From what has been said, it is clear that accurate results can be obtained only when the correct amount of lead is present in the alloy that is cupelled, and when the gold and silver are present in the proper proportion; *i.e.*, it is necessary to know the approximate composition of the alloy before an accurate determination can be made. This is determined by

The Preliminary Assay

For this purpose heat a muffle, Fig. 60, to a cherry-red heat, place a cupel weighing from 6–7 g.* in the back part of it, close the muffle door, and heat the cupel until it has acquired the same color as the muffle. Then place 5 g. of lead upon the cupel, close the muffle until the lead is melted and then, with the aid of tongs, drop into the molten lead 0.25 g. of the accurately-weighed alloy enveloped in a small piece of lead-foil. Close the muffle until the alloy has melted and shows a bright


FIG. 61.

* A good cupel will absorb its own weight of litharge. During the cupellation about one-tenth of the litharge formed is lost by volatilization, so that the weight of litharge absorbed by the cupel is practically that of the original lead button. Fig. 61 represents a cupel, together with its cross-section.

upper surface. With the help of an iron hook, carefully shove the cupel to about the middle of the muffle and leave the door open so that there is a ready access of air into the muffle.

After about 20 minutes the lead will be all absorbed, which is shown by the " blick." The blick is the brightening of the metal which appears when the outer layer of lead oxide that is constantly becoming thinner finally bursts and the bright noble metal shines through. Just before the blick there is a distinct iridescence, so that the point can never be mistaken. At once remove from the muffle and after cooling, observe the color of the button.

(*a*) *If the button is greenish yellow or darker*, it contains less than three parts of silver to one part of gold, in which case add from 4–6 parts of " fine silver " (the proper amount can be usually told by the practised eye) and heat again in a new cupel with 1 g. of lead. Treat the button now obtained with nitric acid and weigh the residual gold.

(*b*) *If the button is pure white*, then three or more parts of silver are present to one part of gold. In this case it is immediately " parted " and the residual gold weighed.

After the approximate amount of gold present has been ascertained,* the analysis proper is made, using the amount of lead as indicated in the following table:

LEAD TABLE

Approximate Percentage of Gold in the Alloy	Amount of Lead Necessary for the Cupellation of 0.25 g. of Alloy
100 per cent	0.25 g.
90 "	2.50 "
80 "	4.00 "
70 "	5.50 "
60 "	6.00 "
50 "	6.50 "
40 or less "	8.50 "

The Final Assay

For the definite determination of the gold and silver, take two portions weighing exactly 0.25 g., the one to serve for the silver determination and the other for the gold. Cupel the former with the cor-

* In assay laboratories the approximate gold contents of the alloy is determined by its streak. A fine-grained piece of silicate is blackened with charcoal. The alloy to be tested is rubbed upon it and the color produced compared with that obtained from alloys containing known amounts of gold. Afterwards these streaks are tested with dilute aqua regia; alloys containing the same amounts of gold are attacked equally readily.

rect amount of lead and determine the weight of the gold-silver button.

If the original alloy was very white, it contains more than 50 per cent (500 thousandths fine) of silver.

If the alloy was greenish yellow, it probably contains 55–75 per cent of noble metal, and silver is present to a considerable extent. If, however, the alloy was a beautiful yellow or reddish yellow, it contains more than 70 per cent of gold.

For a white alloy, therefore, weigh out a quantity of pure silver equal to the weight of gold as indicated by the preliminary assay (inquartated with one part of silver), and cupel this mixture with the same amount of lead as the first portion.

In the case of a greenish yellow alloy, inquartate* with two parts of silver; and for a distinctly yellow or reddish yellow alloy, inquartate with $2\frac{1}{2}$ parts of silver.

Treatment of the Quartered Gold-Silver Button

Remove the gold-silver button from the cupel with the "button tongs," clean with a stiff brush ("button brush"), and hammer upon

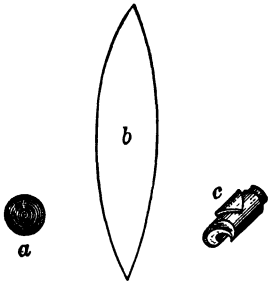


FIG. 62.

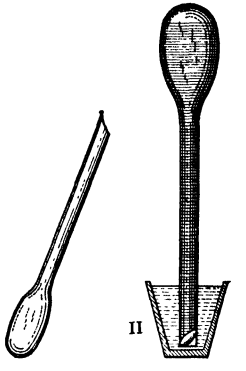


FIG. 63.

an anvil to a round disk about 1 mm. thick (Fig. 61, *a*). Heat this upon a fresh cupel and quickly cool by placing it upon a piece of brass foil and rolling it between two steel rollers to a long strip (Fig. 62, *b*); again heat and roll† up as shown in Fig. 62, *c*. Place this little roll in a small flask (Fig. 63, I), cover with 30–40 ml. of nitric acid (*d*. 1.188)

* Cf. p. 241.

† By hammering the gold-silver alloy, the metal becomes so brittle that it cannot be converted to a smooth-margined roll, and on the subsequent treatment with nitric acid, little pieces would probably drop off. By again heating the metal and then quickly cooling, it regains its original softness.

free from chloride, heat to boiling and keep boiling gently for ten minutes. Pour off the acid, replace by the same quantity of stronger acid (*d.* 1.295) and repeat the above treatment. After this pour off acid and wash the button, decanting three times with distilled water. Fill the flask with water, cover with an annealing cup (or, lacking this, an ordinary porcelain crucible may be used), and quickly invert (Fig. 63, II); the gold will pass into the cup. Remove the flask by first raising its mouth to the level of the water in the crucible and then slide it off at right angles and skilfully turn the flask right side up. Pour off the water from the gold and place the crucible in the back part of the muffle for a short time, whereby the gold is dried and is changed from its former brown and soft condition into a harder, beautiful yellow substance. Cool and weigh. By subtracting the weight of the gold from the weight of the gold and silver together, the amount of silver is obtained.

Determination of Gold in Ores

Principle. — The very finely ground and sifted ore is mixed in a No. 9 French crucible with lead oxide, charcoal, and some suitable slag-forming material. The charcoal reduces a part of the lead oxide to metal which alloys with the noble metal and sinks to the bottom in the form of a button, while the foreign substances pass into the slag. After cooling, break the crucible, hammer off the slag, cupel the lead button, and part the silver-gold button in the same way as before. The noble metal should be extracted with as little lead as possible, for with an unnecessarily large amount of lead some gold is lost during the cupellation.

The amount of lead reduced from the litharge depends largely upon the nature of the ore. Sulfide ores act strongly reducing, as is shown by the following equations:

$$PbS + 2\,PbO = SO_2 + 3\,Pb,$$
$$FeS_2 + 5\,PbO = 2\,SO_2 + FeO + 5\,Pb.$$

In such cases less charcoal (or in some cases none at all) should be added than would be otherwise necessary to produce the right amount of lead. Sometimes, when considerable sulfide is present, it is necessary to neutralize its action by the addition of oxidizing agents.

Reducing ores are recognized by their color: they are gray, bluish-black, or yellow (pyrite, etc.). Reddish-brown ores (Fe_2O_3) usually act oxidizing:

$$Fe_2O_3 + C = CO + 2\,FeO,$$

in which case more charcoal must be added to the charge.

The best results are obtained if the lead button weighs about 18 g. when obtained from 30 g. of ore.* In order that such a button may be obtained, it is usually necessary to make a preliminary assay of the ore. But above all, it is necessary that the purity of the reagents used should be tested.

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* This amount is usually sufficient; with very rich gold ores 10–15 g. is enough, while with very poor ores as much as 120 g. may be used to advantage.

Testing the Reagents

The ordinary reagents necessary for a gold assay are:

1. Litharge (PbO)

Litharge, the most important reagent, is a basic flux, for it forms with the silicic acid of the ore a readily fusible silicate. At the same time, it is a desulfurizing agent, as is shown by the above reaction.

The litharge used must be dry and free from minium, for the latter oxidizes silver, carrying it into the slag, so that low results would be obtained in the silver determination. The litharge should be free from silver (which is almost never the case), or its silver contents must be known; this is determined once for all by the following experiment: Mix 120 g. of litharge, 60 g. of sodium bicarbonate and 2 g. of argols (crude $KHC_4H_4O_6$) upon a sheet of glazed paper and place the mixture in a No. 9 French crucible and cover with a layer of finely-powdered, dry common salt. Place the covered crucible in a hot coke-oven.

As soon as the contents of the crucible have reached the state of quiet fusion, remove the crucible from the fire, gently tap its walls with the tongs, and tap lightly upon its bottom to knock down any small particles of lead adhering to the sides and to make all of the free metal collect together on the bottom in the form of a button.

After cooling break the crucible, remove the slag from the lead button by hammering it upon an anvil, and subject it to cupellation, using a cupel weighing only a few grams more than the button itself. Weigh the resulting silver button and deduct this weight of silver whenever the corresponding amount of litharge is used in an assay.

2. Sodium Bicarbonate ($NaHCO_3$)

3. Anhydrous Borax ($Na_2B_4O_7$)

2 and 3 require no testing.

4. Charcoal

The reducing power is determined as follows: Mix 60 g. of litharge, 15 g. of sodium bicarbonate and 1 g. of charcoal, as in the testing of litharge, in a French crucible No. 9, cover with common salt and fuse. After cooling, determine the weight of the lead button; this expresses in terms of lead the reducing power of the charcoal.

One g. of charcoal should reduce about 30 g. lead.

5. Niter (KNO_3)

serves as an oxidizing agent. Its oxidizing power expressed in terms of lead is determined: Mix 3 g. of niter (potassium nitrate), 60 g. of litharge, 1 g. of charcoal and 15 g. of sodium bicarbonate, fuse as before and determine the weight of the lead button. If under (4) it was found that 1 g. charcoal would reduce P g. lead, and if p g. of lead were obtained in this experiment, then the difference $P - p$ shows the amount of lead that was oxidized by 3 g. niter, or the oxidizing power of the niter.

One g. niter oxidizes about 4 g. lead.

6. Common Salt

Heat table salt in a large Hessian crucible until it melts, and pour the contents of the crucible into a shallow iron mould with a raised edge. Powder and preserve in a stoppered flask.

After the reagents have all been tested the next step is the

Preliminary Assay

Weigh out 5 g. of the finely-powdered and sifted ore and mix with 80 g. of litharge, 20 g. of sodium bicarbonate and 5 g. of borax. Place the mixture in a crucible and cover with a layer of common salt. After fusing, cooling, and hammering off the slag, as already described, weigh the lead button.

Since in an ordinary assay about 30 g. of ore are taken, the weight of the lead button now obtained multiplied by 6 will give the weight of the button from the real assay. Four cases will be considered.

(1) *The lead button weighs* 3 *g.*

A button obtained from 30 g. of ore would weigh 18 g. In this case assay the ore with the following proportions of flux: 80 g. of litharge, 20 g. of sodium bicarbonate and 5 g. of borax.

(2) *The lead button weighs less than* 3 *g.*

Evidently the ore has a slight reducing action, but not enough to yield a button weighing 18 g. when 30 g. of ore are used; it is, therefore, necessary to add charcoal to the flux.

Example. — Assume that the lead button obtained by the preliminary assay weighed 1 g., then the button obtained from 30 g. of ore would weigh 6 g. In order to obtain a button weighing 18 g. it is necessary to add enough charcoal to supply 12 g. of lead. If 1 g. of charcoal was found to reduce 30 g. of lead, then it is necessary to add $12 \div 30$ g. $= 0.4$ g. of charcoal.

(3) *The lead button weighs more than* 3 *g.*

In this case the ore has a strong reducing power, and to obtain the lead button of the right weight it is necessary to add some niter.

Example. — Suppose the button to weigh 6 g.; this would mean a 36-g. button when 30 g. of ore were used; *i.e.*, 18 g. too much lead would be produced. We must add, therefore, enough niter to oxidize this 18 g. of lead. If the oxidizing power of 1 g. of niter was found to be 4 g. of lead, then $18 \div 4 = 4.5$ g. of niter must be added to the flux.

Remark. — Ores which have a very strong reducing power would frequently require the addition of enough niter to cause the contents of the crucible to boil over. In such a case, place 40–50 g. in a " roasting-dish," roast in a muffle, and from this roasted ore take portions for the preliminary and final assays. The results, however, must be expressed in terms of the unroasted ore.

(4) *There is no lead button formed*

The ore is either neutral or possesses an oxidizing action. Repeat the assay using 1 g. of charcoal, and base the final assay from the results now obtained.

Final Assay

For convenience, it is customary to weigh out the ore in *assay ton* units. Ore is usually weighed in avoirdupois tons and gold in troy ounces. The assay report usually gives the ounces troy contained in a ton avoirdupois. Since there are 29,166 troy ounces in an avoirdupois ton, the assay ton is made equal to 29.166 g. Then if one assay ton of ore is used each milligram of gold obtained will represent *one ounce per ton.* For weighing out the ore an inexpensive balance (pulp balance) can be used. It should be capable of taking a load of 200 g. but need not be sensitive to less than 1 mg. For weighing the gold or silver buttons, a *button balance* sensitive to 0.01 mg. should be used.

For the final assay use from 0.1 to 5 assay tons of ore according to the amount of gold present) and the corresponding amount of the various fluxes. Otherwise the procedure is exactly the same as in the preliminary assay. Cupel the lead button and part the weighed silver-gold button as described on p. 243.

PLATINUM, Pt. At. Wt. 195.2

Platinum is best determined as metallic platinum. The following three cases will be considered:

1. The platinum is present in a hydrochloric acid solution either alone or together with other metals, but other platinum metals are absent.

2. The platinum is present alloyed with gold and silver.

3. The platinum is alloyed with small amounts of the platinum metals together with small amounts of base metals.

1. The Platinum is Present in Hydrochloric Acid Solution Either Alone or Together with Other Metals

The platinum is either precipitated from the solution as ammonium chloroplatinate, $(NH_4)_2PtCl_6$, which is decomposed by ignition and the residual platinum weighed; or the platinum is precipitated as metal by the addition of reducing agents to the solution; or finally the platinum is precipitated as sulfide by conducting hydrogen sulfide into the hot solution and changed to platinum by ignition. The two former methods serve to separate platinum from most other metals, while the latter serves to separate platinum only from the metals of the alkali, alkaline earth, and ammonium sulfide groups, and not from members of the hydrogen sulfide group.

(a) *Precipitation of Platinum as Ammonium Chloroplatinate*

Reduce the volume of the solution as much as possible by evaporation, nearly neutralize with ammonia, add an excess of ammonium chloride and considerable alcohol. Allow the mixture to stand twelve hours under a glass bell-jar. Filter through an asbestos filter tube 10–15 cm. long and wash with 80 per cent alcohol until a few drops of the filtrate leave no residue on being evaporated to dryness on a platinum foil. Dry the precipitate by conducting a stream of air, warmed to about 90°, through the tube. After cooling weigh the tube, introduce a plug of ignited asbestos* and again weigh; in this way the weight of the asbestos plug is found. Conduct a stream of dry hydrogen through the tube, and heat the latter carefully until no more hydrochloric acid is evolved and all the ammonium chloride has been driven off; then cool the tube in a desiccator and weigh.

Instead of filtering the precipitate upon asbestos, an unweighed paper-filter may be used. Place the moist precipitate together with the filter in a large porcelain crucible so that the apex of the filter-paper points upward, and heat very carefully, as otherwise there can be a considerable loss by spattering. At first dry the precipitate by gently heating the partly covered and inclined crucible with a tiny flame under the cover until the odor of alcohol has disappeared. Take care not to burn the alcohol. When the alcohol has all evaporated, slowly raise the tempera-

* Ammonium chloroplatinate decrepitates during the heating. To prevent loss of substance heat it between two asbestos plugs.

ture until the crucible is at a strong red heat. During the whole operation there must be no visible escape of vapors from the crucible. The decomposition is complete when there is no longer a penetrating odor arising from the crucible. Now place the crucible in an upright position and ignite with free access of air until the carbon from the filter-paper is completely burned. Often a slight deposit of platinum* will be found in the upper part of the crucible and upon the cover, so that the latter must always be weighed with the crucible.

Remark. — If it seems likely that the precipitate of ammonium chloroplatinate is contaminated with other substances (*e.g.*, sodium chloride, etc.) the precipitate can be dissolved in water after it has been washed with alcohol and dried. The platinum may then be determined, as described on p. 63, by precipitating with mercury, washing with dilute hydrochloric acid and then with water, and finally weighing.

The results obtained by this method are satisfactory but somewhat lower than the true values; the following process is more accurate:

(*b*) *Precipitation of Platinum by Reducing Agents*

Free the solution from any excess of acid by evaporation and transfer to an Erlenmeyer flask the neck of which is ground to fit a return-flow condenser. Neutralize the solution with ammonia, add an excess of formic acid and a little ammonium acetate, dilute to 200 ml. and heat to about 80° C. on the water-bath until the evolution of carbon dioxide has nearly ceased. Now connect the flask with the return-flow condenser, and boil for twenty-four hours. Filter off the precipitated metal, wash with dilute hydrochloric acid, then with water, dry, ignite, and weigh.

Determination of Platinum in Alloys

Platinum is now used a great deal in jewelry and there are so many useful alloys of platinum that the analysis has become of importance. The platinum content is almost always determined by dry assay.

Weigh out 0.1 g. of the alloy and make a trial assay to determine the approximate platinum content. Cupel twice with 1 g. portions of lead at a high temperature (well back in the hot muffle), weigh the resulting button and part with sulfuric acid as described below.

* By means of the dry distillation of the filter, carbon monoxide is formed, and by the decomposition of the ammonium chloroplatinate chlorine is set free. These two gases act upon the metallic platinum and form volatile compounds ($PtCl_2.CO$, $PtCl_2.2\ CO$, and $2\ PtCl_2.3\ CO$), which, however, are later decomposed by the aqueous vapor. This causes the deposit of platinum in the upper part of the crucible. In order to avoid loss, a large crucible should be used.

For the analysis proper, weigh out 0.25 g. of alloy, add 1.25 g. of pure silver and the same quantity of copper. Cupel at a white heat using 15 g. of lead if the alloy is nearly pure platinum and reducing the quantity of lead by 0.15 g. for each per cent of alloyed metal but using at least 2 g.

After the cupellation place the button on a fresh cupel and heat 2–5 minutes in the hottest part of the muffle. Hammer out the button and roll it until it is 0.2 mm. thick. Part the button in a small Jena flask using 20–30 ml. of concentrated sulfuric acid which has been diluted with 22 per cent of water by volume. Heat the metal with the sulfuric acid for 15 minutes at 240°. Nitric acid could not be used for the parting as it dissolves some platinum as well as silver. By boiling platinum with pure concentrated sulfuric acid, 7.7 mg. are dissolved in an hour but the presence of reducing agent prevents the dissolving. By keeping the temperature at 240° there is no appreciable loss of platinum.

After the heating allow the acid to cool, carefully decant off the liquid and repeat the acid treatment twice more. To avoid loss by bumping during the second and third treatments, wind a piece of pumice with platinum wire and drop it into the flask. After the third treatment, decant off the acid and wash the residual platinum twice by decantation with water. During the decantation some platinum always flows off with the liquid. Save the washings, therefore, filter through a small filter, ignite and weigh in a crucible. Transfer the most of the platinum to a porcelain crucible, rinse off the pumice and evaporate off the water. Ignite and weigh.

Separation of Platinum from Gold

Parting with sulfuric acid leaves gold, if present, with the platinum. Parting with nitric acid does not dissolve platinum in the absence of silver but if three parts by weight of silver are present for each part of gold and platinum, the last metal gradually dissolves.

Procedure. — Cupel the platinum-gold button, obtained by the above method of assaying, with three times its weight of pure silver and 1 g. of lead. Hammer and roll the resulting button and part with 6 *N* nitric acid. Weigh the button, inquartate with 3 parts of silver and again cupel with 1 g. of lead. This time part with 9.5 *N* nitric acid. Repeat the inquartation and parting until a constant weight of gold is obtained.

Instead of separating gold and platinum in this way, the button can be dissolved in aqua regia and the gold precipitated by ferrous sulfate

as described on p. 239 or the gold may be thrown down from an alkaline solution by means of hydrogen peroxide. To determine the platinum, precipitate it as sulfide by introducing hydrogen sulfide into the hot, acid filtrate and weigh as metal after ignition in a porcelain crucible.

3. Analysis of Commercial Platinum, according to Deville and Stas

Heat 5 g. of the platinum alloy* for five hours at about 1000° with ten times as much lead in a crucible of purified gas-carbon embedded in a clay crucible filled with charcoal. After cooling, treat the lead button with very dilute nitric acid until there is no longer any gas evolved.

In this way a **solution, A,** is obtained, containing about 98.4 per cent of the lead used, all the palladium and copper, and small amounts of platinum, rhodium, and iron, and a **residue, B,** consisting of a black metallic powder, which is filtered off, and will contain the remainder of the platinum and rhodium with all of the iridium and ruthenium.

1. *Treatment of the Nitric Acid Solution A*

Precipitate the lead by adding a slight excess of sulfuric acid, and filter. If the lead sulfate is pure white, wash it with 2 *N* sulfuric acid. If it is not absolutely white, wash it with a solution of ammonium carbonate until it becomes so; small amounts of lead are dissolved by this operation. Concentrate this last wash liquid, therefore, to precipitate lead carbonate, filter, and after making acid with hydrochloric acid, add the solution to the main filtrate.

Evaporate to about 100 ml., and when cold pour into a saturated solution of ammonium chloride. Heat to boiling and allow to cool again. Filter off the ammonium chloroplatinate and wash with a saturated solution of ammonium chloride; in this way, the greater part of the platinum is obtained.

Boil the filtrate from the platinum precipitate with formic acid and ammonium acetate as described on p. 249, *b*. In this way the remainder of the platinum, the palladium, and the rhodium will be precipitated. Filter off these metals, and determine the copper and iron in the filtrate in the usual way. Dry the formic acid precipitate (consisting of a black metallic powder) and fuse with potassium pyrosulfate in a porcelain crucible. Treat the melt with water, decant the solution from the unattacked platinum and wash alternately with ammonium carbonate and nitric acid (to remove traces of lead sulfate), then with dilute hydrofluoric acid, and finally with water. Dry and weigh the

* All commercial platinum contains other platinum metals, especially iridium.

platinum. The filtrate from the platinum contains palladium and rhodium. Precipitate the former by adding mercuric cyanide, and boiling until the odor of hydrocyanic acid has disappeared. Wash the voluminous, yellowish-white precipitate of palladous cyanide first by decantation, and then upon the filter. Dry, and ignite at first cautiously and then strongly over the blast until the paracyanide is completely destroyed; finally heat in a current of hydrogen (as in the case of copper sulfide, p. 185) to reduce any palladium that has been oxidized by the previous treatment. As soon as the flame is removed at once cut off the supply of hydrogen to prevent its being absorbed by the metal. Weigh the cold palladium.

Precipitate the rhodium from the filtrate by means of formic acid, as before, dry the deposited metal, ignite in a stream of hydrogen, allow to cool in the gas, and weigh.

2. *Treatment of the Residue B*

Heat the washed residue with dilute aqua regia (2 vol. nitric acid, 8 vol. hydrochloric acid, and 90 vol. water), and in this way **solution C** is obtained, which contains the rest of the lead, platinum, and rhodium, and **residue D**, consisting of lamellæ of iridium and ruthenium.

3. *Treatment of the Solution C*

After evaporating to a small volume, remove the lead by sulfuric acid. Evaporate the filtrate from the lead sulfate to dryness, take up the residue in hydrochloric acid, and precipitate the platinum by pouring into a cold saturated solution of ammonium chloride, continuing as described under 1, p. 248. The platinum precipitate contains a little rhodium, and after washing it with a saturated solution of ammonium chloride, place at one side for the time being.

Evaporate the filtrate, together with the wash water, until more platinum and rhodium separate out on cooling. Filter and wash this precipitate as before.

Place both filters, together with the precipitates, in a small, weighed porcelain dish, dry, and reduce at as low a temperature as possible, in a stream of illuminating gas, and heat somewhat in a muffle to remove the carbon from the filter. Weigh the metal thus obtained (platinum + rhodium). For the separation of the rhodium from the platinum, heat the spongy metal in the same dish with potassium pyrosulfate, gradually raising the temperature until a dull-red heat is obtained. After cooling, extract the melt with water, filter off the unattacked platinum (it may still contain small amounts of rhodium), wash, and again fuse with potassium pyrosulfate. Repeat this operation until

the rhodium is completely extracted, which is known by the melt showing no yellow color after ten minutes.

Wash, ignite, and weigh the platinum as described under 1.

The combined filtrates from the platinum contain rhodium and still a little platinum. Add once more ammonia, acetic and formic acids, and boil the solution for a long time. Filter off the precipitated metal, ignite and weigh. Fuse this precipitate at a red heat with potassium pyrosulfate, and extract the cold melt with water. If a residue remains after this treatment, filter off, weigh, and treat with dilute aqua regia. If it dissolves, it is platinum; if it does not, it is rhodium.

Dilute the filtrate from the ammonium chloroplatinate, which contained some rhodium, add formic acid and ammonium acetate, and gently boil for two or three days in an Erlenmeyer flask connected with a return-flow condenser. The liquid evaporates somewhat in spite of the condenser, and it is necessary to replace the evaporated part from time to time with a dilute solution of ammonium formate. In this way small amounts of platinum and rhodium are precipitated. Filter them off and separate by fusion with potassium bisulfate as before. In the filtrate there are likely to be present traces of platinum, rhodium, and iron.

First remove the iron by the addition of chlorine water and afterward ammonia; filter off the ferric hydroxide, ignite, and weigh. To remove the last traces of platinum and rhodium, evaporate this last filtrate to dryness, heat the residue with nitric acid to remove the ammonium chloride completely, and then boil for a long time with formic acid and ammonium acetate. Wash the traces of metal thus obtained with hydrofluoric acid and add to the main portion of platinum and rhodium.

Treatment of the Residue D

Filter off the undissolved, gray lamellæ (consisting of iridium, ruthenium, and small amounts of iron) obtained after the above treatment with dilute aqua regia. Dry, ignite in an atmosphere of hydrogen or illuminating gas, and weigh.

Fuse the weighed metal in a pure gold crucible with potassium nitrate and carbonate. For this purpose, place a previously melted mixture of 3 g. potassium nitrate and 10 g. potassium carbonate in the crucible, add the metal, and heat the mixture for two hours at a dull-red temperature. In this way the ruthenium is changed completely into water-soluble potassium ruthenate, K_2RuO_4, and the iridium is oxidized to Ir_2O_3; the latter forms, to some extent, a soluble compound with the alkali.

Extract the melt with water, and pour the solution, together with the suspended Ir_2O_3,* into a stoppered cylinder, allow the precipitate to settle, and decant off the clear liquid into a retort.

Repeatedly cover the residue remaining in the cylinder with a dilute solution of sodium hypochlorite and sodium carbonate, until the yellow color is completely removed. Add the decanted liquid to the main solution in the retort. This solution contains all the ruthenium and a part of the iridium. Saturate with chlorine in the cold, distil and receive the distillate in a mixture of alcohol (distilled over potassium) and pure hydrochloric acid.

After the distillation is complete, evaporate the alcoholic distillate to dryness and reduce the ruthenium chloride thus obtained to metal by heating in a stream of hydrogen. After weighing, test the purity of the ruthenium. It should dissolve completely in a concentrated solution of sodium hypochlorite.

Evaporate the liquid remaining in the retort to a small volume, add the insoluble residue that remained in the cylinder after the above treatment with sodium hypochlorite solution and boil the mixture with caustic soda solution, with the addition of a little alcohol, until all of the iridium is precipitated.

Filter off the dark-blue precipitate, consisting of iridium oxide and small amounts of ferric hydroxide, wash, and strongly ignite. Dissolve out the contaminating ferric oxide by heating with hydrochloric acid containing some ammonium iodide, and wash the residual iridium oxide successively with water, chlorine water, and hydrofluoric acid, to remove gold that came from the crucible and silicic acid from the caustic soda. Ignite in hydrogen and weigh the iridium.

Precipitate the iron in the hydrochloric acid extract as ferric hydroxide, ignite, and weigh. Test its purity by heating in a stream of hydrogen and hydrochloric acid, to see if it can be completely changed to ferrous chloride and volatilized as such.

F. Mylius and F. Förster† have recommended that platinum be tested for small amounts of impurity by taking three separate portions each weighing 10 g. Test the first portion for palladium, iridium, and ruthenium according to the lead procedure just described of Deville and Stas. The second portion serves for the iron determination; dissolve the metal in aqua regia, precipitate the platinum metals by formic acid, and determine the iron in the filtrate. In the third portion determine rhodium, silver, copper, and lead by volatilizing the

* Cf. W. Palmaer, *Z. anorg. Chem.*, **10**, 332 (1896).

† *Ber.* **1892**, p. 665.

platinum as $PtCl_2CO$ at 238° (temperature of boiling quinoline) in a stream of carbon monoxide and chlorine, and determining the other metals in the residue.

Remark. — The determination of the iron in a separate portion is to be recommended, for in the lead procedure some iron is always obtained from the carbon crucible.

PALLADIUM, Pd. At. Wt. 106.7

Palladium is usually determined as metal. In most cases it is a matter of depositing palladium from an aqua regia solution. The following methods for precipitating palladium are best accomplished by having the palladium present in the bivalent, palladous condition; this is accomplished by repeatedly evaporating the solution with concentrated hydrochloric acid on the water-bath. From the slightly acid solution of palladous chloride, metallic palladium can be precipitated completely by the action of sodium formate or carbon monoxide.

(*a*) Precipitation of Palladium by Formic Acid

To the fairly dilute solution add sodium formate solution, cover with a watch glass and heat carefully over a free flame. Carbon dioxide is evolved and shortly the palladium is precipitated as a fine black powder: $PdCl_2 + HCO_2Na = NaCl + HCl + CO_2 +$ **Pd.** The finely-divided metal is appreciably soluble in hydrochloric acid. After the evolution of gas has ceased, therefore, add sodium carbonate solution until a neutral or faintly alkaline reaction is obtained. Filter and wash the palladium with hot water. Place the moist filter and precipitate in a porcelain crucible and carefully ignite, finally using the full heat of the burner. Cool and weigh. As a rule, there is a slight superficial oxidation of the metal as shown by blue or violet colorations but the increase in weight is so small that it can be neglected.

(*b*) Precipitation of Palladium by Carbon Monoxide

Conduct carbon monoxide into the cold, faintly acid solution. $PdCl_2 + CO + H_2O = 2\,HCl + CO_2 +$ **Pd.** After the precipitation is complete, add sodium carbonate solution and continue as described in the previous method.

(*c*) Precipitation of Palladium as Palladous Cyanide

Nearly neutralize the solution with sodium carbonate and add an excess of mercuric cyanide: $PdCl_2 + Hg(CN)_2 = HgCl_2 +$ **$Pd(CN)_2$.** Heat on the water bath until there is no more odor of hydrocyanic

acid, allow the light yellow precipitate to settle, wash it by decantation and on the filter with cold water. Dry, ignite and weigh as Pd.

(*d*) Precipitation of Palladium as Palladous Nitrosonaphthol

Treat the faintly acid solution of palladous salt with a saturated solution of α-nitroso-β-naphthol in 50 per cent acetic acid. A voluminous, reddish-brown precipitate of $Pd(C_{10}H_6NO_2)_2$ results but the other platinum metals are not precipitated. Wash the precipitate with hot water and weigh as Pd according to the directions given under (*a*).

Separation of Palladium from Platinum

Method of Cohn and Fleissner

This method depends upon the insolubility of ammonium chloroplatinate in alcohol and the solubility of the corresponding palladous compound.

Evaporate the aqua regia solution repeatedly with hydrochloric acid to remove all nitric acid and reduce the palladium to the palladous condition. Treat the concentrated solution with an excess of 10 per cent ammonium chloride solution and evaporate nearly to dryness on the water-bath. Moisten the residue with a few drops of water, add 30 per cent ammonium chloride solution, stir and allow to stand 30 minutes. Filter, wash the precipitate with 30 per cent ammonium chloride solution and finally with alcohol. Ignite the precipitate carefully and weigh as platinum. To the filtrate add nitric acid and evaporate slowly on the water-bath; a red crystalline precipitate of $(NH_4)_2PdCl_6$ is formed. Cool, filter, wash with strong ammonium chloride solution, ignite and weigh as palladium.

(*b*) *Method of W. Schmidt*

Precipitate the palladium from weak hydrochloric acid solution with α-nitroso-β-naphthol as described above. In the filtrate precipitate the platinum with sodium formate according to p. 249.

SELENIUM, Se. At. Wt. 79.2

Selenium is usually determined as the element itself. Three cases are to be considered:

I. The selenium is present as alkali selenite or as selenious acid.
II. The selenium is present as alkali selenate or as selenic acid.
III. The selenium is present as potassium selenocyanide.

I. *The selenium is present as selenite or as free selenous acid.* — Make the solution acid with hydrochloric acid, saturate with sulfur dioxide gas, boil, filter through a Gooch crucible, and wash first with water, then with alcohol. Dry the residue at 105° and weigh.

Remark. — The precipitation of selenium by sulfur dioxide is quantitative whether the solution is concentrated or dilute, whether it contains much or little hydrochloric acid. This latter fact is of importance in the separation of selenium from tellurium, for the latter element is not precipitated by sulfur dioxide when considerable hydrochloric acid is present (cf. p. 259).

In the presence of nitric acid the precipitation of selenium by sulfurous acid is incomplete. In such cases, the nitric acid may be removed by boiling with hydrochloric acid in a flask with a return-flow condenser. Evaporation in an open vessel is not permissible as considerable selenium is volatilized even in the presence of dissolved alkali chloride. It is safer to precipitate the selenium with hydrazine sulfate or hydrazine hydrate when nitric acid is present.

Add ammonium hydroxide to the nitric acid solution until it is faintly ammoniacal and then make slightly acid with hydrochloric acid. Cover the Erlenmeyer flask with a watch-glass, add an excess of hydrazine sulfate or hydrate and boil until the precipitated red selenium coagulates and changes into the easily filtrable gray modification with a clear supernatant solution. Filter into a Gooch or Munroe crucible, wash with hot water and then with alcohol, dry at 105° and weigh as selenium.

Phosphorous acid does not precipitate selenium from cold, dilute, strongly acid solutions; this fact is made use of in the separation of selenium from mercury (cf. p. 261).

II. *The selenium is present as alkali selenate or as free selenic acid.* — As selenium in the form of selenic acid is not precipitated by sulfur dioxide, phosphorous acid, or hydrogen sulfide, it must be first reduced to selenous acid by long-continued boiling with hydrochloric acid (cf. Vol. 1); the above procedure is then followed. This tedious operation is unnecessary, however, if the precipitation is effected with hydrazine hydrate or sulfate as described under I.

III. *The selenium is present as potassium selenocyanide.* — Treat the concentrated solution with hydrochloric acid, boil, allow to settle, and filter the precipitate through a Gooch crucible. Dry at 105° and weigh.

Remark. — From very dilute solutions of potassium selenocyanide, selenium separates out only very slowly according to this method; it is therefore advisable to concentrate the solution as much as possible, but when this cannot be done, the boiling with hydrochloric acid should be continued for some time and the liquid allowed to stand before filtering.

In practice, selenium is obtained usually in none of the above forms, but as impure selenium (selenium sponge) or as selenide, and by the treatment of these substances one or the other of the above selenium compounds is obtained.

If the selenium or selenide is made to react with concentrated nitric acid,* or aqua regia, all of it is dissolved in the form of selenous acid (not selenic acid), and the selenium can be precipitated with hydrazine hydrate or sulfate as described under I.

If the finely powdered selenium or selenide is intimately mixed with two parts sodium carbonate and one part potassium nitrate, placed in a nickel crucible, covered with a layer of sodium carbonate and potassium nitrate and heated gradually until it fuses, all the selenium forms alkali selenate and on extracting the melt with water it goes into solution; in this way it is separated from most of the remaining oxides. The solution, however, often contains small amounts of lead. In order to remove the latter, treat the filtrate with hydrogen sulfide, and again filter; free the solution from hydrogen sulfide by boiling, strongly acidify with hydrochloric acid, boil until no more chlorine is evolved and precipitate the selenium by sulfur dioxide according to II.

Remark. — The mixture must be heated very slowly, as otherwise some selenium is likely to be lost by volatilization.

Selenium and very many selenium compounds may be satisfactorily determined as follows: Fuse the dry, finely powdered sponge at low as a temperature as possible in a current of hydrogen† with twelve times as much potassium cyanide. After the mass has fused quietly for about 15 minutes, allow it to cool in hydrogen. Extract with water, heat the solution to boiling, and analyze according to III.

It is necessary to boil the solution of potassium selenocyanide before acidifying it, for small amounts of potassium selenide (K_2Se) are almost always present, and on acidifying with hydrochloric acid this is decomposed with evolution of hydrogen selenide. On boiling, the potassium selenide is changed to potassium selenocyanide according to the equation:

$$2\,K_2Se + 2\,KCN + 2\,H_2O + O_2 = 4\,KOH + 2\,KCNSe.$$

* Mercury cyanide is unacted upon by nitric acid, but is dissolved by aqua regia.

† A Rose crucible (Fig. 45, p. 185) is used, or a round-bottomed flask with a long neck made of difficultly fusible glass, from which the air is replaced by hydrogen. In the latter case the delivery-tube must be so wide that the neck of the flask is nearly filled with it.

TELLURIUM, Te, At. Wt. 127.5

Tellurium is usually determined as the element itself.

If sulfur dioxide is conducted into a hydrochloric acid solution containing tellurous acid, black tellurium is precipitated quantitatively, *provided the solution does not contain too much acid.* If tellurous acid is dissolved in 200 ml. of hydrochloric acid, *d.* 1.175, no tellurium will be precipitated on passing sulfur dioxide into the cold solution. If, however, the solution is diluted with an equal volume of water and sulfur dioxide is passed into the boiling solution, all the tellurium will be precipitated. Filter off the precipitate, wash with water until free from chlorides, then with alcohol, dry at 105° and weigh. The oxidation of the tellurium during the drying is so slight that it can be disregarded.

From solutions of telluric acid, tellurium is not precipitated by means of sulfur dioxide. From such solutions the precipitation can be accomplished after boiling for a long time with a return-flow condenser with strong hydrochloric acid which reduces telluric acid. According to Gutbier, this reduction is unnecessary if hydrazine hydrochloride or hydrate is ued to precipitate the tellurium.

$$2\,H_6TeO_6 + 3\,(N_2H_4.2\,HCl) = 12\,H_2O + 6\,HCl + 3\,N_2 + 2\,\mathbf{Te}.$$

Lehner and Homberger prefer to use both hydrazine hydrochloride and sulfurous acid. Their procedure is as follows: — To the solution of tellurite, tellurate or the corresponding acids, containing about 0.5 g. of tellurium, add 25 ml. of 3 *N* hydrochloric acid, 10 ml. of a 15 per cent solution of hydrazine hydrochloride and 35 ml. of saturated sulfur dioxide solution. Boil 5 minutes, filter, wash with hot water till free from chloride, then with alcohol, dry at 105° and weigh as tellurium. The entire analysis can be made in an hour.

Separation of Selenium and Tellurium from the Metals of Groups III, IV, and V

By conducting sulfur dioxide into the solution fairly acid with hydrochloric acid, the selenium and tellurium will be quantitatively precipitated while the other metals remain in solution.

Separation of Selenium and Tellurium from the Metals of Group II

(a) From Copper, Bismuth, and Cadmium

Pass sulfur dioxide into the boiling solution, acid with hydrochloric acid, whereby all of the selenium and tellurium and usually some of the bismuth are precipitated. Filter and wash the precipitate with

hot water. Dissolve it in nitric acid, evaporate the solution to dryness, take up in concentrated hydrochloric acid, dilute with a little water and precipitate with hydrogen sulfide. Wash the precipitate, consisting of the sulfides of selenium, tellurium and bismuth, and treat with sodium sulfide solution; selenium and tellurium pass into solution while the bismuth remains behind as its brown sulfide and is filtered off.

Make the solution containing the selenium and tellurium acid with nitric acid, carefully evaporate to dryness and boil the residue with 200 ml. of hydrochloric acid, *d.* 1.175, until there is no longer any evolution of chlorine. Filter off the deposited sulfur through a Gooch crucible, and saturate the filtrate with sulfur dioxide gas; all the selenium is in this way precipitated. Filter off the selenium through a Gooch crucible and wash successively with 10 *N*, 6 *N* and 2 *N* hydrochloric acid, and finally with absolute alcohol. Dry the precipitate at 105° and weigh. Dilute the filtrate with an equal volume of water and precipitate the tellurium by passing sulfur dioxide into the boiling solution. Wash this precipitate with water until free from chlorides, then with absolute alcohol, dry at 105° and weigh.

Remark. — The above method is suitable for the separation of selenium and tellurium from small amounts of bismuth, but does not effect a good separation of selenium (and tellurium) from copper. In this case, more or less copper selenide is formed according to the conditions, and this compound is not decomposed quantitatively by sodium sulfide.* The following method of B. Brauner and B. Kuzma† is more satisfactory.

Precipitate the tellurium and selenium in a pressure flask, by means of SO_2, filter off the precipitate, which is contaminated with copper, antimony and bismuth (using a Gooch crucible), wash, dissolve in nitric acid, evaporate the solution to dryness and take up the residue in caustic potash solution (1:5). To the alkaline solution in an Erlenmeyer flask upon a water-bath, add little by little 4–6 g. of ammonium persulfate, whereby the potassium tellurite is oxidized to potassium tellurate and the selenite to selenate. When all the persulfate has been added, boil the solution to decompose the excess of persulfate, make acid with sulfuric acid and allow to cool. Now, add 100 ml. of H_2S-water, expel the excess of the H_2S by passing CO_2 through the solution, filter off the precipitated CuS (Bi_2S_3, Sb_2S_3) and treat as described on p. 219. Boil the filtrate with hydrochloric acid to reduce

* Cf. E. Keller, *J. Am. Chem. Soc.*, **19**, 771.

† Ber., **1907**, 3362.

the telluric acid to tellurous acid, reduce the solution by SO_2 and analyze as described above.

The first filtrate from the impure Te and Se will contain the greater part of the Cu, Bi, etc.

(*b*) *From Antimony, Tin and Arsenic*

If considerable antimony is present, add tartaric acid to the solution, and precipitate the selenium and tellurium by boiling with sulfur dioxide.

According to Muthmann and Schröder* this method of separating tellurium from antimony is not quantitative; some antimony is always precipitated with the tellurium. A. Gutbier,† however, finds that a perfect separation can be accomplished by means of hydrazine hydrochloride (not the sulfate).

(*c*) *From Mercury*

Dissolve the mercury selenide, or telluride, in aqua regia, add chlorine water, and dilute the solution largely with water. Add phosphorus acid;‡ after twenty-four hours standing, the mercury is precipitated completely as mercurous chloride, and can be determined as such according to p. 174. Make the filtrate slightly alkaline with potassium hydroxide, evaporate nearly to dryness, dilute and separate the selenium from the tellurium according to the method of Keller (see p. 262).

(*d*) *From Gold and Silver*

The separation of selenium and tellurium from silver offers no difficulty, inasmuch as the latter can be precipitated by hydrochloric acid and determined as the chloride.

Precipitate the gold as described on p. 239 by oxalic acid and the selenium and tellurium in the filtrate by means of sulfur dioxide. The three metals may also be precipitated together by sulfur dioxide, weighed, and the selenium and tellurium afterward volatilized by roasting, leaving the gold behind.

Tellurium may be separated from gold by precipitating the latter with ferrous sulfate. In the case of selenium, however, it is also precipitated quantitatively by ferrous sulfate from solutions strongly acid with hydrochloric acid.

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* *Z. anorg. Chem.*, **14**, 433 (1897).

† *Z. anorg. Chem.*, **32**, 263 (1902).

‡ Selenous and tellurous acids are not precipitated by phosphorous acid from dilute hydrochloric acid solution, but are precipitated from hot concentrated solutions.

Separation of Selenium from Tellurium

*A. Method of E. Keller**

Keller's method is based upon the fact that tellurous acid is not precipitated from solutions strongly acid with hydrochloric acid while selenium is precipitated quantitatively.

Procedure. — Dissolve the mixture of the two elements, obtained by precipitation with sulfur dioxide, in nitric acid and carefully evaporate to dryness. Treat the dry mass with 200 ml. of hydrochloric acid (*d.* 1.18), boil to remove the nitric acid and saturate with sulfur dioxide. Filter off the precipitated selenium through a Gooch crucible, wash first with a mixture of 90 vol. HCl (*d.* 1.18) and 10 vol. water, then with dilute hydrochloric acid, then with water until free from chloride and finally with absolute alcohol. Dry the selenium at 105° and weigh. Dilute the filtrate with an equal volume of water, heat to boiling, precipitate the tellurium by sulfur dioxide and treat like the selenium.

According to Keller, this method gives satisfactory results, as long as the amount of tellurium present does not exceed 5 g. Even then the separation can be effected by increasing the amount of acid to 450 ml.

B. The Potassium Cyanide Method

Fuse the precipitate of selenium and tellurium with 12 times as much of pure (98 per cent) potassium cyanide, in an atmosphere of hydrogen, as described on p. 258. The tellurium is nearly all changed to potassium telluride, K_2Te (a small amount of potassium tellurocyanide is probably formed), while the selenium is changed for the most part into potassium selenocyanide, and to a slight extent into potassium selenide.

Dissolve the brown melt in water, and pass a slow current of air through the solution; the K_2Te is quantitatively decomposed according to the equation

$$2\,K_2Te + 2\,H_2O + O_2 = 4\,KOH + 2\,Te.$$

After standing 12 hours filter off the tellurium through a Gooch crucible, wash with water, then with absolute alcohol, dry at 105° and weigh.

Heat the colorless filtrate to boiling,† in order to change any potassium selenide into the double cyanide; make acid with hydrochloric acid under a good hood (*hydrocyanic acid!*), filter and determine the selenium according to p. 257.

* *J. Am. Chem. Soc.*, **19**, 771.

† Cf. p. 258.

Remark. — This method gives slightly low results for tellurium and high values for selenium. This is due to the fact that a little potassium tellurocyanide is formed by the fusion and this compound is not decomposed by the current of air, but is subsequently precipitated with the selenium on acidifying the solution.

Determination of Selenium and Tellurium in Crude Copper

Many copper ores contain selenium and tellurium, and the crude copper obtained from such ores always contains these elements. The amount present may be determined, according to Keller,* as follows: According to the amounts of selenium and tellurium present, take 5–100 g. of the copper for analysis. Dissolve the sample in nitric acid, and add an excess of ammonia to precipitate the phosphorus, arsenic, antimony, tin, bismuth, selenium, and tellurium together with the ferric hydroxide; the copper is held in solution by the excess of ammonia. Filter off the precipitate and wash with dilute ammonia-water until the copper is completely removed. Dissolve the precipitate in hydrochloric acid and saturate this solution with hydrogen sulfide in the cold; selenium and tellurium together with arsenic, antimony, tin, and bismuth are thrown down as sulfides and are separated by filtration from the iron and phosphorus. Treat the precipitate thus obtained with sodium sulfide solution and filter. The filtrate contains all the selenium and tellurium in the presence of arsenic, antimony, and tin as sulfo salts. Make acid with nitric acid and carefully evaporate to dryness. Dissolve the residue in 200 ml. of hydrochloric acid (*d.* 1.18) and treat as described on p. 262, A.

MOLYBDENUM, Mo. At. Wt. 96.0

Form: Molybdenum Trioxide, MoO_3

If the molybdenum is present as ammonium molybdate, heat a weighed portion in a spacious porcelain or platinum crucible, at first carefully and later to a dull red heat; this leaves the molybdenum trioxide behind in the form of a dense powder, appearing yellow when hot and almost white when cold. There is no danger of losing any of the molybdenum by volatilization, provided the dull red heat is not exceeded.

If the molybdenum is present as alkali molybdate, change it to mercurous molybdate or to its sulfide, and then analyze as described below.

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* *J. Am. Chem. Soc.*, **22**, 241.

Precipitation of Molybdenum as Mercurous Molybdate

In the course of analysis it is frequently necessary to determine molybdenum in alkali molybdates obtained by fusion with an alkali carbonate.

Neutralize the greater part of the alkali carbonate with nitric acid, and to the slightly alkaline solution add a barely acid solution of mercurous nitrate until no further precipitation is effected. Heat the liquid to boiling, allow the black precipitate, consisting of mercurous carbonate and mercurous molybdate, to settle, filter and wash with a dilute solution of mercurous nitrate. Dry the precipitate, transfer as completely as possible to a watch-glass, and dissolve the precipitate remaining on the filter in hot dilute nitric acid into a large porcelain crucible. Evaporate the solution to dryness, add the main portion of the precipitate to the residue, and heat the whole very carefully over a low flame until the mercury is completely volatilized, and weigh the residual molybdenum trioxide.

Remark. — It was formerly customary to add a slight excess of mercurous nitrate solution and then to add mercuric oxide to neutralize the excess of nitric acid (the solution of mercurous nitrate contains free nitric acid). According to the above procedure of Hillebrand, the addition of mercuric oxide is wholly superfluous, for the basic mercurous carbonate suffices to remove the slight amount of free nitric acid.

Precipitation of Molybdenum as Molybdenum Sulfide

The precipitation of molybdenum as the sulfide can take place in two ways: either the acid solution may be precipitated by hydrogen sulfide gas, or the solution of ammonium sulfo-molybdate may be acidified with dilute acid.

(*a*) *Precipitation of Molybdenum Sulfide from Acid Solutions*

Place the molybdenum solution, slightly acid with sulfuric acid,* in a small pressure-flask and saturate in the cold with hydrogen sulfide. Close the flask, heat on the water-bath until the precipitate has completely settled, and filter after it has become cold. Wash the precipitate with very dilute sulfuric acid and finally with alcohol until the acid has been completely removed. Place the moist filter in a large porcelain crucible and dry upon the water-bath. Cover the crucible and heat very carefully over a small flame until no more hydrocarbons are expelled. Then remove the cover, burn off the carbon from the sides of the crucible at as low a temperature as possible, and,

* In some cases, *e.g.*, for the separation of Mo from Ba, Sr, and Ca, it is necessary to effect the separation in a *hydrochloric* acid solution.

by raising the temperature gradually, change the sulfide to oxide. The operation is finished when no more sulfur dioxide is formed. After cooling, add a little mercuric oxide suspended in water to the contents of the crucible, stir the mixture well, evaporate to dryness on the water-bath, remove the mercuric oxide by gentle ignition, and weigh the residue of molybdenum trioxide. The mercuric oxide helps to remove particles of unburned carbon.

It is much easier to transform the molybdenum trisulfide into the oxide as follows: Filter off the sulfide into a Gooch crucible, wash with water containing sulfuric acid, and then with alcohol, and dry at 100° C. Place the crucible within a larger nickel one, cover with a watch-glass,* and carefully heat over a small flame whereby the sulfide is for the most part changed to the oxide. As soon as the odor of sulfur dioxide can no longer be detected, remove the watch-glass and heat the open crucible to a constant weight. The molybdenum oxide thus obtained always contains traces of SO_3, and consequently has a bluish appearance. The results, nevertheless, are excellent.

(*b*) *Precipitation of Molybdenum Sulfide from Alkaline Solution*

To the molybdenum solution add an excess of ammonium hydroxide and saturate the solution with hydrogen sulfide until it assumes a bright-red color. Make acid with sulfuric acid and treat the precipitate as described under (*a*).

The Separation of Molybdenum from the Alkalies

can take place by precipitation as mercurous molybdate or as sulfide, as described above.

Separation of Molybdenum from the Alkaline Earths

Fuse the substance with sodium carbonate, extract the melt with water and filter. The solution contains all the molybdenum as alkali molybdate, while the alkaline earths remain undissolved as carbonates. From the aqueous solution determine the molybdenum by one of the above methods.

Separation of Molybdenum from the Metals of the Ammonium Sulfide Group

Precipitate the molybdenum as sulfide (preferably from a sulfuric acid solution) by treatment with hydrogen sulfide under pressure (see p. 264). If the solution contains titanium, it is better to first add am-

* To avoid loss by decrepitation.

monia and ammonium sulfide, whereby the metals of Group III will be precipitated and the molybdenum will remain in solution in the form of its sulfo salt. After filtration, precipitate the molybdenum as sulfide by the addition of acid (see p. 265, *b*).

Separation of Molybdenum from the Metals of Group II

(*a*) *From Lead, Copper, Cadmium, and Bismuth*

Make the solution alkaline with sodium hydroxide, add sodium sulfide, digest some time in a closed flask, and filter. The molybdenum remains in solution as its sulfo salt, while the other metals are precipitated as sulfides. After filtering, acidify the solution with sulfuric acid and heat in a pressure-flask until the precipitate has settled and the supernatant liquid appears colorless. After allowing to cool, filter off the molybdenum sulfide and convert to oxide, as described on p. 265.

(*b*) *From Arsenic*

Add ammonium hydroxide to the solution, which must contain the arsenic as arsenic acid, and precipitate the arsenic by magnesia mixture (see p. 201) and filter. Make the filtrate acid with sulfuric acid and precipitate the molybdenum as sulfide as described on p. 265.

Separation of Molybdenum from Phosphoric Acid

Precipitate the phosphoric acid from the ammoniacal solution as magnesium ammonium phosphate (see phosphoric acid) and the molybdenum as sulfide in the filtrate (cf. p. 264, *a*). Another way is to saturate the ammoniacal solution with hydrogen sulfide, acidify with hydrochloric acid, and then precipitate the molybdenum as sulfide. In this filtrate precipitate the phosphoric acid as magnesium ammonium phosphate under the customary conditions.

Determination of Molybdenum in Steel

Dissolve 2–3 g. of drillings or chips in 50 ml. of 6 *N* nitric acid, evaporate to dryness and heat in a porcelain dish until the ferric nitrate is well decomposed. During the heating the oxides are for the most part dislodged from the sides of the dish. Transfer the loose particles to an agate mortar, mix with 12 g. of sodium peroxide and transfer to a well-scoured nickel or iron crucible containing a little sodium peroxide on the bottom. Rub the dish, mortar and spatula with more sodium peroxide and transfer the peroxide to the crucible. Finally add a little

sodium hydroxide solution to the dish, heat nearly to boiling, rinse into a beaker and set it aside.

Cover the crucible and heat with a small flame until the sodium peroxide melts, then raise the temperature and heat to dull redness for 15 minutes. Allow the crucible to cool, place it in a beaker, add 150 ml. of hot water and cover the beaker with a watch-glass. The mass dissolves quickly and most of the excess peroxide is decomposed. Add the reserved alkaline solution, remove the crucible, washing it thoroughly, and heat the contents of the beaker for about an hour on the water-bath. If the solution then shows a green color due to manganate, or a purple color due to permanganate, cool, add a little more sodium peroxide and stir. This serves to reduce manganate and permanganate to manganese dioxide. Dilute the solution to 200 ml., allow it to cool, and when well settled, decant the supernatant liquid through a filter. Wash twice by decantation with 50 ml. portions of hot water and then on the filter until the washings are neutral to red litmus paper.

The insoluble residue may still contain a little molybdenum. Place the filter and its contents in the same crucible that was used before, heat till the carbon is consumed and fuse with 8 g. of a mixture of equal parts sodium carbonate and peroxide. Treat the melt as before and add the filtrate to that previously obtained.

If the molybdenum content is considerable (over 5 per cent) dilute in a calibrated flask and use an aliquot part for the molybdenum determination. Otherwise use the entire filtrate which contains beside all the molybdenum, any vanadium, tungsten, phosphorus, silicon, etc., that was originally present.

Neutralize the greater part of the alkali with dilute sulfuric acid, evaporate to 100 ml., cool and stir in 25 ml. of concentrated ammonium hydroxide. Saturate the solution with hydrogen sulfide and continue as described on p. 265.

After adding the acid to precipitate MoS_3, it is well to introduce hydrogen sulfide and heat while passing the gas to make sure that all the molybdenum is precipitated as sulfide.

Remarks. — If tungsten is present, add tartaric acid before adding sulfuric acid to the ammonium sulfide solution. This prevents the precipitation of tungsten sulfide.

If vanadium is present, the ignited molybdenum oxide has a dark color. After weighing the impure MoO_3 treat with sodium hydroxide solution and determine the vanadium volumetrically. Deduct the corresponding weight of V_2O_5 from that of the impure MoO_3.

If arsenic is present, remove it by adding magnesia mixture before introducing hydrogen sulfide.

The filtrate from the molybdenum sulfide precipitate will be violet or bluish green if chromium and vanadium are present: only part of the vanadium is precipitated with the molybdenum.

Pure molybdenum trioxide is light yellow when cold. On adding a drop of concentrated sulfuric acid and evaporating off the excess, a beautiful blue color is obtained. This test is very sensitive but may not be obtained if the molybdenum sulfide precipitate was not washed thoroughly to dissolve out sodium salts.

TUNGSTEN, W. At. Wt. 184.0

Tungsten is determined as its trioxide, WO_3.

If the tungsten is present as ammonium tungstate, as mercurous tungstate, or as tungstic acid, it can be changed by ignition in the air to yellow tungsten trioxide. Care should be taken not to heat strongly or some of the tungstic acid will be lost by volatilization. The crucible should be uncovered and the full heat of the burner should not be used. When ignited over a Méker burner in a covered platinum crucible, a slow volatilization of tungstic acid takes place. There is danger of some tungsten being reduced by ignition of ammonium tungstate.

If the tungsten is present as alkali tungstate, the tungstic acid may be precipitated as such, or by means of mercurous nitrate as mercurous tungstate; by ignition the yellow trioxide is obtained and weighed.

Precipitation of Tungstic Acid

Moisten the residue with 20 ml. of concentrated hydrochloric acid, add 10 ml. of concentrated nitric acid and evaporate carefully to 10 or 15 ml. Rinse down the cover glass and sides of the container with water and dilute to about 150 ml. Add 5 ml. of cinchonine hydrochloride solution (prepared by dissolving 12.5 g. of cinchonine in 100 ml. of 6 *N* acid) and heat on the hot plate for 30 minutes or longer, stirring occasionally and keeping the temperature just below boiling.

Allow the tungstic acid to settle and then decant the solution through a filter containing some pulp made by digesting ashless filter paper with acid. Wash the precipitate 3 times with the above cinchonine hydrochloride solution diluted 100-fold. Transfer the precipitate to the filter and continue washing till free from alkali salt. Ignite at a low temperature in an open crucible and weigh the residual WO_3.

Remark. — It is difficult to precipitate tungsten acid by simple evaporation with acid. Sodium tungstate, Na_2WO_4, unites to some extent with free tungstic acid to form an acid tungstate, $Na_2W_4O_{13}$ and this is not easily decomposed by acids. By heating with ammonium hydroxide the acid tungstate can be converted back to

normal tungstate but on adding acid some more of the acid tungstate is likely to form.

Cinchonine hydrochloride prevents the formation of the acid tungstate and also prevents the formation of colloidal solutions upon washing. During the ignition the organic material is all consumed so that the presence of cinchonine in the precipitate does no harm.

Tungstic acid is slowly volatilized by heating at a high temperature. The filter should be consumed at as low a temperature as possible and the heating stopped when the carbon is all gone.

Precipitation of Tungsten as Mercurous Tungstate

This method, proposed by Berzelius,* has often been used to precipitate tungsten from a solution of sodium tungstate obtained by fusion with alkali carbonate. Like the phosphates, however, many tungstates are incompletely decomposed by fusion with sodium carbonate so that for the determination of tungsten in ores and in alloy steels it is better to decompose the material with acid and precipitate tungstic acid with the aid of cinchonine hydrochloride, as described above.

Procedure. — Add a few drops of methyl orange to the solution of alkali tungstate and add nitric acid till the indicator turns pink. Boil to expel carbonic acid, allow to cool and add an excess of mercurous nitrate solution. The yellow precipitate settles quickly and the supernatant liquid should appear as clear as water. After standing three or four hours, filter off the precipitate, wash with water containing mercurous nitrate (5 ml. saturated mercurous nitrate solution diluted with water to 100 ml.) dry, ignite in a porcelain crucible under a good hood, using the flame of a Bunsen burner, and weigh as WO_3.

Precipitation of Tungsten as Benzidine Tungstate†

If a neutral solution of sodium tungstate is treated with benzidine hydrochloride, a white flocculent precipitate of benzidine tungstate is formed and the precipitate is insoluble in water containing benzidine hydrochloride; when formed in the cold it is hard to filter and, on being washed with pure water, tends to run through the filter. If the precipitate is formed from a hot solution, however, it comes down in a more compact condition and after cooling‡ can be easily filtered and washed without loss with water containing benzidine hydrochloride. The moist precipitate on being heated to 800° yields a residue of WO_3.

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* *Jahresber.*, **21**, II, 143. Cf. O. v. der Pfordten, *Ann.*, **222**, 152 (1883).

† G. v. Knorre, *Ber.*, **38**, 783 (1905).

‡ Since benzidine tungstate is appreciably soluble in hot water containing benzidine hydrochloride, it is necessary in all cases to postpone the filtration until the solution is cold.

The precipitation can also take place satisfactorily from a cold solution if, before adding the precipitant, a little dilute sulfuric acid or alkali sulfate is added to the solution. In this case a mixture of crystalline benzidine sulfate and amorphous benzidine tungstate is formed which can be filtered after standing 5 minutes. The benzidine sulfate is entirely volatile, so that equally good results are obtained by either of the above two procedures.

If the tungsten is present as tungstate after fusing with sodium carbonate, dissolve the melt in water, add a little methyl orange to the clear solution, then hydrochloric acid until the pink color is obtained, and finally 10 ml. of 0.1 *N* sulfuric acid. Benzidine hydrochloride gives a precipitate which can be filtered in five minutes. Wash with dilute benzidine hydrochloride until the evaporation of a few drops of the filtrate on platinum foil leaves no weighable residue. Ignite the moist precipitate as described above.

Preparation of the Benzidine Solution

Triturate 20 g. of commercial benzidine in a mortar with water, wash into a beaker with about 400 ml. of water, treat with 25 ml. hydrochloric acid (*d.* 1.2) and heat until solution is complete and a brown liquid is formed. Filter and dilute to one liter. Of this solution, 5.6 ml. are sufficient to precipitate 0.1 g. of WO_3.

If the analysis is carried out with the aid of sulfuric acid, it is necessary to add at least one milliliter of the benzidine solution for 10 ml. of 0.1 *N* sulfuric acid added.

Preparation of the Wash Liquid

Dilute 10 ml. of the above solution with distilled water to a volume of 300 ml.

Determination of Tungsten in Chrome-Tungsten Steel*

Decompose 1–2 g. of steel by treatment with 50 ml. of 6 *N* hydrochloric acid. When all the iron is dissolved add 2 ml. of concentrated nitric acid to oxidize the iron and tungsten. Digest until the tungstic acid is bright yellow. Dilute to 150 ml. and add 5 ml. of cinchonine solution (125 g. of cinchonine dissolved in one liter of 6 *N* hydrochloric acid). Digest at 90–95° C. for 30 minutes or longer with occasional stirring.

* This method has been recommended by the Bureau of Standards at Washington, D. C.

Filter and wash the precipitate as described on p. 268. Ignite the precipitate gently in a platinum crucible until the carbon of the filter is burned off, treat with a few drops of dilute sulfuric acid and a few cubic centimeters of hydrofluoric acid, evaporate, ignite to not above 800° and weigh. Fuse the impure tungstic acid with sodium carbonate, dissolve the melt in water, filter off the ferric oxide and chromic oxide, wash thoroughly, return to the thoroughly washed crucible, and ignite. Repeat the fusion with a small amount of sodium carbonate, filter, wash, ignite, and weigh. Deduct this weight from that of the impure tungstic acid.

Remark. — Sometimes a little chromium is present in the impure tungstic acid. In that case the aqueous extract of the fusions will be yellow and the chromium content can be determined by colorimetric comparison.

Determination of Tungsten in Ores*

Procedure. — Weigh out about 1 g. of the finely ground ore into a 400 ml. beaker. Moisten the sample with 5 ml. of water and add 100 ml. of concentrated hydrochloric acid. Cover the beaker and digest at about 60° for at least an hour. Stir from time to time to prevent the formation of any crust. Then evaporate slowly to about 50 ml. Add 40 ml. more of strong hydrochloric acid and 20 ml. of concentrated nitric acid and evaporate to about 10 ml. During these operations, especially when fresh acid is added, stir the material at the bottom of the beaker so that it does not become encrusted.

Rinse down the cover-glass and the sides of the beaker and dilute with water to about 150 ml. If, by accident, the solution was evaporated to dryness during the above treatment, add 20 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid to the residue and evaporate to 10 or 15 ml.

To the diluted solution add 5 ml. of cinchonine hydrochloride solution (cf. p. 268) and heat on the hot plate for 30 minutes or longer. The solution should be at a temperature just below the boiling-point and should be stirred occasionally.

Allow the tungstic acid anhydride to settle and then decant the solution through a filter which contains some pulp made by digesting ashless filter paper with acid. Wash the precipitate three times with a solution containing 10 ml. of the above cinchonine solution to a liter of hot water. Then transfer the precipitate to the filter and wash with this same, diluted cinchonine solution.

* Recommended by J. A. Holliday and found satisfactory by collaborative work in 17 different laboratories in 1918 under the direction of W. F. Hillebrand.

Wash the tungstic anhydride back into the original beaker by a jet of water, using about 25 ml. to accomplish this. Add 6 ml. of concentrated ammonia solution and heat gently, with the beaker covered, for about 10 minutes to convert all the tungstic acid into ammonium tungstate. Rinse down the sides of the beaker with hot, dilute ammoniacal ammonium chloride solution (200 ml. of concentrated ammonia, 800 ml. of water and 10 ml. of concentrated hydrochloric acid). Stir up the contents of the beaker and filter through the same filter that was used for the previous filtration. Collect the filtrate in a 400 ml. beaker and wash the original beaker and filter with the hot ammoniacal solution. The presence of a little ammonium chloride in this ammoniacal solution prevents colloidal silicic acid from passing into the filtrate.

The residue on the filter is usually free from tungsten, but it should be tested by giving it the same treatment as that of the original ore. Ammonium and sodium salts tend to prevent the complete precipitation of tungstic acid, so that it is important, next, to remove the excess ammonia. After this has been evaporated off, add 20 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid and evaporate to about 15 ml. Dilute with 150 ml. of water and precipitate the remainder of the tungstic acid by treatment with cinchonine solution as described above.

After filtering and washing the precipitate as before, ignite it carefully in a weighed platinum crucible. The presence of the paper pulp causes the precipitate to form a porous, friable mass and makes it easy to oxidize the carbon. If the ignition is made in a muffle, the introduction of oxygen is advantageous. After burning off the carbon, at as low a temperature as possible, weigh the precipitate and correct for silica by the usual treatment with hydrofluoric acid.

If the tungstic acid is heated over the full flame of the burner, some of it will be lost by volatilization. After the removal of the silica, the residue should be heated to dull redness for only one minute. Heated in the muffle, the maximum temperature should not exceed 800°. The ignited tungsten trioxide, WO_3, should have a clean, lemon-yellow color.

To test the residue insoluble in ammonia for tungsten, ignite it in an iron crucible and fuse the ash with a small quantity of sodium peroxide mixed with a little sodium carbonate. Reducible metals are likely to ruin a platinum crucible if the residue and filter paper are heated in it. Extract the melt with water and filter. Acidify the aqueous extract with hydrochloric acid, add 5 ml. of cinchonine hydrochloride solution and heat for several hours to see if any yellow tungstic acid anhydride is formed.

Separation of Molybdenum from Tungsten

(*a*) *The Sulfuric Acid Method*

This method, proposed by M. Ruegenberg and E. F. Smith,* depends upon the fact that unignited molybdic acid is readily dissolved by warming with sulfuric acid (*d.* 1.38), while tungstic acid is not.

W. Hommel† tested this method in the author's laboratory, and could not obtain good results except by digesting the moist oxides with *concentrated* sulfuric acid, and afterward diluting with three times as much water.

Procedure. — (α) Both acids are present in a moist, freshly precipitated state.

Cover the mixture with concentrated sulfuric acid in a porcelain dish and heat over a free flame. By this means, usually a small amount of the tungstic acid is oxidized to the blue oxide, so that the yellow precipitate of tungstic acid is tinted with green. On adding one or two drops of dilute nitric acid, the green color disappears and the tungstic acid is of a pure yellow color. After digesting for half an hour, the separation is complete. Cool, dilute the liquid with three times its volume of water, filter, wash with water containing sulfuric acid, then two or three times with alcohol, ignite (after burning the filter by itself) in a porcelain crucible, and weigh as WO_3.

Precipitate the molybdenum in the filtrate by passing hydrogen sulfide into the sulfuric acid solution in a pressure-flask, and treat the precipitate as described on p. 265.

If only a little sulfuric acid is used for the separation, the filtrate from the tungstic acid can be evaporated in a platinum dish, the sulfuric acid driven off for the most part, and the residue washed into a weighed platinum crucible with ammonia, and then evaporated, ignited, and weighed. In case large amounts of molybdenum are present, however, it is always safer to precipitate the molybdenum as sulfide.

(β) *Tungsten and Molybdenum are Present in the Form of their Ignited Oxides*

These ignited oxides cannot be separated by treatment with sulfuric acid. According to W. Hommel, they can readily be brought into solution by heating for half an hour on the water-bath with concentrated ammonia in a pressure-flask, shaking frequently.

After cooling, wash the contents of the flask, whether dissolved or not, into a porcelain dish, evaporate to dryness, and treat as described under (α).

It is still better to fuse the ignited oxides with four times as much sodium carbonate, and treat the melt as described under (α).

* *J. Am. Chem. Soc.*, **22**, 772.

† *Inaug. Dissert.*, Giessen, 1902.

(*b*) *Sublimation Method**

If a mixture of the trioxides of tungsten and molybdenum, or of their alkali salts, is heated at 250–270° in a current of dry hydrochloric acid, the molybdenum is volatilized completely as $MoO_3.2\,HCl$, which collects on the cooler parts of the tube as a beautiful, white, wool-like sublimate, while the tungsten trioxide remains behind in the boat.

Procedure. — Weigh out about 0.3 g. of the oxides of the two elements, or their sodium salts, into a porcelain boat, and place the latter in a tube made of difficultly fusible glass, of which one end is bent vertically downward and is connected with a Péligot tube containing a little water. Insert the horizontal arm of the tube through a drying-oven (to serve as an air-bath) (see Fig. 28, p. 48), and connect with an apparatus for generating hydrogen chloride gas. Pass this gas through a flask containing concentrated hydrochloric acid, and then through concentrated sulfuric acid. As soon as the temperature has reached about 200° the sublimation of the molybdenum begins. From time to time drive over the sublimate that collects in the combustion tube toward the Péligot tube† by carefully heating with a free flame, to see whether any more molybdenum is being volatilized. After heating for 1.5–2 hours, the operation is usually complete. Remove the boat containing tungsten trioxide, or the latter with sodium chloride, and in case only the former is present, weigh after drying in a desiccator over caustic potash. In case, however, sodium chloride is present (when the tungsten was originally present as sodium tungstate) remove this by treatment with water, and weigh the filtered WO_3.

For the determination of the molybdenum, wash out the sublimate in the tube by means of water containing a little nitric acid, and carefully evaporate the nitric acid solution of the entire sublimate to dryness in a porcelain dish. Dissolve the residue in ammonia, wash into a porcelain crucible, evaporate to dryness, and change to WO_3 by gentle ignition.

(*c*) *The Tartaric Acid Method of H. Rose*

To the aqueous solution of the alkali salts of the two metals add considerable tartaric acid and an excess of sulfuric acid. Precipitate the molybdenum according to p. 264, by hydrogen sulfide in a pressure-flask. Filter off the molybdenum sulfide and change by roasting in the

* Péchard, *Compt. rend.*, **114**, p. 173, and **46**, p. 1101.

† By the absorption of the $MoO_3.2\,HCl$ in the water of the Péligot tube, the brick-red acid chloride, $Mo_3O_5Cl_3$, is often formed:

$$3[MoO_3.2\,HCl] + 2\,HCl = 4\,H_2O + Mo_3O_5Cl_3.$$

This substance is insoluble in hydrochloric acid, but readily soluble in nitric acid.

air to the trioxide. For the determination of the tungsten, destroy the tartaric acid by repeated evaporation with nitric acid, filter off the precipitated tungstic acid and change by ignition to the trioxide.

Remark. — This method gives correct results, but is not so satisfactory as the preceding one on account of the time consumed in removing the tartaric acid.

Analysis of Tungsten Bronzes

The analysis of these alkali salts of complex tungsten acids, discovered by Wöhler in 1824,* offered for a long time considerable difficulty on account of the fact that acids do not decompose them very readily.

By fusion with alkalies in the air, or better still in the presence of potassium nitrate, the tungsten bronzes can be converted without difficulty into normal alkali tungstate, and the tungsten determined by one of the methods already described. It is obvious that the alkalies cannot be determined in the same sample, so that Philipp† proceeded as follows:

Treat the bronze with ammoniacal silver nitrate solution. The WO_2 is thereby oxidized to WO_3 and an equivalent amount of silver is precipitated, but the whole of the tungsten remains in solution in the form of alkali and ammonium tungstates. In the filtrate obtained after filtering off the deposited silver, precipitate the tungstic acid by treatment with nitric acid and determined as WO_3. After removing the excess of silver, by precipitating it as the chloride, evaporate the filtrate to dryness with the addition of sulfuric acid, and weigh the alkali as sulfate.

Although the above method affords satisfactory results in the analysis of bronzes containing comparatively little tungsten, it is wholly inadequate in the case of bronzes rich in tungsten. The method of Brunner,‡ which follows, is applicable in all cases. It is based upon the fact that the bronzes can be transformed very easily, and without loss of alkali, into normal tungstates by heating with ammonium persulfate, or ammonium acid sulfate.

Procedure. — Treat 0.5 g. of the finely-powdered bronze in a porcelain crucible with 2 g. of alkali-free ammonium sulfate and 2 ml. of concentrated sulfuric acid§, heating carefully over a small flame. During the heating frequently shake the contents of the crucible about a little by cautiously moving the crucible. The escape of gases from the crucible soon ceases and when sulfuric acid vapors begin to be evolved, the decomposition of the bronze results.

With sodium and lithium bronzes, the fused mass appears greenish, whereas with a potassium bronze the color is yellowish white. After a part of the ammonium sulfate has been volatilized, allow the mass in the crucible to cool, add another gram of ammonium sulfate and 1 ml. of

* *Pogg. Ann.*, **2**, 350.

† *Ber.*, **15**, 500 (1882).

‡ *Inaug. Dissert.*, Zürich, 1903.

§ If ammonium persulfate is used the addition of sulfuric acid is unnecessary. The only objection to the use of the persulfate lies in the fact that the commercial salt often contains some potassium persulfate.

concentrated sulfuric acid. Again heat the contents of the crucible as before until sulfuric acid fumes come off thickly; then allow the crucible to cool.

Soften the greenish or yellowish-white residue by treatment with water and rinsing into a porcelain dish. After adding 50 ml. of concentrated nitric acid, digest the contents of the evaporating dish on the water-bath for 3 or 4 hours, and then, after diluting with water, filter off the residue of pure yellow tungstic acid.

To recover the small amount of tungstic acid remaining in the filtrate, evaporate as far as possible on the water-bath, allow to cool, dilute with a little water, carefully treat with an excess of ammonia, again evaporate on the water-bath and treat as described on p. 268.

Evaporate the final filtrate from the tungstic acid determination to dryness, expel ammonium salts by ignition and weigh the residue of alkali sulfate (cf. pp. 57 and 58)

Separation of Tungsten from Tin*

Mix 1 g. of the finely powdered mineral in an iron crucible with 8 g. of sodium peroxide, and carefully fuse the mixture over a Bunsen burner for about 15 minutes. After cooling, soften the melt with water and transfer into a 250-ml. flask (if lead is present, conduct carbon dioxide into the solution for a few minutes), dilute the solution to the mark, mix well and filter through a dry filter, rejecting the first few ml. of the filtrate.

For the determination of the tungstic acid, take 100 ml. of the filtrate and proceed as described on p. 268.

For the determination of the tin, use a second 100 ml. of the original alkaline solution. Treat with 45 ml. of concentrated hydrochloric acid, to precipitate tungstic and stannic acids. Add 2 or 3 g. of pure zinc to change the tungstic acid to the blue oxide and reduce the stannic acid to metallic tin. Allow the mixture to stand quietly for an hour at a temperature between 50° and 60°. The tin then goes into solution as stannous chloride, and the greater part of the tungsten remains undissolved in the form of the blue oxide. Filter off the latter, and wash. In this way the whole of the tin should be obtained in an acid solution, in the presence of a small amount of tungsten, which does no harm. Dissolve the blue oxide on the filter, however, in hot, dilute ammonia solution to make sure that it contains no trace of metallic tin. If it does, dissolve the small particle of tin in a little hydrochloric acid and add the resulting solution to the main solution of the tin.

* Cf. H. Augenot, *Z. angew. Chem.*, **19**, 140 (1906).

Now dilute the solution with water and precipitate the tin as stannous sulfide by introducing hydrogen sulfide gas. Filter off the precipitate, ignite in a porcelain crucible and weigh as SnO_2 (see p. 215). Or, dissolve the moist precipitate of stannous sulfide in potassium hydroxide solution and determine tin by electrolysis (see p. 219).

According to Donath and Müller* a mixture of stannic oxide and tungstic acid may be separated as follows: Ignite the mixture with powdered zinc for 15 minutes in a covered porcelain crucible. After cooling, heat the spongy mass in the crucible in a beaker with 4 *N* hydrochloric acid (1:2) until there is no more evolution of hydrogen perceptible. Allow the solution to cool somewhat and add powdered potassium chlorate little by little until the blue tungsten oxide is completely transformed to yellow tungstic acid, and the liquid no longer shows any blue tinge. Dilute with $1\frac{1}{2}$ times as much water, and after standing 24 hours filter off the tungstic acid, washing the precipitate first with dilute nitric acid and then with one per cent solution of ammonium nitrate. Dry, ignite and weigh as WO_3. Determine the tin in the filtrate as above.

Separation of Tungstic Acid from Silica

When a mixture of tungstic and silicic acid is at hand, such as is obtained by evaporation with nitric acid, the silicic acid may be removed by treating the ignited residue with hydrofluoric acid and a large excess of sulfuric acid. The separation does not succeed, however, in the mixture of oxides as obtained after precipitation with mercurous nitrate; for in this case the silicic acid is so enveloped with tungstic acid that some of the former is not volatilized as fluoride. In such cases, as Friedheim† has shown, excellent results may be obtained by the

Method of Perillon‡

Place the mixture of ignited oxides in a platinum boat and heat to redness in a stream of dry hydrogen chloride. Thereby the tungsten is volatilized, probably as an acid chloride, which can be recovered in a receiver containing dilute hydrochloric acid; the silica remains behind in the combustion tube.

Frequently the tungsten is reduced to a blue lower oxide, which is not volatile in a current of hydrochloric acid gas. In such cases, after the apparatus has been allowed to cool, replace the hydrogen chloride by air, and heat the contents of the boat in a current of air. Again allow

* *Wiener Monatshefte*, **8**, 647 (1887).

† *Z. anorg. Chem.*, **45**, 398 (1905).

‡ *Bull. soc. l'industrie miner.*, 1884.

the tube to cool, replace the air by hydrogen chloride, and once more heat the tube to redness. Repeat the process if necessary until finally a residue of pure white SiO_2 is obtained. Evaporate the tungstic acid hydrochloride in the receiver to dryness with nitric acid, filter off the precipitated WO_3, ignite and weigh. Unless the current of hydrogen chloride gas is perfectly free from air, the platinum boat will be strongly attacked.

VANADIUM, V. At. Wt. 51.0

Vanadium is determined as the pentoxide, V_2O_5. The most convenient method for determining vanadium is a volumetric process, and will be discussed in the chapter on volumetric analysis.

If vanadium is present as ammonium or mercurous vanadate, it can be easily changed to the pentoxide by ignition; the latter is a reddish-brown fusible substance which solidifies as a radiating, crystalline mass. If vanadic sulfide is carefully roasted in the air, it is also changed quantitatively to the pentoxide.

In the analysis of most minerals containing vanadium, the vanadium is separated from the other metals present by fusing with a mixture of six parts sodium carbonate and one part potassium nitrate. After cooling, the melt is extracted with water, whereby the sodium vanadate goes into solution while most of the metals are left behind in the form of oxides or carbonates. If phosphorus, arsenic (molybdenum, tungsten), and chromium are present, these elements also dissolve on treating the melt with water in the form of the sodium salts of the corresponding acids.

In practice, therefore, the vanadium is usually met with as the sodium salt of vanadic acid, and it is a matter of separating it from the aqueous solution obtained after fusing with sodium carbonate and potassium nitrate, and of separating it from the other acids which are likely to accompany it (phosphoric, arsenic, and chromic acids).

Precipitation of Vanadic Acid from the Solution of Sodium Vanadate

There are two good methods for the separation of vanadic acid from a solution of an alkali vanadate: the Rose method, according to which the vanadium is precipitated as mercurous vanadate, and that of Roscoe, by which it is precipitated as lead vanadate. The Berzelius-Hauer method,* in which the vanadium is precipitated as ammonium metavanadate, was found by Holverscheidt† to give low results, but Gooch

* *Pogg. Ann.*, **22**, 54 and *J. prakt. Chem.*, **69**, 388.

† Dissertation, Berlin, 1890.

and Gilbert,* as well as E. Campagne,† obtained correct results by working in an ammoniacal solution, which was saturated with ammonium chloride.

1. *The Mercurous Nitrate Method of Rose*

Nearly neutralize the alkaline solution with nitric acid and then add, drop by drop, a nearly neutral solution of mercurous nitrate‡ until, after the precipitate has settled, a further addition of the reagent causes no precipitation. Heat to boiling, allow the gray-colored precipitate to settle, filter and wash with water containing a few drops of mercurous nitrate solution. Ignite under a good hood, and weigh the residue of V_2O_5.

Remark. — In neutralizing the alkaline solution of the vanadate with nitric acid, the solution must on no account be made acid, for in this case nitrous acid (from the nitrate fusion) will be set free and the latter reduces some of the vanadate to a vanadyl salt and the latter is not precipitated by mercurous nitrate. In order to avoid passing over the neutral point, Hillebrand recommends fusing with a weighed amount of sodium carbonate and adding the amount of nitric acid that has been found necessary by a blank test to neutralize this. The method gives good results but under these conditions chromate, molybdate, arsenate, tungstate and phosphate will be precipitated so that it is useful only in the absence of chromium, molybdenum, tungsten, etc. The same is true of the following method of Roscoe.

2. *The Lead Acetate Method of Roscoe*§

Principle. — If a solution weakly acid with acetic acid is treated with lead acetate, orange-yellow lead vanadate is precipitated quantitatively. The lead vanadate, however, does not possess a constant composition, so that the amount of vanadium present cannot be determined by weighing the precipitate. After being washed, it is dissolved in as little nitric acid as possible, the lead precipitated as lead sulfate, and the vanadium determined in the filtrate by evaporating the latter, driving off the excess of sulfuric acid, and weighing the residual V_2O_5.

Procedure. — Nearly neutralize the solution from the sodium carbonate and potassium nitrate fusion with nitric acid as described in the previous method. Stir in it an excess of lead acetate solution; the voluminous precipitate will soon coagulate and settle to the bottom of the beaker leaving a perfectly clear supernatant liquid. The precipitate is at first orange-colored, but on standing it gradually becomes yellow and finally perfectly white. Filter and wash with water containing acetic acid until a little of the filtrate will leave no residue on evapora-

* *Z. anorg. Chem.*, **32**, 175 (1902).

† *Ber.*, **1903**, 3164.

‡ The mercurous nitrate should leave no residue on being heated strongly.

§ *Ann. Chem. Pharm., Suppl.*, **8**, 102 (1872).

tion. Wash the precipitate into a porcelain dish, dissolve the part remaining on the filter in as little as possible of hot, dilute nitric acid, and add the solution to the main part of the precipitate, to which add enough nitric acid to dissolve it completely. Then add an excess of sulfuric acid, evaporate on the water-bath as far as possible, and finally heat over a free flame until dense fumes of sulfuric acid are evolved. After cooling, add 50–100 ml. of water, filter off the lead sulfate and wash with dilute sulfuric acid until 1 ml. of the filtrate will show no yellow color with hydrogen peroxide. The lead sulfate should be white and free from vanadium; it will be so provided enough sulfuric acid was used and the mass was not heated until absolutely dry before diluting with water. Evaporate the filtrate containing all the vanadic acid in a porcelain dish to a small volume, transfer to a weighed platinum crucible, evaporate further on the water-bath, and finally in an air-bath until all the sulfuric acid is removed. Ignite the contents of the open crucible for some time* at a faint-red heat and finally weigh as V_2O_5.

Remark. — Instead of decomposing the lead vanadate by means of sulfuric acid, Holverscheidt recommends precipitating the lead as sulfide by means of hydrogen sulfide and determining the vanadium in the filtrate. For this purpose boil the blue-colored filtrate from the lead sulfide precipitate (which contains some vanadyl salt) to expel the excess of hydrogen sulfide and filter off the deposited sulfur. Add a few drops of nitric acid, evaporate the solution to dryness, and change the reddish-yellow hydrate of vanadic acid by gentle ignition into the pentoxide of vanadium.

Lead may also be separated from the vanadic acid as lead chloride. In this case the procedure recommended on page 233 is followed.

The separation of vanadium as the sulfide by acidifying a solution of an alkali vanadate that has been treated with an excess of ammonium sulfide is not admissible, for only a part of the vanadium is precipitated as the brown sulfide, the rest remaining in solution in the form of vanadyl salt. H. Rose called attention to the inaccuracy of this method, but this has not prevented its being recommended in some of the recent works on analytical chemistry. The author has carefully tested the method and found it useless.

Separation of Vanadium from Arsenic Acid

Most minerals containing vanadium also contain arsenic, and after extracting the melt, obtained by fusion with sodium carbonate and niter, *with water*, both elements go into solution. For their separation, make the solution acid with dilute sulfuric acid and introduce sulfur dioxide into the hot liquid; the vanadic acid is reduced to vanadyl salt and the arsenic to arsenious acid. After boiling to remove the excess of sulfur dioxide, saturate the solution with hydrogen sulfide and filter off the

* On expelling the sulfuric acid, there is finally formed some green and brown crystals of a compound of vanadic acid with sulfuric acid; these are decomposed only at a faint-red heat.

precipitate of arsenic trisulfide. Remove hydrogen sulfide from the filtrate by boiling, evaporate with nitric acid to form vanadic acid again, make the solution alkaline with sodium carbonate, and determine the vanadium by one of the above methods.

Separation of Vanadium from Phosphoric Acid

If the aqueous solution obtained after the soda-niter fusion contains phosphoric as well as vanadic acid, both are precipitated by mercurous nitrate. By igniting and weighing the washed precipitate the sum of the $V_2O_5 + P_2O_5$ is obtained. When P_2O_5 is present the V_2O_5 does not melt, but only sinters together. Fuse the ignited oxides with an equal weight of sodium carbonate, dissolve the melt in water, make the solution acid with sulfuric acid and boil with sulfurous acid to reduce the vanadic acid to vanadyl sulfate; the latter will be recognized by the pure blue color which the solution assumes. Pass carbon dioxide into the boiling solution until the excess of sulfurous acid is removed, and then allow to cool. To the cold solution, now about 100 ml. in volume, add 200 ml. of a 75 per cent solution of ammonium nitrate and 50 ml. of ammonium molybdate solution (cf. Remark, below). Heat the solution to about 60°, set aside and allow to stand for one hour. Decant the clear liquid through a filter, and wash three times by decantation with 50 ml. of the proper wash liquid (see *Phosphoric Acid*). Dissolve the precipitate by pouring 10 ml. of 8 per cent ammonia through the filter into the beaker containing the bulk of the precipitate and finally wash the filter with 30 ml. of water. To this solution add 20 ml. of a 34 per cent ammonium nitrate solution and 1 ml. more of ammonium molybdate, heat just to boiling, and reprecipitate the phosphoric acid by the addition of 20 ml. of hot 25 per cent nitric acid. Determine the phosphoric acid by the method of Woy (see *Phosphoric Acid*). Deduct the amount of P_2O_5 found from the sum of the oxides to get the weight of V_2O_5.

Remark. — A. Gressly tested this method in the author's laboratory and made the interesting observation that if about 0.15 g. of V_2O_5 was present with 0.1 g. P_2O_5, no trace of the latter could be detected according to the procedure of Woy, not even on boiling the solution. On the other hand, an immediate precipitation was produced if a stronger solution of ammonium molybdate were used (75 g. of ammonium molybdate dissolved in 500 ml. of water) and this solution poured into 500 ml. of nitric acid, *d.* 1: 2.

The above-described separation gives correct results only when the vanadium is present as vanadyl sulfate; if vanadic acid is present it is precipitated with the phosphoric acid. If the solution is allowed to stand after the addition of the ammonium molybdate, the vanadyl sulfate is gradually oxidized to vanadic acid; the precipitate therefore should not be allowed to stand long before filtering. A method for determining phosphorus in vanadium steel will be on page 283.

Separation of Vanadium from Molybdenum

Precipitate the molybdenum as sulfide from sulfuric acid solution by the action of hydrogen sulfide under pressure as described on p. 264. Ignite and weigh as MoO_3.

Boil off hydrogen sulfide from the filtrate and determine vanadium as described under the Separation of Vanadium from Arsenic Acid on p. 280.

Determination of Vanadium and Chromium in Iron Ores and Rocks

As vanadium often occurs in many ores of iron and in rocks, although in very small amounts, it is often of interest and of importance to be able to determine it in such cases. For this purpose, W. F. Hillebrand* proceeds as follows:

Fuse 5 g. of the finely powdered mineral with 20 g. sodium carbonate and 3 g. potassium nitrate over the blast-lamp. Extract the fused mass with water, add a few drops of alcohol to reduce the green manganite and filter off the residue.†

The aqueous solution contains sodium vanadate and often phosphate, chromate, molybdate, aluminate, and considerable silicate as well. First of all, remove the aluminium and the greater part of the silicic acid by nearly neutralizing the alkaline solution with nitric acid.‡ It is very important not to make the solution acid at this point on account of the reducing action of the nitrous acid set free from the nitrite formed during the fusion. Evaporate the nearly neutral solution to approximate dryness, take up in water, and filter.§

Treat the cold alkaline solution with an almost neutral solution of mercurous nitrate until no further precipitation takes place. The somewhat voluminous precipitate contains, besides mercurous carbonate, also mercurous chromate, vanadate, molybdate, arsenate, and phosphate, if the corresponding elements are present in the mineral. If the precipitate is too bulky, cautiously add a little nitric acid, and then a drop of mercurous nitrate in order to see if the precipitation is complete.

Heat the liquid to boiling, filter, wash the precipitate with water containing ammonium nitrate, dry, and ignite in a platinum crucible at as

* *U. S. Geol. Survey Bull.*, 700.

† If considerable vanadium is present, the insoluble residue may contain vanadium and should be fused with soda-niter again.

‡ Determine the amount of nitric acid necessary to neutralize 20 g. of sodium carbonate by a blank test.

§ The residue of aluminium hydroxide and silicic acid rarely contains vanadium, but often does contain chromium. If it is desired to determine the latter, evaporate the residue to dryness with hydrofluoric and sulfuric acids, fuse the dry mass with soda and niter again, and add the aqueous solution of the melt to the main solution.

low a temperature as possible. Fuse the ignited residue with a little sodium carbonate, extract the melt with water and, if yellow-colored, filter into a 25-ml. flask and determine the amount of chromium colorimetrically by comparing its color with a carefully-prepared solution of potassium chromate.

Then slightly acidify the solution with sulfuric acid, and precipitate the molybdenum, arsenic, and traces of platinum by hydrogen sulfide in a pressure-flask. Filter off the precipitated sulfides, carefully ignite the filter together with the precipitate in a porcelain crucible, add a few drops of sulfuric acid and heat the crucible again until the acid is almost completely removed. On cooling the mass is colored a beautiful blue if molybdenum is present.

Expel hydrogen sulfide from the filtrate by boiling and introducing carbon dioxide at a volume of not over 100 ml. Then titrate the *hot* solution to a pink color with 0.01 *N* potassium permanganate solution (cf. Vol. Anal.). To obtain absolutely accurate results, reduce the solution again with sulfur dioxide and repeat the titration. The latter result is usually a trifle lower and should be taken as correct.

$$5\,V_2O_2(SO_4)_2 + 2\,KMnO_4 + 22\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + 10\,H_3VO_4 + 6\,H_2SO_4.$$

This method gives correct results only when the amount of chromium present is very small, which is true in most cases.

In case more than 5 mg. of chromium are present a correction must be made, for a measurable amount of permanganate is used up in oxidizing the chromium. This is determined by taking a solution containing the same amount of chromate as the analyzed solution, reducing it with sulfurous acid, and titrating with permanganate. The amount of permanganate now used must be subtracted from the amount used in the analysis, and from the difference the amount of vanadium can be calculated.

Determination of Vanadium and Molybdenum in Steel

*Modified Method of A. A. Blair**

Dissolve 2 g. of the steel in 50 ml. 6 *N* nitric acid, evaporate to dryness and bake the residue to decompose nitrates. Take up with hydrochloric acid and carry out the Rothe ether separation as described on p. 169. Practically all of the molybdenum will be dissolved in the ether and all the chromium, vanadium and nickel will be in the aqueous acid solution.

To determine molybdenum, evaporate the ether solution nearly to

* *J. Am. Chem. Soc.* **30**, 1228.

dryness by carefully heating over warm water, away from any flame. Add 10 ml. of sulfuric acid and again evaporate to remove hydrochloric acid. Cool, dilute with 100 ml. of water and reduce the ferric salt by adding ammonium bisulfite. Boil off the excess of sulfurous acid, cool, transfer to a pressure flask, saturate with hydrogen sulfide and determine molybdenum as MoO_3 according to page 264.

Take the aqueous-acid extract from the ether separation for the determination of vanadium. Remove the dissolved ether by heating on the water-bath, add nitric acid in excess and evaporate to remove hydrochloric acid. When the solution is almost sirupy, add 20 ml. of hot water and heat with a few drops of sulfurous acid to reduce any chromic acid that may have been formed, but take care not to reduce the vanadium. Boil and slowly pour the hot solution, while stirring, into an excess of a boiling 10 per cent solution of sodium hydroxide. One ml. of the alkali will neutralize about 0.4 ml. of 6 *N* nitric acid. Boil a few minutes, allow the precipitate to settle, filter and wash with hot water till free from alkali. The precipitates contain hydroxides of iron, chromium, nickel, copper, manganese, etc., and the filtrate contains sodium vanadate. To remove traces of chromium, make acid with nitric acid, boil and again neutralize with hot caustic soda. Make this last filtrate acid with acetic acid, heat to boiling and precipitate the vanadium with hot lead acetate solution. Filter off the yellow lead vanadate precipitate, dissolve it in hot dilute hydrochloric acid and, if much lead is present, evaporate the solution nearly to dryness, cover with alcohol and filter off the lead chloride. Evaporate off the alcohol and titrate the vanadium as in the preceding method.

In most cases it is unnecessary to remove the lead. Evaporate the hydrochloric acid solution to dryness, add 50 ml. of 12 *N* hydrochloric acid and again evaporate nearly to dryness. Add 10 ml. of concentrated sulfuric acid and evaporate to fumes. Cool, dilute to 150 ml., heat to 60° and titrate slowly with permanganate. One ml. of 0.1 *N* permanganate reacts with 0.00510 g. of vanadium.

Remark. — For the routine analysis of vanadium in steel, the American Society of Testing Materials has sanctioned the determination of vanadium without removing chromium. In this case, after the removal of the ether in the above procedure, add 25 ml. of concentrated sulfuric acid and evaporate to fumes. Cool, add 25 ml. of water and a slight excess of 2.5 per cent permanganate solution. Add 15 ml. of concentrated hydrochloric acid, again evaporate to fumes, cool, dilute to 150 ml. and titrate with permanganate at 60°.

Campagne* showed that good results can be obtained by reducing the vanadium by evaporation with hydrochloric acid when not more than 0.1 g. of vanadium is present. The reduction with sulfurous acid, as in the preceding method, is safer.

* *Compt. rend.*, **137**, 570 (1903).

METALS OF GROUP I

SILVER, LEAD, MERCUROUS MERCURY (AND THALLIUM)

The determination of lead and mercury has already been considered; it remains only to discuss the determination of silver.

SILVER, Ag. At. Wt. 107.88

Forms: AgCl and Ag

Determination as Silver Chloride, AgCl

Heat the solution, slightly acid with nitric acid, to boiling and precipitate the silver by the addition of hydrochloric acid, drop by drop, until no more precipitate is formed. Allow the precipitate to settle in a dark place, filter through a Gooch crucible and wash, first with water containing a little nitric acid until the chloride test can no longer be obtained and then twice with alcohol or water to remove the nitric acid. Dry the precipitate at 100° and finally at 130° till a constant weight is obtained. If it is not desired to use a Gooch crucible for this determination, filter off the silver chloride upon an ordinary washed filter, wash as before and dry at 100°. Transfer as much of the precipitate as possible to a weighed porcelain crucible, burn the filter (as described on p. 32) and add the ash of the filter to the main portion of the precipitate. Moisten with a little nitric acid and a drop or two of concentrated hydrochloric acid, dry on the water-bath and heat over a free flame until the silver chloride begins to melt. Weigh after cooling in a desiccator.

*Solubility of Silver Chloride.** One liter of water dissolves 0.00154 g. AgCl at 20° and 0.0217 g. at 100°. In water containing a *little* hydrochloric acid, the AgCl is less soluble than in pure water but as the quantity of hydrochloric acid is increased, the solubility of AgCl rises rapidly. Thus 1 liter of 1 per cent HCl dissolves only 0.0002 g. AgCl at 21°, but 1 liter of 5 per cent HCl dissolves 0.0003 g. and 1 liter of 10 per cent HCl dissolves 0.0555 g. AgCl. By melting the silver chloride there is always loss by volatilization.

Determination as Metal, Ag

Metallic silver is obtained by the ignition of silver oxide, carbonate, cyanide or the salt of an organic acid. In the latter case, the substance must be heated very cautiously at first in a covered crucible. When

* G. S. Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

the organic substance is completely charred, remove the cover from the crucible and heat until the carbon is completely burned; then weigh the crucible.

From the chloride, bromide (but not the iodide) and sulfide, the metal can be obtained by igniting in a current of hydrogen. The reduction of the chloride, bromide, and iodide can be effected very conveniently by passing the electric current through the substance after it has been melted together. Place the porcelain crucible containing the silver halide in a crystallizing dish and near it place a second crucible containing a little mercury and a small piece of zinc. Upon the silver salt place a small disk of platinum foil, fastened to a platinum wire which dips into the mercury in the other crucible. Fill the crystallizing dish with 1.5 *N* sulfuric acid so that the crucible is entirely covered with the acid and allow to stand over night. Next morning all of the silver salt will be found to be reduced. Remove the crucible from the acid, wash with water, dry, ignite and weigh. By this simple method, E. Lagutt obtained excellent results. If the silver halide has not been fused to a compact mass, small particles of the silver precipitate are likely to float around during the operation, and escape reduction.

Separation of Silver from Other Metals

As almost all metal chlorides* are soluble in dilute hydrochloric acid, silver is usually separated from the other metals by the addition of hydrochloric acid to the solution. If the solution contains mercurous salts these are oxidized before the addition of the hydrochloric acid by boiling with nitric acid.

For the separation of silver from gold and platinum in alloys consult pp. 239, 244 and 250.

Electrolytic Determination of Silver

Silver may be deposited from nitric acid solutions, from ammoniacal solutions and from potassium cyanide solution.

From nitric acid solution, the electrolysis succeeds under the following conditions: — 0.5 g. of silver in 150 ml. of 0.1 *N* nitric acid electrolyzed at 55–60° with the voltage kept between 1.35 and 1.38

* Thallous chloride is difficultly soluble in water. If thallium is present precipitate the silver from a nitrate solution by means of H_2S, ignite in a stream of hydrogen, and weigh as metal. To determine the thallium, evaporate the filtrate to dryness, dissolve the residue in a little water and precipitate the thallium by the addition of potassium iodide. Wash the thallous iodide precipitate with dilute potassium iodide solution, then with alcohol, dry at 150° and weigh as TlI.

volts. Add 5 ml. of alcohol to the bath to prevent the formation of peroxide at the anode. From 6–8 hours are required to precipitate the last traces of silver. Wash the electrode without interrupting the current and dry at 100°.

Determination of Silver in Alloys with Baser Metals by Dry Assay

The cupellation of a silver alloy is carried out in much the same way as discussed under the Determination of Gold. Use 0.5 g. of the alloy and first determine the approximate silver content by a trial assay. Cupel with 5 g. of lead and weigh the resulting button as described on p. 241. If the silver is 50 per cent or less use 8 g. of lead for the final assay. For each per cent of increase in silver content, use 0.1 g. less of lead until the content corresponds to 80 per cent silver. Then decrease the weight of lead more rapidly with increase in the silver content, using 3.5 g. of lead for a 90 per cent alloy, 2.3 g. of lead for a 93.5 per cent alloy, 1.75 g. of lead for a 95 per cent alloy and only 0.6 g. of lead for nearly pure silver. Unless care is taken to adjust the lead carefully to the silver content, the loss of silver during cupellation is likely to be serious.

For the final assay, cupel 0.5 g. of the alloy with the suitable quantity of lead and weigh the button. Correct for loss of silver by volatilization and absorption by the cupel, by cupelling in the same way and at the same time the corresponding quantities of pure silver and copper. Without this correction, the results are usually 0.4–1.1 per cent too low.

GRAVIMETRIC DETERMINATION OF THE ACID CONSTITUENTS (ANIONS)

GROUP I

HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, HYDROCYANIC, FERROCYANIC, FERRICYANIC, THIOCYANIC, AND HYPOCHLOROUS ACIDS

HYDROCHLORIC ACID, HCl. Mol. Wt. 36.47

Form: Silver Chloride, AgCl

A. The chlorine is present in solution either as free hydrochloric acid or as a chloride soluble in water.

B. It is present in the form of an insoluble chloride.

A. The Chloride is Present in Aqueous Solution

If only metals of the alkali or alkaline earth groups are present, make the cold solution slightly acid with nitric acid, slowly add silver nitrate with constant stirring until the precipitate coagulates and further addition of the reagent produces no more precipitation. Now heat the liquid to boiling, allow the precipitate to settle in the dark, filter through a Gooch crucible, and treat exactly as described in the determination of silver, p. 285.

If the aqueous solution contains a chloride of a heavy metal, it is not always possible to follow the above procedure. If, for example, substances are present which on boiling are changed to insoluble basic salts, it is evident that the precipitate of silver chloride would be contaminated with these substances and too high results would be obtained. This is particularly true of stannic and ferric salts. Ferrous salts, on the other hand, in case only little nitric acid is present, reduce silver nitrate to metallic silver on heating the solution; if enough nitric acid is present to prevent the reduction to silver, the danger of forming basic salts still remains to be feared. In such cases the precipitation is effected as before from a cold solution and the subsequent heating is omitted.

In all cases, however, it is better to first remove the heavy metal by precipitation with ammonia, caustic soda or sodium carbonate.

Example: Analysis of Commercial Tin Chloride

Tin chloride is obtained either as a solid salt corresponding to the formula $SnCl_4 + 5\,H_2O$, or as a concentrated aqueous solution. As both the solid salt and its concentrated solution are very hygroscopic, it is necessary to weigh out the portion for analysis from a stoppered vessel. It is best to proceed as follows:

Place a large sample of the substance (about 10 g.) in a tared weighing beaker, stopper and weigh. Dissolve in about 10 ml. of water, shaking until a homogeneous sirup is obtained. Again weigh the beaker and its contents. Weigh 4 more weighing beakers and into each place about 2 ml. of the sirup. Quickly stopper each beaker and weigh.

Determination of Tin. — Wash the contents of one of the weighing beakers into a 400–500-ml. beaker, dilute to about 300 ml. and add a few drops of methyl orange indicator solution, whereby the liquid is colored red. Add ammonium hydroxide solution (free from chloride) until the color of the solution is changed to yellow (an excess of ammonia must be carefully avoided for tin hydroxide is somewhat soluble in ammonia). To the neutral solution add 10 ml. of 3 *N* ammonium nitrate solution, boil one or two minutes, filter, wash with water containing ammonium nitrate, and weigh as SnO_2.

Determination of Chlorine. — Make the filtrate from the tin hydroxide precipitate acid with nitric acid, and precipitate in the cold with silver nitrate. Then heat the solution to boiling and, after the precipitate has settled, filter through a Gooch crucible, wash with cold water containing a little nitric acid, then with cold water or alcohol, dry at 130° C., and weigh.

The amount of tin and chlorine present is computed as follows: Let A = weight of the original solid salt, B = weight of the solid salt mixed with a little water; a = weight of the concentrated solution taken for analysis; p = weight of SnO_2 obtained and q = weight of silver chloride.

Then $$\frac{\text{Sn} \times p \times B \times 100}{SnO_2 \times a \times A} = \text{per cent Sn}$$

and $$\frac{\text{Cl} \times q \times B \times 100}{AgCl \times a \times A} = \text{per cent Cl.}$$

This analysis may be accomplished much more rapidly by a volumetric process. (Consult Vol. Anal.)

If antimony or stannous compounds are present, the above procedure cannot be used. It has been proposed to add tartaric acid to the solution, then dilute with water and precipitate the chlorine with silver nitrate. It is better, however, to proceed as follows: Precipitate the

antimony by hydrogen sulfide, remove the excess of the latter by passing carbon dioxide through the solution, filter and wash the precipitate with hot water. Make the filtrate slightly ammoniacal, add a little hydrogen peroxide or potassium percarbonate (both reagents must be free from chloride) and boil the solution until the excess of the peroxide is destroyed. By this treatment traces of hydrogen sulfide remaining in the solution are oxidized to sulfuric acid. After cooling, make acid with nitric acid, and determine the chlorine as described above.

According to this method, chlorine may be determined in the presence of large amounts of hydrogen sulfide without difficulty.

It is less practical to proceed as follows: Add an excess of ammonium hydroxide to the filtrate from the antimony sulfide and precipitate the hydrogen sulfide by the addition of ammoniacal silver nitrate solution. Filter off the deposited silver sulfide, wash with ammonia, and precipitate the silver chloride from the filtrate by acidifying with nitric acid.

B. Analysis of an Insoluble Chloride

Boil the substance with sodium carbonate solution* (free from chloride), and determine the chlorine in the filtrate as described above.

Some chlorides, *e.g.*, silver chloride, many minerals such as apatite,† sodalite, and rocks containing the latter, are not decomposed by boiling them with sodium carbonate. In such cases, the substance must be *fused* with sodium carbonate.

Mix silver chloride with three times as much sodium carbonate and heat in a porcelain crucible until the mass has sintered together. Extract with water, filter off the insoluble silver, and determine the chlorine in the filtrate as under (*a*).

For the determination of chlorine in rocks, fuse 1 g. of the finely-powdered material with four or five times as much sodium carbonate (or with a mixture of equal parts sodium and potassium carbonates) at first over a Bunsen burner, afterward over a Méker burner or the blast-lamp. Extract the melt with hot water. After cooling, add methyl orange indicator solution, acidify with nitric acid and allow to stand overnight. If silicic acid has precipitated out by the next morn-

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* Mercurous chloride is decomposed only slowly by sodium carbonate solution, but readily acted upon by potassium or sodium hydroxide.

† According to Jannasch, chlorine in apatite may be determined by treating the finely powdered mineral with nitric acid and silver nitrate on the water-bath. Everything goes into solution with the exception of silver chloride, which is filtered off and weighed. (This does not apply to a sample of apatite contaminated with silica or silicates.)

ing, add a little ammonia, boil the solution, filter, and wash with hot water. Add a little nitric acid to the cold filtrate and determine the chlorine as above.

If there is no separation of silicic acid on acidifying the water extraction of the fusion with nitric acid,* precipitate the chlorine at once from the cold solution.

Free Chlorine

If it is desired to determine gravimetrically the amount of chlorine in a sample of chlorine water, it is not feasible simply to add silver nitrate, for all of the chlorine is not precipitated as silver chloride; a part of it remains in solution as soluble chloric acid:

$$3\,Cl_2 + 3\,H_2O + 5\,AgNO_3 = 5\,AgCl + HClO_3 + 5\,HNO_3.$$

The chlorine, therefore, must be changed to hydrochloric acid or to one of its salts before attempting to precipitate with silver nitrate. This may be accomplished in several ways:

1. Transfer a definite amount of the chlorine water by means of a pipet to a flask containing ammonia water and after mixing heat the solution to boiling. After cooling acidify with nitric acid and precipitate with silver nitrate. The ammonia converts the chlorine to ammonium chloride.

$$8\,NH_4OH + 3\,Cl_2 = 6\,NH_4Cl + N_2 + 8\,H_2O.$$

2. Treat the chlorine water with an excess of sulfurous acid, make the solution ammoniacal, add hydrogen peroxide, and boil the liquid until the excess of hydrogen peroxide is removed. Cool, acidify with nitric acid, dilute with water, and precipitate the chlorine by means of silver nitrate.

3. Treat the chlorine water with dilute sodium hydroxide solution, and add an aqueous solution of sodium arsenite (arsenic trioxide dissolved in sodium carbonate) until a drop of the liquid will not turn a piece of iodo-starch paper blue. Then make acid with nitric acid and precipitate the chlorine by a soluble silver salt.

If the solution contains both free chlorine and hydrochloric acid determine the total chlorine by one of the above methods, and the free chlorine in a separate sample by a volumetric process (see Iodimetry.)

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* According to W. F. Hillebrand, there is no separation of silicic acid to be feared from 1 g. of the substance.

Determination of Chlorine in Non-electrolytes (Organic Compounds)

*A. Method of Carius**

Principle. — The method is based upon the fact that all organic compounds are decomposed by heating with concentrated nitric acid at a high temperature under pressure. If the substance contains halogen, sulfur, phosphorus, or arsenic, it is first set free as such, but on account of the reducing action of the nitrous acid formed it is then changed over into its hydrogen compound. The latter, however, is partly oxidized by the nitric acid. The reaction is therefore a reversible one. If, on the other hand, the substance is heated under the same conditions with nitric acid in the presence of silver nitrate, the halogen hydride is converted into silver halide as fast as it is formed and the halogen is in this case quantitatively changed into its silver salt. Sulfur, phosphorus, and arsenic are oxidized in the same way to sulfuric, phosphoric, and arsenic acids and any metals present form nitrates.

Procedure for the Halogen Determination

Take a tube made of difficultly fusible glass about 50 cm. long, 2 cm. in diameter, with walls about 2 mm. thick. Seal one end, clean thoroughly and dry by sucking air through it.

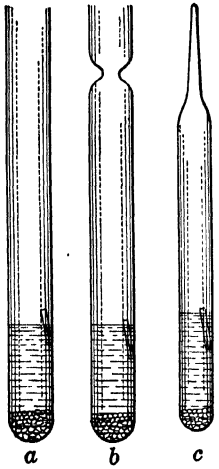


FIG. 64.

Transfer about 0.5 g. of powdered silver nitrate (or in the case of substances rich in halogen as much as 1 g. may be used) to the tube by pouring the powder through a cylinder made by rolling up a piece of glazed paper and shoving the paper into the tube until it reaches about the middle of it. Pour into the tube through a funnel whose stem is about 40 cm. long, about 40 ml. of pure nitric acid (*d.* 1.5) free from chlorine. In this way only the lower half of the tube is wet with the acid. Incline the tube to one side and introduce a small glass tube, closed at one end and containing from 0.15–0.2 g. of the substance (this smaller tube should be about 5 cm. long and 5 mm. wide). As soon as the tube containing the substance has reached the acid, it remains suspended (Fig. 64, *a*). It is very important that the substance should not come in contact with the acid before the tube is closed at the upper end, as otherwise there is likelihood of some halogen escaping.

Now heat the upper end of the tube very cautiously in the flame of the blast-lamp until the tube begins to soften and thicken (Fig. 64, *b*). Then draw out into a thick-walled capillary 3–5 cm. long, and fuse the end together (Fig. 64, *c*).

* *Ann. Chem. Pharm.*, **136**, 129 (1865) and *Z. anal. Chem.*, **4**, 451 (1865).

After the tube has become cold, envelop it in asbestos paper, carefully shove it into the iron mantle of a " bomb furnace," and gradually heat. Aliphatic substances are usually decomposed by heating 4 hours at 150–200°; substances of the aromatic series usually require from 8–10 hours' heating at 250–300°, while in some cases an even longer heating at a higher temperature is necessary. The time and temperature must be found out for each substance by experiment. The decomposition is complete when on cooling the contents of the tube neither crystals nor drops of oil are to be recognized.* Regulate the heating so that after 3 hours the temperature of about 200° is reached, after 3 hours more 250–270°, and finally after another 3 hours a temperature of about 300° is attained.† After the heating is finished, allow the tube to cool completely in the furnace, remove the iron mantle together with the tube, and by slightly inclining the mantle bring the capillary of the tube out into the open air. In most cases a drop of liquid will be found in the point of the latter. In order not to lose this, carefully heat the outer point of the capillary with a free flame, and by this means drive back the liquid into the other part of the tube. Now heat the point of the capillary more strongly‡ until the glass softens, and a hole is blown in the soft glass as a result of the pressure within the tube. The gas escapes with a hissing sound. When the contents of the tube are at the atmospheric pressure, make a scratch upon it with a file just below the capillary, and touch this with a hot glass rod, whereby the tube usually breaks and the upper part can be removed. Then carefully pour out the contents of the tube into a fairly large beaker, without breaking the little tube into which the substance was weighed, and wash out the inner part of the tube as well as its capillary with water. Dilute the liquid in the beaker to about 300 ml. and heat to boiling. After cooling, filter off the insoluble silver halide through a Gooch crucible and, after washing and drying at 130°, determine its weight.

If it is thought that the precipitate is contaminated by fragments of broken glass, as is often the case even with careful work, decant the clear liquid through a filter, wash the residue by decantation with very dilute nitric acid to the disappearance of the silver reaction, and dissolve the

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* Sometimes, with substances rich in sulfur, crystals of nitrosyl sulfuric acid are formed and adhere to the sides of the tube. They are easily distinguished from crystals of the undecomposed substance.

† Such a high pressure is often attained that the tube bursts as soon as it is heated very hot. In such cases heat to only 200°, allow to cool, open the capillary and release the pressure. Then fuse together again and heat to the desired temperature.

‡ Before heating, the tube and the hand should be wrapped in a towel to avoid accidents.

residue (except when it is silver iodide) in warm ammonia water. Filter the solution through the same filter, but collect the filtrate this time in a fresh beaker. After washing the filter with dilute ammonia, acidify the filtrate with nitric acid, heat to boiling, and after allowing the silver chloride or bromide to settle in the dark, filter through a Gooch crucible, dry at 130°, and weigh.

In the case of silver iodide, it cannot be dissolved in ammonia and in this way separated from splinters of glass. In this case filter off the precipitate, together with the glass, through an ordinary washed filter (not a Gooch crucible), wash with dilute nitric acid, then once with alcohol in order to remove the nitric acid, and dry at 100°. Transfer as much of the precipitate as possible to a watch-glass, burn the filter, and drop the ash into a weighed porcelain crucible. Add a little dilute nitric acid (to change any reduced silver into the nitrate), evaporate off the liquid on the water-bath, add a few drops of water and a drop of pure hydriodic acid, and again evaporate the contents of the crucible to dryness. Now add the main part of the precipitate, heat until it begins to fuse, and weigh. Cover the mass in the crucible with pure dilute sulfuric acid, add a piece of chemically pure zinc, and allow the crucible to stand overnight. After this time the silver iodide will be completely reduced to metallic silver. Remove the zinc, and wash the residue by decanting several times with water until the iodide reaction can no longer be detected. Warm the residue with dilute nitric acid upon the water-bath, in order to dissolve the silver, filter the solution through a small filter; wash the latter with water and dry. Ignite this filter in a crucible and weigh the residue (the glass). This second weight deducted from the former gives the amount of silver iodide present.

This method is also suitable for obtaining lead and mercury from organic compounds in a form which can be precipitated by hydrogen sulfide.

The method of Carius is by far the best for the determination of halogens in organic substances when only one of the halogens is present. If two or three of them are present at the same time, the "lime method" is to be preferred.

B. The Lime Method

Into a glass tube made of difficultly fusible glass (about 40 cm. long, 1 cm. wide and closed at one end), introduce a layer of lime (free from chloride) from 5–6 cm. long, then about 0.5 g. of substance, and finally 5 cm. more of lime. Mix the substance thoroughly with the lime by means of a copper wire wound into a spiral. Nearly fill the tube with

lime, place on its side, and gently tap, so that a small canal is formed above the lime. Place the tube in a small combustion furnace (cf. Carbon) and heat. First heat the front end of the tube, free from substance, to a dull redness, then the back end, and afterwards light the other burners, one after another, until finally the whole tube is at a dull-red heat. After cooling, transfer the contents of the tube to a large beaker and dissolve the lime in dilute nitric acid free from chlorine. Filter off the carbon, and precipitate the halogen with silver nitrate.

If the lime contains calcium sulfate, this is reduced to sulfide, so that some silver sulfide is likely to be precipitated with the silver halide. In this case treat the solution with hydrogen peroxide (free from halogen) before enough nitric acid has been added to make the solution acid, boil the liquid to remove the excess of the reagent, then acidify, filter, and precipitate with silver nitrate.* In the analysis of substances rich in nitrogen, it is possible that some soluble calcium cyanide will be formed. In this case care must be taken that the silver precipitate contains no silver cyanide (cf. Separation of Cyanogen from Chlorine-Bromine, and Iodine, p. 303).

C. The Sodium Peroxide Method

Heat 0.2–0.3 g. of the substance with a mixture of 10 g. of powdered potassium hydroxide and 5 g. sodium peroxide in a nickel or iron crucible. Heat first in the hot closet at 85°. After some time remove the crucible from the closet and heat over a small flame, gradually raising the temperature until the flux is melted. Cool, extract the melt with water, filter and determine the halogen as silver salt after adding nitric acid.

Remark. — For an excellent volumetric method for determining chlorine see the Volhard method.

HYDROBROMIC ACID, HBr. Mol. Wt. 80.93

Form: Silver Bromide, AgBr

Hydrobromic acid is determined exactly the same as hydrochloric acid. This is also true of the determination of free bromine, and bromine in non-electrolytes.

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* W. Biltz (*Chem. Ztg.*, **1903**, Rep. 142) separates the halides from sulfide by treating the precipitated silver salts with an ammoniacal sodium thiosulfate solution, whereby the silver halide goes into solution, from which the silver is precipitated as silver sulfide, by adding ammonium sulfide, and determined as silver.

HYDRIODIC ACID, HI. Mol. Wt. 127.93

Forms: Silver Iodide, AgI, and Palladous Iodide, PdI_2

(*a*) *Determination as Silver Iodide*

The determination of hydriodic acid is carried out in exactly the same way as the analysis of hydrochloric acid. If it is desired to filter the silver iodide through an ordinary washed filter instead of through a Gooch crucible, the procedure described on p. 285 is used, converting the reduced metal to iodide by dissolving in nitric acid and adding hydriodic acid. In case there is no hydriodic acid at one's disposal, place the main portion of the precipitate in a weighed porcelain crucible and heat until it begins to melt and then weigh. Place the filter ash in another crucible, and treat with nitric and hydrochloric acids, whereby the silver and any unreduced iodide are changed to silver chloride. Weigh the silver chloride and add the equivalent amount of silver iodide to the weight of the main part of the precipitate.

(*b*) *Determination as Palladous Iodide*

This important method for the separation of iodine from bromine and chlorine is carried out as follows:

Make the solution acid with hydrochloric acid, and add palladous chloride solution until no more precipitate is formed. After standing one or two days in a warm place, filter off the brownish-black precipitate of palladous iodide through a Gooch crucible, or through a tared filter that has been dried at 100°, wash with warm water, dry at 100° and weigh as PdI_2.

According to Rose, the PdI_2 may be changed to palladium by igniting in a current of hydrogen, and from the weight of the palladium the amount of iodine calculated.

SEPARATION OF THE HALOGENS FROM ONE ANOTHER

1. Separation of Iodine from Chlorine

(*a*) *The Palladous Iodide Method*

Determine the iodine as palladous iodide, and in a second sample determine the sum of the chlorine and iodine from the weight of their insoluble silver salts.

(*b*) *Method of Gooch*

This method depends upon the fact that in a dilute acid solution of the 3 halides, nitrous acid reacts only with the iodide:

$$2\,KI + 2\,KNO_2 + 4\,H_2SO_4 = 4\,KHSO_4 + 2\,NO + 2\,H_2O + I_2.$$

Iodine is liberated and escapes from the solution on boiling. In one sample, therefore, precipitate the halogens together in the form of their silver salts, in a second sample determine the amount of the chlorine after setting free the iodine by means of nitrous acid, and determine the amount of iodine by difference. In order to obtain correct results by this method, the solution must be very dilute when it is boiled to expel the iodine; otherwise some chlorine escapes.

Procedure. — Dissolve 0.5 of the halide mixture in 600 ml. of water in a liter flask, treat with 2–3 ml. of dilute sulfuric acid, add 0.5–1 g. of solid potassium nitrite (free from halogen), and boil the solution until entirely colorless; in most cases this is accomplished in about three-quarters of an hour. Then add silver nitrate solution, and allow the resulting precipitate to settle. Filter through a Gooch crucible, and weigh.

(c) *Method of Jannasch**

Jannasch proceeds in exactly the same way as Gooch, but instead of letting the iodine escape, he collects in it an aqueous solution of sodium hydroxide and hydrogen peroxide, whereby it is transformed to sodium iodide and can be subsequently determined as silver iodide. In the other solution the chlorine is determined in the usual way.

Procedure. — Place the solution containing 0.5 g. of the two halides in a $1\frac{1}{2}$-liter round-bottomed flask and dilute to a volume of 600–700 ml. Like a wash-bottle, provide this flask with one glass tube reaching to the bottom, through which vapor can be conducted into the flask, and with another shorter tube for the escape of gas. Connect this second tube with an Erlenmeyer flask for a receiver, and this in turn with a Péligot tube. Place about 50 ml. of pure 5 per cent sodium hydroxide solution in the Erlenmeyer flask, add an equal volume of hydrogen peroxide free from chlorine, and cool the mixture by surrounding the flask with ice or snow. Likewise fill the Péligot tube with a suitable amount of caustic soda and hydrogen peroxide. Now add from 5–10 ml. of 6 *N* sulfuric acid and 10 ml. of 10 per cent sodium nitrite solution to the solution containing the halides. Immediately close the flask, and heat the contents over a free flame while at the same time conducting steam into it. As soon as the liquid begins to boil, the space above is filled with violet vapors of iodine, which are gradually driven over into the Erlenmeyer flask, where, with evolution of oxygen, they are completely absorbed by the hydrogen peroxide solution. The iodine is changed into sodium iodide and sodium hypoiodite by means of the dilute alkali:

$$I_2 + 2\,NaOH = NaI + NaIO + H_2O.$$

* *Z. anorg. Chem.* I, 144, and *Prakt. Leit. der Gewichts-analyse.*

The sodium hypoiodite, however, is reduced by the hydrogen peroxide to sodium iodide:

$$NaIO + H_2O_2 = H_2O + O_2 + NaI.$$

When all the iodine is driven over into the receiver (which is always the case after the solution in the flask has become colorless and has been boiled for twenty minutes longer), remove the delivery-tube between the distilling-flask and the Erlenmeyer flask, wash the liquid within with hot water into the Erlenmeyer and stop the current of steam. Add the contents of the Péligot tube to the Erlenmeyer flask and heat the solution to boiling to remove the excess of hydrogen peroxide. After cooling, make the liquid acid with a little sulfuric acid; this always causes a yellow coloration due to free iodine.* Treat the solution, therefore, with a few drops of sulfurous acid, to decolorize it. Add an excess of silver nitrate and a little nitric acid, boil the liquid, and filter the silver iodide into a Gooch crucible. Dry at 130° and weigh.

For the chlorine determination, transfer the contents of the distilling-flask to a beaker and determine the chlorine as silver chloride.

Determination of the Halogens by Indirect Analysis

2. Determination of Bromine together with Chlorine

Principle. — In this method the sum of the weights of the silver salts of the 2 halogens is first determined and afterwards the silver bromide is converted to silver chloride by heating in a current of chlorine.

Procedure. — To the neutral solution containing about 0.5 g. of halides add a little nitric acid (free from chlorine) and precipitate in the cold by the addition of a slight excess of silver nitrate. Heat the liquid to boiling, with frequent stirring, cool after the precipitate has coagulated, and filter off the precipitate into a 15 cm. long, asbestos filter-tube made of difficultly fusible glass. Dry the precipitate at 150° and weigh after cooling.

For the transformation of the bromide into chloride, shove the asbestos forward a little in the tube by means of a glass rod (in order that the gas may pass through it more readily), fasten the tube in a

* If the above directions are closely followed, there should not be much separation of iodine. It may be caused by the presence of a small amount of nitrous acid which is not oxidized to nitric acid by hydrogen peroxide; or, if the contents of the Erlenmeyer flask are not kept cool, appreciable amounts of sodium iodate ($NaIO_3$) are formed, and the latter is not reduced by hydrogen peroxide. In this case there is a separation of a considerable amount of iodine on acidifying the solution, but the addition of sulfurous acid changes it to iodide without loss.

slightly inclined position, and pass a current of dry chlorine gas through it. At the same time cautiously heat the tube by moving a small flame back and forth. During the first half hour the precipitate should not be heated hot enough to melt it; finally, however, raise the temperature until it *begins* to melt, after which replace the chlorine by air, cool and again weigh.

If p represents the weight of silver chloride and bromide first obtained, q the weight after the precipitate has been completely changed to chloride, x the weight of silver chloride in the first precipitate and y the weight of silver bromide, then $x + y = p$ and $x + \frac{\text{AgCl}}{\text{AgBr}} y = q$. Since $\frac{\text{AgCl}}{\text{AgBr}} = 0.7633$, the solution of the above two equations gives $y = 4.224\ (p - q)$ and $x = p - y$, from which the percentage of chlorine and bromine can be computed.

3. Determination of Iodine together with Chlorine

The same procedure is used as above described.

If p represents the weight of silver iodide + silver chloride, q the weight after the silver has been converted to chloride, x the weight of silver chloride and y the weight of silver bromide in the first precipitate, $y = 2.567\ (p - q)$ and $x = p - y$.

4. Determination of Bromine in the Presence of Iodine

In this case p represents the weight of the silver bromide and silver iodide, q as before the corresponding weight of silver chloride, x the weight of silver iodide in the first precipitate and y the weight of silver bromide,

$$x + y = p, \qquad \frac{\text{AgCl}}{\text{AgI}} x + \frac{\text{AgCl}}{\text{AgBr}} y = q$$

$$x = 4.996\ p - 6.545\ q$$

$$y = p - x.$$

5. Determination of Iodine, Bromine and Chlorine

In one portion of the substance determine the weight, p, of silver salts obtained by precipitation and change this over to silver chloride of weight q. In another portion of the same weight of original substance, determine the weight t of palladous iodide corresponding to the iodine content. Then if x represents the weight of silver chloride and y the

weight of silver bromide in the first precipitate, the following relationships hold:

$1.303\,t$ = weight of silver iodide in the first silver precipitate and $0.7951\,t$ is the corresponding weight of silver chloride.

$p - 1.303\,t$ = weight of silver bromide and silver chloride in the first precipitate

$q - 0.7951\,t$ = weight of silver chloride in the second precipitate equivalent to the chloride and bromide.

$$x + y = p - 1.303\,t \qquad x + 0.7633\,y = q - 0.7951\,t$$
$$y = 4.224\,[(p - 1.303\,t) - (q - 0.7951\,t)]$$
$$x = p - 1.303\,t - y.$$

Instead of determining the iodine as palladous iodide it may be removed as on p. 297, *b*, by treatment with nitrous acid and the weight of the silver bromide + silver chloride obtained.

Another method* depends upon the fact that treatment of silver halides with potassium dichromate and concentrated sulfuric acid causes the following decompositions:

$$6\,AgCl + K_2Cr_2O_7 + 14\,H_2SO_4 = 6\,AgHSO_4 + 2\,KHSO_4 + 2\,Cr(HSO_4)_3 + 7\,H_2O + 3\,Cl_2\uparrow.$$

$$6\,AgBr + K_2Cr_2O_7 + 14\,H_2SO_4 = 6\,AgHSO_4 + 2\,KHSO_4 + 2\,Cr(HSO_4)_3 + 7\,H_2O + 3\,Br_2\uparrow.$$

$$2\,AgI + 2\,K_2Cr_2O_7 + 18\,H_2SO_4 = 2\,AgHSO_4 + 4\,KHSO_4 + 4\,Cr(HSO_4)_3 + 8\,H_2O + 2\,HIO_3.$$

All the bromine and chlorine can be distilled off but the silver and all the iodine remain behind. By introducing SO_2 into the diluted acid, the iodic acid is reduced to hydriodic acid and silver iodide precipitates. After filtering this off, the remaining silver can be precipitated as iodide. Thus for the determination of the three unknowns, three simultaneous equations can be formulated.

Procedure. — Precipitate a mixture of silver chloride, bromide and iodide in the usual manner, filter into a small asbestos filtering tube and weigh after drying at 150°. Call the weight of original substance *A* and that of the mixed halides *a*. Place the dry precipitate together with the asbestos in an Erlenmeyer flask and for each 0.3 g. of silver salt add 2 g. of pure, potassium dichromate and 30 ml. of concentrated sulfuric acid. Heat 2 hours at 95°. Toward the last, pass a stream of air through the liquid until all of the chlorine and bromine has been

* Bech, *Chem. Ztg.*, **39**, 405 (1915), Baubigny, *Compt. rend.*, **127**, 1219 (1898).

expelled. The decomposition takes place more rapidly if the precipitate is treated with the oxidizing mixture without drying it except by suction but this necessitates the determination of the mixed silver salts in a separate sample. After the oxidation of the silver salts is complete, dilute with 300 ml. of water, filter off the asbestos and to the filtrate add sodium bisulfite solution drop by drop until a faint permanent odor of sulfur dioxide is obtained. Filter off and weigh the silver iodide precipitate; call this weight b. In the filtrate precipitate the rest of the silver by adding potassium iodide. Call this weight c. Compute the percentages of chlorine, bromine and iodine as follows:

$$\frac{54.06\ b}{A} = \text{per cent iodine}$$

$$\frac{63.8\ c - 80.0\ (a - b)}{A} = \text{per cent chlorine}$$

$$\frac{179.8\ (a - b) - 109.7\ c}{A} = \text{per cent bromine.}$$

HYDROCYANIC ACID, HCN. Mol. Wt. 27.02

Forms: Silver Cyanide, AgCN, and Metallic Silver, Ag

Free hydrocyanic acid as well as the cyanides of the alkalies and alkaline earths are decomposed quantitatively by silver nitrate with the formation of insoluble silver cyanide.

If, therefore, it is desired to determine gravimetrically the amount of cyanide present in an aqueous solution of hydrocyanic acid or of an alkaline cyanide, treat the cold solution with an excess of silver nitrate, stir, make faintly acid with nitric acid, allow the precipitate to settle and filter through a weighed filter, dry at 110° and weigh. To confirm the result, place the silver cyanide in a porcelain crucible burn the filter in a platinum spiral, add its ash to the main portion of the precipitate, and ignite the contents of the crucible, at first gently and finally more strongly but not enough to melt the silver. Cool and weigh the silver.

By the decomposition of the silver cyanide, difficultly volatile paracyanide is formed, but this is gradually burned away by igniting the contents of the open crucible.

Example: Determination of Hydrocyanic acid in Bitter-almond Water. — Bitter-almond water contains cyanogen as free hydrocyanic acid and as ammonium cyanide, but the greater part is present as mandelic acid nitrile, $C_6H_5CH(OH)CN$. The latter compound is not decomposed in aqueous solution by means of silver nitrate, but is readily acted upon by the latter if the solution is made ammoniacal after the addition of the silver nitrate and then made acid.

The gravimetric determination of the cyanogen present is performed according to the method of Feldhaus* as follows:

Treat 100 g. of bitter-almond water with 10 ml. of a 10 per cent silver nitrate solution, add 2–3 ml. of concentrated ammonium hydroxide and immediately acidify with nitric acid. Allow the precipitate to settle, and determine the HCN as described above.

Liebig's volumetric method is much more satisfactory for this determination (see Part II, Precipitation Analyses).

If it is desired to determine the amount of cyanogen in a solid alkali cyanide, dissolve a weighed amount of the salt in water containing silver nitrate, and make the solution acid with nitric acid and treat the precipitate as above.

If the cyanide is dissolved in water before the addition of the silver nitrate, there is always a slight loss of hydrocyanic acid.

Some complex cyanides are quantitatively decomposed by silver nitrate, *e.g.*, those of nickel, zinc, and copper (the latter only slowly); while others such as the ferro- and ferricyanides of the alkalies (and mercuric cyanide) are not.

Determination of Cyanogen in Mercuric Cyanide, Method of Rose

Mercuric cyanide is a non-electrolyte and is consequently not precipitated by silver nitrate, but it is acted upon by hydrogen sulfide with the formation of insoluble mercuric sulfide and hydrocyanic acid:

$$Hg(CN)_2 + H_2S = HgS + 2\,HCN$$

This reaction, however, cannot take place in neutral or acid solutions on account of the volatility of the hydrocyanic acid; it must be performed in an alkaline solution. In order to avoid the introduction of an excess of hydrogen sulfide into the solution, the following procedure is necessary:

Treat the aqueous solution of the mercuric cyanide with about twice as much zinc sulfate dissolved in ammonia. If this should cause a turbidity, add enough ammonia to clear it up and slowly add hydrogen sulfide water. This causes at first a brown precipitate which becomes black on stirring. Continue the addition of hydrogen sulfide water until the upper liquid shows a *pure white* precipitate of zinc sulfide. The zinc sulfate, therefore, serves, as it were, as an indicator, inasmuch as the pure white precipitate will not be formed until the mercury is completely precipitated. Filter off the precipitated sulfides and wash

* *Z. anal. Chem.* **3**, 34 (1864).

with dilute ammonia. The filtrate contains all of the hydrocyanic acid. Add to it an excess of silver nitrate, make acid with nitric acid, filter and determine the weight of silver in the silver cyanide as described on p. 301.

Determination of Hydrocyanic Acid and Halogen Hydride in the Presence of One Another, according to Neubauer and Kerner*

Treat the solution with silver nitrate in the cold, add nitric acid to faintly acid reaction and heat to coagulate the precipitate. Filter, dry at 130° and in this way determine the total weight of the silver salts. Place a definite amount of the precipitate in a porcelain crucible, heat until it is completely melted, and reduce with zinc and sulfuric acid as described on p. 294. Dilute with water, filter off the metallic silver and para-cyanogen and determine the halogen in the filtrate according to p. 288 *et. seq.*

The above separation can be more satisfactorily effected by means of a volumetric process (see Precipitation Analyses).

THIOCYANIC ACID, HCNS. Mol. Wt. 59.08

Forms: $Cu_2(CNS)_2$, AgCNS, $BaSO_4$

1. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$

To the solution of thiocyanate, which is neutral or slightly acid with hydrochloric or sulfuric acid, add 20–50 ml. of a saturated solution of sulfurous acid, and copper sulfate solution with constant stirring until a slightly greenish tint is imparted to the liquid. After standing a few hours, filter the precipitate into a Munroe crucible, wash with cold water containing sulfurous acid, then once with alcohol, and dry at 130° to constant weight.

2. Determination as Silver Thiocyanate, AgCNS

This excellent method for estimating thiocyanic acid is only applicable in the absence of the halogen acids, or hydrocyanic acid.

Treat the dilute solution of the alkali thiocyanate in the cold with a slight excess of silver nitrate solution, which has been acidified with nitric acid. After stirring well, filter off the precipitate into a Munroe crucible, wash with water, then with a little alcohol, dry at 130° and weigh.

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* *Ann. Chem. Pharm.*, **101**, 344 (1857).

3. Determination as Barium Sulfate

In the absence of all other compounds containing sulfur, thiocyanic acid can be determined with accuracy by oxidizing it and precipitating the sulfuric acid formed as barium sulfate. Bromine water is the most suitable oxidizing agent for this purpose. Treat the alkali thiocyanate solution with an excess of bromine water, heat for from 30–60 minutes on the water-bath, acidify the solution with hydrochloric acid, precipitate the sulfuric acid by means of barium chloride, and weigh as barium sulfate (see Sulfuric Acid).

Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another (Borchers)*

In one portion determine by volumetric titration the quantity of silver nitrate necessary to precipitate both of the acids (see Precipitation Analysis) and in a second portion determine the weight of barium sulfate formed after the oxidation of the thiocyanic acid. From the latter weight compute the quantity of thiocyanic acid present and also the weight of silver nitrate that would be required to precipitate it. If this weight is subtracted from the weight of silver nitrate required to precipitate both of the acids, the quantity of silver nitrate equivalent to the hydrocyanic acid present is obtained.

Determination of Thiocyanic Acid together with Halogen Hydrides (Volhard)

In one portion determine the thiocyanic acid as barium sulfate after oxidation. Heat a second portion in a closed tube with concentrated nitric acid and silver nitrate (Carius Method,† p. 292), filter off and weigh the mixture of silver halides and change to silver chloride as described on p. 298. Fuse a third portion with sodium carbonate and potassium nitrate, dissolve the alkali salts in water and determine the iodine as palladous iodide (see p. 296). From the data thus obtained, compute the relative quantities of the three halides (see p. 299).

FERROCYANIC ACID, $H_4Fe(CN)_6$. Mol. Wt. 215.9

Form: Silver Cyanide, AgCN

The most accurate procedure for the analysis of complex cyanides is to determine the carbon and nitrogen by elementary analysis (which see).

* *Reportorium der anal. Chemie*, 1881, p. 130.

† Instead of using the Carius method, the halogens and thiocyanate may be precipitated by silver nitrate, filtered through a Gooch crucible, dried at 160° and weighed.

Determination as Silver Cyanide (Rose-Finkener)

This method depends upon the fact that all salts of ferrocyanic acid on being heated with yellow mercuric oxide give up their cyanogen to the mercury, forming soluble mercuric cyanide, while the iron is changed to insoluble ferric hydroxide. Thus Prussian blue is decomposed as follows:

$$Fe_4[Fe(CN)_6]_3 + 9\ HgO + 9\ H_2O = 9\ Hg(CN)_2 + 4\ Fe(OH)_3 + 3\ Fe(OH)_2$$

Treat a weighed amount of the substance with water and an excess of mercuric oxide. Boil until the blue color has completely disappeared, filter off the iron precipitate with the excess of mercuric oxide and determine the cyanide in the filtrate according to p. 302.

On filtering off the insoluble oxides, at first a clear filtrate is obtained, but on washing some of the precipitate usually passes through the filter. By washing with a solution containing a dissolved salt, preferably mercuric nitrate, it is possible, however, to obtain a clear filtrate. Even then the operation is tedious, so that it is better to dilute the liquid containing the precipitate suspended in it to 100 ml., and use a filtered aliquot of 50 ml. for the determination of the cyanide according to p. 302. This introduces a slight error because the volume of the precipitate is neglected although the error is largely compensated by adsorption errors.

Soluble ferrocyanides may be determined satisfactorily by titration with potassium permanganate (cf. Part II, Oxidation and Reduction Methods). For the determination of the iron and other metals, heat the substance with concentrated sulfuric acid, dissolve the residue after evaporation in water, and analyze the solution in the usual way.

FERRICYANIC ACID, $H_3Fe(CN)_6$. Mol. Wt. 214.9

The ferricyanides are analyzed in the same way as the ferrocyanides.

HYPOCHLOROUS ACID, HClO. Mol. Wt. 52.47

Hypochlorous acid is always determined volumetrically and will be discussed in Part II of this book, under Oxidation Methods.

GROUP II

NITROUS, HYDROSULFURIC, ACETIC, CYANIC, AND HYPOPHOSPHOROUS ACIDS

NITROUS ACID, HNO_2. Mol. Wt. 47.02

Nitrous acid is either determined volumetrically, gasometrically, or colorimetrically. The two former methods will be discussed in Parts II and III of the book.

Colorimetric Determination, of Peter Griess

This method serves only for the determination of extremely small amounts of nitrous acid (*e.g.*, in drinking-waters), and depends upon the formation of intensively colored azo-dyes.

Inasmuch as azo-compounds are formed only when nitrous acid is present, they can all be used in testing for this acid, but the different substances do not prove equally sensitive as reagents. Thus in the production of tri-amino-azo-benzene (Bismarck brown) not less than 0.02 mg. of nitrous acid in a liter can be detected, while according to the following procedure 0.001 mg. in a liter can be detected with certainty. To carry out the determination two solutions are necessary, one of sulfanilic acid and one of α-naphthylamine. Both substances are dissolved in acetic acid* and prepared according to the directions of Ilosvay† as follows:

1. Dissolve 0.5 g. of sulfanilic acid in 150 ml. of dilute acetic acid.

2. Boil 0.1 g. of solid α-naphthylamine with 20 ml. of water, pour off the colorless solution from the bluish-violet residue, and add 150 ml. of dilute acetic acid.

Mix these two solutions.‡ It is not necessary to protect the reagent from the action of light, but it is desirable to keep impure air away from it. As long as the solution remains colorless it can be used. If it comes in contact with nitrous acid, which is often present in the air, the reagent becomes red, and in this case it must be decolorized by shaking with zinc-dust before using.

Besides the above reagent, it is necessary to prepare a solution of sodium nitrite of known strength. For this purpose add silver nitrate solution to a concentrated solution of commercial potassium nitrite,

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* P. Griess used dilute sulfuric acid to set free the nitrous acid. Ilsovay showed that if acetic acid were used the reaction was much more sensitive.

† *Bull. chim.* [2] **2**, 317.

‡ Lunge, *Zeitschr. f. angew. Chem.*, 1899, Heft 23.

filter off the precipitated silver nitrite and wash a few times with cold water. To obtain absolutely pure silver nitrite dissolve the precipitate in as little hot water as possible and quickly cool. Place the mass of crystals in a funnel provided with a platinum cone and, after draining off the mother-liquor by suction, wash with a small amount of distilled water. Place the silver nitrite in a calcium chloride desiccator and allow to dry in the dark. As soon as it has become dry (shown by its having assumed a constant weight) dissolve exactly 0.4047 g. in a liter flask with hot distilled water. Add 0.2–0.3 g. of pure sodium chloride (*i.e.*, a little more than the theoretical amount) to convert the silver nitrite into silver chloride and sodium nitrite. Cool, dilute the solution to exactly one liter with pure water, shake well, and allow the precipitate to settle. After this, pipet off 100 ml. of the clear liquid into a second liter flask and dilute up to the mark with water free from nitrous acid. One ml. of this solution contains 0.01 mg. N_2O_3.

Procedure for the Determination

Place 50 ml. of the water to be examined in a cylinder, such as is shown on p. 74, add 5 ml. of the reagent, and mix the contents of the cylinder with the aid of the stirrer shown in Fig. 33. Place the cylinder in water heated to 70–80°. If as much as 0.001 mg. of nitrous acid is present in a liter of the water tested, the red coloration will appear within 1 minute; with relatively larger amounts (*e.g.*, as much as 1 mg. per liter) the solution is simply colored yellow, unless a concentrated solution of naphthylamine is used. Meanwhile in three other cylinders place respectively 0.1 ml., 0.5 ml., and 1 ml. of the solution containing a known amount of sodium nitrite; dilute each with water up to the mark and treat with the reagent in the same way. As soon as a distinct red coloration is apparent, compare the colors with that produced by the water to be analyzed. If the color of the unknown water lies between two of the standards — *e.g.*, between that produced with 0.1 and 0.5 ml. of the standard — then prepare 3 more standards containing, say, 0.2, 0.3, and 0.4 ml. of the known solution. When the color of the unknown solution is matched, then the water contains the same amount of nitrous acid as the standard.

If the water contains considerable nitrous acid (*e.g.*, over 0.3 mg. per liter), the red coloration will be so dark that the colorimetric determination cannot be performed with certainty. In this case dilute a definite volume of the water with distilled water and determine the nitrous acid present in this diluted water.

Tromsdorff recommends for the determination of nitrous acid in drinking-water the use of zinc iodide of starch, and comparing the blue color produced by the nitrous acid (cf. Vol. I.) If 0.1 mg. of nitrous acid is present in a liter, the blue color produced can be distinctly seen; with 0.4 mg. per liter, however, the color is so intense that it is unsuited for a colorimetric determination. This method is not to be recommended because in the first place it is far less sensitive than the Griess method, and second because it can easily lead to error inasmuch as a blue color will be often produced when there is no nitrous acid present. Traces of hydrogen peroxide or ferric salts, which are likely to be present in a drinking-water, will also cause the solution of zinc iodide of starch to turn blue.

HYDROSULFURIC ACID, H_2S. Mol. Wt. 34.08

Forms: Barium Sulfate, $BaSO_4$, Hydrogen Sulfide, H_2S, and colorimetrically

There are four cases to be considered:

I. The determination of free hydrogen sulfide.

II. The determination of sulfur in sulfides soluble in water.

III. The determination of sulfur in sulfides insoluble in water but decomposable by dilute acids with evolution of hydrogen sulfide.

IV. The determination of sulfur in insoluble sulfides.

I. Determination of Free Hydrogen Sulfide

(*a*) *Determination of Hydrogen Sulfide in Gas Mixtures*

If it is desired to know the per cent of hydrogen sulfide present in a mixture of gases, the analysis is best made volumetrically (see Part II, Iodimetry), but it is possible to accomplish the same end by a gravimetric process.

Connect the source of the gas by means of rubber tubing with a ten-bulb Meyer absorption-tube shown in Fig. 46, p. 196,* which contains a solution of ammoniacal hydrogen peroxide free from sulfuric acid. Connect the other end of the absorption-tube with an aspirator, *i.e.*, a large bottle of about 4–5 liters capacity filled with water and closed by means of a double-bored stopper. Through 1 hole of the stopper pass a right-angled glass tube which reaches just below the bottom of the stopper in the bottle, and connected at other end with the absorp-

* Usually two of these tubes are used in order to make sure that none of the gas escapes absorption.

tion-tube. Through the other hole in the stopper place a glass tube reaching to the bottom of the bottle. Likewise bend the upper end of this tube, and connect with a rubber tube to serve as a siphon; on the lower end of the rubber tube place a screw-cock.

Before beginning the experiment, remove the air in the rubber tubing between the source of gas and the absorption-tube by conducting the gas to be analyzed through it. When this is accomplished connect the tubing with the absorption-tube. Now allow water to run slowly from the aspirator into a vessel graduated in liters; after from 2–5 liters of the water have run out, close the aspirator by screwing up the cock on the siphon arm. Pour the contents of the absorption-tube into a beaker, slowly heat to boiling, and keep at this temperature for 5–10 minutes. Evaporate the solution on the water-bath to a small volume, add a little hydrochloric acid, filter the solution if necessary, and precipitate the sulfuric acid at a boiling temperature with a boiling solution of barium chloride. After the precipitate has settled, filter it off, ignite wet in a platinum crucible, and weigh as barium sulfate.

Both at the beginning and end of the experiment it is necessary to note the temperature of the room and the barometer reading. Use the mean of these readings for the calculation. Compute the amount of hydrogen sulfide present in the gas as follows:

The volume of water which has flowed out of the aspirator represents the volume of the gas that has been sucked through the apparatus less the amount absorbed by the ammoniacal hydrogen peroxide solution. Let V represent the volume of water in liters which has flown from the aspirator and p the weight of barium sulfate found.

Since one gram molecule of barium sulfate corresponds to one gram molecule of hydrogen sulfide and the latter assumes at 0° and 760 mm. pressure a volume of 22.16 liters,* we have:

$$V_1 = \frac{22.16 \cdot p}{BaSO_4} = \text{the volume of the hydrogen sulfide absorbed.}$$

Now the volume (V) of the gas that passed through the apparatus was at $t°$ and B mm. pressure and was saturated with water vapor; whereas V_1 refers to the dry gas at 0° C. and 760 mm. pressure. It is necessary, therefore, to reduce V to 0° C. and 760 mm. pressure.

$$V_0 = \frac{V \cdot (B - w)\, 273}{760\,(273 + t)}.$$

* According to Leduc, *Comptes rendus*, **125**, 571 (1897) the density of H_2S (referred to air = 1) is 1.1895, from which the molecular volume is computed as 22.159 liters.

The volume of the gas drawn through the apparatus is then:

$$V_0 + V_1;$$

and we have: $\frac{V_1 \cdot 100}{V_0 + V_1}$ = the per cent by volume of hydrogen sulfide present.

(*b*) *Determination of Hydrogen Sulfide Present in Solution*

By means of a pipet measure out a definite volume of the solution and allow it to run into ammoniacal hydrogen peroxide while constantly stirring with the pipet. Heat to boiling, acidify with hydrochloric acid, and determine the amount of sulfate by precipitation with barium chloride.

II. Determination of Sulfur in Sulfides Soluble in Water

(α) Treat the solution with an excess of ammoniacal hydrogen peroxide water, slowly heat to boiling and keep at this temperature until the excess of the reagent is destroyed. Then precipitate the sulfuric acid with barium chloride and weigh as barium sulfate.

(β) Treat the solution with bromine water until a permanent brown color is obtained, heat, make acid with hydrochloric acid, and determine the sulfuric acid as barium sulfate.

If the solution contains thiosulfate, sulfide, and sulfate, as is likely to be the case after standing in the air for some time, precipitate the sulfide sulfur by means of cadmium acetate and determine the sulfur in the precipitate as under III, or oxidize the cadmium sulfide with either bromine water or fuming nitric acid, and determine the sulfuric acid formed as barium sulfate.

The determination of thiosulfate, sulfide, and sulfite sulfur will be discussed in Part II of this book under Iodimetry.

III. The Determination of Sulfur in Sulfides Soluble in Dilute Acids

Principle. — The hydrogen sulfide is evolved by treatment of the sulfide with dilute acid, and absorbed in ammoniacal hydrogen peroxide solution as under I; or the hydrogen sulfide is absorbed in caustic soda solution and the sodium sulfide formed analyzed according to II; or finally the gas may be absorbed in a weighed tube containing pumice soaked with copper sulfate solution, in which case the gain in weight represents the amount of gas absorbed.

Evolution and Absorption of the Hydrogen Sulfide

In the case of sulfides rich in sulfur take 0.25–0.50 g. of the substance for analysis, and of sulfides containing less sulfur use a correspondingly larger amount. Place the substance in an Erlenmeyer

flask (Fig. 65, *a*), break the connection between the flask and the receiver and expel the air from *K* by conducting hydrogen gas through the delivery tube and out through the open stop-cock of *T*. After a rapid current of hydrogen has passed through the apparatus for about 5 minutes, partly fill the receivers *V* and *P* with an ammoniacal solution of hydrogen peroxide* (about 3–4 per cent H_2O_2); placing about 100 ml. of the solution in *V* and about 10–20 ml. in *P*.

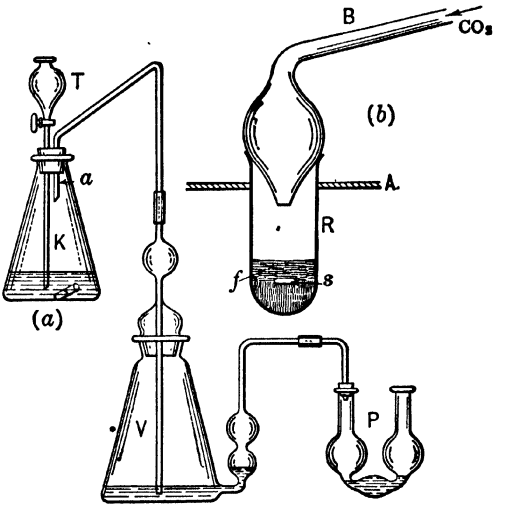


FIG. 65.

Now connect the receiver, *V*, with the delivery-tube from the evolution-flask *K*, and conduct hydrogen from *T* through the whole apparatus for 5 minutes more in order to remove as much as possible of the air from the receivers. After this, introduce about 20 ml. of boiled water into *K* through *T* so that the substance is entirely covered, then slowly add 6 *N* hydrochloric acid to the contents of the flask and promote the decomposition by warming somewhat. When the evolution of the gas has ceased, heat the contents of *K* to gentle boiling and pass a slow current of hydrogen† through the apparatus from *T* for 20 minutes; then remove the flame and continue the current of hydrogen for 15 minutes longer. At the end of this time, the hydrogen sulfide will be completely driven over into *V*.‡

* Instead of hydrogen peroxide, the receivers can contain 100 ml. of dilute sodium hydroxide solution (250 g. to 1 liter). After the decomposition is complete transfer the contents of the receiver to a beaker, add 30–50 ml. of bromine water, make the solution acid with hydrochloric acid and boil while passing carbon dioxide through it until the excess of bromine is completely expelled. Then precipitate the sulfuric acid formed with a hot solution of barium chloride. Instead of oxidizing the sodium sulfide to sodium sulfate it can be titrated with iodine (cf. Iodimetry).

† Prepare the hydrogen from zinc and sulfuric acid in a Kipp generator. Wash the gas first with an alkaline lead solution to remove traces of hydrogen sulfide and then with water.

‡ By the absorption of the hydrogen sulfide in the ammoniacal solution of hydrogen peroxide the latter is always colored somewhat yellow owing to the formation of a little ammonium disulfide. This yellow color can be distinctly seen in the delivery-

Wash the contents of the two receivers into a beaker and slowly heat to boiling in order to effect the complete oxidation of the thiosulfuric and sulfurous acids and to expel the excess of the hydrogen peroxide. Finally make the solution acid with hydrochloric acid and determine the sulfuric acid as barium sulfate.

This method yields excellent results and can be applied to the

Determination of Sulfur in Iron and Steel

Inasmuch as the amount of sulfur present is small, a large amount of the substance must be taken for the analysis. For pig iron 2–5 g. are sufficient, while with steel 5 g., and with wrought iron, as much as 10 g. should be used.

The determination is carried out in the same way as before, except in this case concentrated hydrochloric acid should be used; allow this to act upon the iron at once without first covering it with water, and continue boiling for 10 minutes after the gas evolution has ceased and all of the iron has dissolved.

Instead of collecting the evolved hydrogen sulfide in ammoniacal hydrogen peroxide, it is often more convenient to absorb it in ammoniacal cadmium solution, or in caustic soda solution, and determine the sulfur volumetrically by an iodimetric process as will be described later.

Bamber Method for Determining Sulfur in Iron and Steel

On account of the uncertainty in obtaining all the sulfur present in iron or steel by the above evolution method, the Committee on Standard Methods for the Analysis of Iron of the American Foundrymen's Association, have recommended the following method, which is that proposed by Bamber.

Dissolve 3 g. of drillings in concentrated nitric acid. After the iron is completely dissolved, add 2 g. of potassium nitrate, evaporate to dryness on the water-bath, and ignite the dry residue over an alcohol lamp to a red heat. After the ignition, add 50 ml. of a 1 per cent solution of sodium carbonate, boil for a few minutes, and filter, washing the precipitate with hot 1 per cent sodium carbonate solution. Make the filtrate acid with hydrochloric acid and again evaporate to

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tube, where it dips into the solution in the receiver and later disappears owing to further oxidation:

$$(NH_4)_2S_2 \rightarrow (NH_4)_2S_2O_3 \rightarrow (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4.$$

When the color can no longer be detected, it is a sign that the greater part of the hydrogen sulfide has been driven over.

dryness. Moisten the residue with 2 ml. of concentrated hydrochloric acid and add 50 ml. of water. Heat to boiling and filter. Dilute the filtrate to 100 ml. and precipitate hot with barium chloride solution.

During the determination great care should be taken to prevent the absorption of fumes containing sulfur. For this reason a gas flame should not be used at any stage in the process.

The following method is recommended by the Bureau of Standards.

Determination of Sulfur in Iron and Steel without Removing the Iron

Dissolve 4.57 g. of the sample in 50 ml. of concentrated nitric acid in a covered beaker or flask. Add 0.5 g. of sodium carbonate, evaporate to dryness and bake for 1 hour on the hot plate. Add 30 ml. of concentrated hydrochloric acid and repeat the evaporation and baking. Add another 30 ml. of hydrochloric acid (*d.* 1.20) and evaporate to a sirupy consistency. Add 5 ml. of concentrated hydrochloric acid, 10 ml. of water, 5 g. of 20–30 mesh zinc, free from sulfur, and heat on the steam-bath until the iron is reduced to ferrous chloride, adding more acid if necessary. Filter from the silica and undissolved zinc, dilute to 100 ml. and add 10 ml. of 10 per cent barium chloride. Let stand 18–24 hours, filter, wash once or twice with cold 2 per cent hydrochloric acid and then with hot water until free from chlorides. A blank should be carried through all steps of the determination. The corrected weight of the ignited barium sulfate multiplied by 3 is equal to the percentage of sulfur.

The following method has also been found to give good results.

Meinicke Method for Sulfur in Iron and Steel

Dissolve 4.57 g. of the metal in 25 ml. of potassium-cupric chloride solution (300 g. $KCl.CuCl_2$ and 100 ml. concentrated hydrochloric acid per liter). Filter off the residue, containing all the sulfur, using an asbestos filter. Wash 2 or 3 times with 5 per cent hydrochloric acid and then return residue and asbestos pad to the beaker and cover with 20 ml. of concentrated nitric acid. Heat and add potassium chlorate until all carbonaceous matter is destroyed. Add 5 ml. of concentrated hydrochloric acid to dissolve the precipitated manganese dioxide and again filter through asbestos. Evaporate the solution to dryness, take up in 10 ml. of hydrochloric acid and evaporate to dryness again. Take up in 10 ml. of 2 per cent hydrochloric acid and 20 ml. of water and filter through paper. Precipitate the sulfuric acid in the boiling filtrate, containing 1 per cent hydrochloric acid by volume, with 2 ml. of hot 10 per cent barium chloride solution. Digest a short time on

the hot plate and filter. Wash the barium sulfate with hot water until free from chlorides, ignite slowly, and weigh. The weight of barium sulfate in grams multiplied by 3 is equal to the percentage of sulfur. Run a blank on all reagents, carrying out every step of the procedure.

Determination of Sulfur in Cast Iron and Steel. (Noyes and Helmer*)

Dissolve 5 g. of the metal by dropping the borings slowly into a cold mixture of 200 ml. of water and 8 ml. of bromine. When the iron is all dissolved, heat to boiling and filter. Fuse the residue with sodium carbonate and a little potassium nitrate. Extract with water, filter and test to see if any precipitate is obtained with hot barium chloride added to the acidified solution. If a precipitate is obtained, ignite and weigh.

Pour the original solution of the iron, which contains the greater part of the sulfur as sulfuric acid, into 130 ml. of 6 *N* ammonium hydroxide in a 500 ml. measuring flask. Dilute to the mark, mix and filter off 250 ml. for the analysis. Make slightly acid with hydrochloric acid and in a volume of 100 ml. precipitate with hot barium chloride.

Method of Krug†

Dissolve 5 g. of the metal in 50 ml. of concentrated nitric acid. When the iron has all dissolved, add 0.25 g. of potassium nitrate, evaporate to dryness and bake the residue. Take up in hydrochloric acid and carry out the Rothe ether separation as described on p. 169. After removing the ether precipitate the sulfuric acid with hot barium chloride reagent.

Colorimetric Determination of Sulfur in Iron and Steel‡

Principle. — The hydrogen sulfide evolved from a weighed sample is passed through a cloth which has been wet with a solution of cadmium acetate. The hydrogen sulfide reacts with the cadmium salt to form yellow cadmium sulfide and the intensity of the color is proportional to the amount of hydrogen sulfide.

If a grams of substance produce a certain shade then it would take $2a$ grams of a substance containing half as much sulfur to duplicate it, or in other words, the relations hold, $as = a's'$, where a and a' represent the amount of substance taken for the analysis and s and s' the percentage of sulfur present. In the first place, then, a scale must be prepared of different shades representing different percentages of sulfur.

* *J. Am. Chem. Soc.*, **23**, 675 (1901).

† *Stahl und Eisen*, **25**, 887 (1905).

‡ J. Wiborgh: *Stahl and Eisen*, 6 (1866), 240.

For this purpose, Wiborgh uses the apparatus shown in Fig. 66. It consists of a 250–300 ml. Erlenmeyer flask *A* with a side-arm funnel *T* and with a ground-glass connection between the cylinder *B*. The latter is about 20 cm. long, and is from 5.5–6.0 cm. wide at the top and about 8 mm. at the bottom. The upper edge of the cylinder is rounded over and ground perfectly smooth. Upon this upper edge are placed two rubber rings of the same inner diameter as the glass cylinder. Between these two rings is laid a circular piece of cloth *C* that has been dipped in a solution of cadmium acetate, and upon the upper rubber ring is placed a wooden ring *H* which is held firmly against the edge of the cylinder by means of three clamps *K* (only two are shown in the illustration).

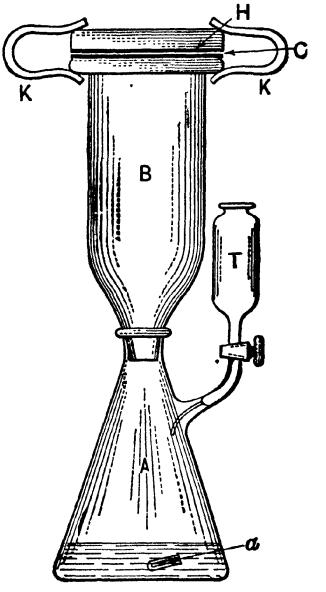


FIG. 66

Fill the flask *A* not quite half full with distilled water, boil a few minutes to remove the air, take away the flame and drop into the flask a weighing-tube containing a definite amount of a sample whose sulfur content is known. Insert the cylinder, with the cadmium acetate cloth in position, in the neck of the flask, and boil gently until the cloth is uniformly moistened with the aqueous vapor which is seen to pass through it. The water must not be boiled too strongly and the cloth must not be allowed to puff up, for in that case it will become distorted and afterward an unevenly colored surface will be obtained. After boiling for 3 or 4 minutes, cautiously add 6 *N* sulfuric acid, drop by drop, to the contents of the flask (3 ml. for each 0.1 g. of iron) through the funnel *T*. The evolution of hydrogen sulfide begins at once and is recognized by the cadmium acetate cloth becoming yellow. After the acid has all been added, continue boiling until there is no more gas evolved from the substance, and then for 10 minutes more in order to completely expel it from the solution.

Now remove the piece of cloth and place it upon a piece of white filter-paper, so that the side which was toward the flask is on top. In the same way prepare a scale of six different shades corresponding to 0.02 mg., 0.04 mg., 0.08 mg., 0.12 mg., 0.20 mg. and 0.28 mg. of sulfur, etc. For the determination proper, weigh out from 0.1–0.8 g. of the substance (according to its supposed sulfur content) and treat

in the same way. If with a sample of 0.2 g. a shade corresponding to Tint No. 5 is obtained, the sample contains 0.2 mg. of sulfur.

Remark. — The above process is very simple and to be recommended in case a large number of sulfur determinations are to be made, as is the case in iron and steel laboratories. It is to be noted, however, that an accurate value is obtained only when all the sulfur is present in a form such that it is evolved as hydrogen sulfide on treatment with acid.

IV. Determination of Sulfur in Insoluble Sulfides

For this analysis the sulfur is either oxidized to sulfuric acid and determined as barium sulfate, or the sulfide is converted into a soluble sulfide which is analyzed as described above.

The oxidation of the sulfide can take place:

(*a*) *In the Dry Way.*

(*b*) *In the Wet Way.*

(A) OXIDATION IN THE DRY WAY

1. *Fresenius' Method: Fusion with Sodium Carbonate and Potassium Nitrate*

Intimately mix 0.5 g. of the finely powdered sulfide in a spacious nickel crucible with 5 g. of sodium carbonate and 1.25 g. of potassium nitrate, cover with a thin layer of sodium carbonate and heat at first gently, then hotter until the contents of the crucible are melted; keep at this temperature for 15 minutes. After cooling, extract the melt with water, filter, boil the residue with 2 per cent sodium carbonate solution and finally wash with water to the disappearance of the alkaline reaction. To the filtrate in a covered beaker add an excess of hydrochloric acid, boil, expel carbon dioxide, and evaporate to dryness. To remove all of the nitric acid, treat the dry mass with 10 ml. concentrated hydrochloric acid and again evaporate to dryness. Moisten this last residue with 1 ml. of concentrated hydrochloric acid, add 100 ml. of water, heat to boiling and filter. Dilute the filtrate to 350 ml., heat to boiling and precipitate with 24 ml. of normal barium chloride solution which is diluted to 100 ml. and added as quickly as possible while stirring vigorously (cf. Sulfuric Acid).

2. *Sodium Peroxide Method**

The above method has long been accepted as a standard method for determining sulfur in pyrite and other insoluble sulfides but equally

* W. Hempel, *Z. anorg. Chem.*, **3**, 193 (1893); J. Clark, *J. Chem. Soc.*, **63**, 1079 (1893); Höhnel, *Arch. Pharm.*, **232**, 222; C. Glaser, *Chem.-Ztg.*, **18**, 1448; Fournier, *Revue générale de chimie, pure et appliquée*, **1903**, 77; List, *Z. angew. Chem.*, **1903**, 414.

good results can be obtained by substituting sodium peroxide as the oxidizer and the procedure is shorter.

Procedure. — Mix 0.5 g. of pyrite with 5 g. of pure sodium peroxide and 4 g. of sodium carbonate in a nickel or iron crucible. Cut an opening in a piece of asbestos board (at least 4 inches square) sufficiently large to allow two-thirds of the crucible to project below the asbestos. The purpose of this shield is to keep the products formed by the combustion of the gas from reaching the mouth of the crucible. Heat the contents of the crucible gently for 10 minutes so that the mass softens and bakes together and then raise the temperature until the crucible is exposed to the full heat of the Tirrill burner for 20 minutes.

Allow the contents of the crucible to cool and place in a small beaker with 150 ml. of hot water. When the sodium salts are all dissolved, remove the crucible and add 5 ml. of concentrated hydrochloric acid, to which liquid bromine has been added till the acid is saturated. The purpose of the bromine is to make sure that the oxidation of the sulfur is complete.* It is necessary to add acid as otherwise the hot sodium hydroxide solution is likely to destroy the filter paper. After heating to boiling, filter the solution and wash the residue of ferric hydroxide free from sulfate.

Carefully neutralize the filtrate with 6-normal hydrochloric acid, and add 2 ml. in excess. Heat the solution till all the bromine is expelled, dilute to 250 ml. and precipitate the sulfuric acid as in the previous method.

3. *Method of Böckmann*

Fuse 0.5 g. of pyrite with a mixture of 21 g. of sodium carbonate and 4 g. of potassium chlorate. Heat gently at first and gradually raise the temperature until no more oxygen is evolved. Cool, extract with water, filter and precipitate the sulfate as in the two preceding methods.

4. *Oxidation by Chlorine (Rose)*

This important method is used less to determine the amount of sulfur present in insoluble sulfides than it is to effect the solution of the sulfide for the separation and determination of the metals. As an example of this sort of an analysis we will consider the

Analysis of Tetrahedrite (Fahlerz)

Tetrahedrite is a sulfo-salt corresponding to the general formula $4\,MS \cdot R_2S_3$ in which M is Cu_2, Ag_2, Fe, Zn, or Hg_2, and R is As, Sb, or Bi.

* A black residue may denote ferrous sulfide or nickelic oxide. It may be tested for sulfur by dissolving in hydrochloric acid and bromine and adding barium chloride to the diluted solution.

Place 0.5–1.0 g. of the powdered substance into a porcelain boat *S*, Fig. 67, shove this into the decomposition tube *R* and also insert the diffusion tube, *d*, which is just small enough to fit into *R*. Both ends of *d* are sealed so that the tube *R* is nearly stopped up at this point. Put the decomposition tube into a drying closet, as shown in Fig. 53, p. 209, and connect one end through the stop-cock *H* with the purification tubes *A*, *B*, *C*, and *D* and the other end with the vessels *E* and *G*. The flask *E* contains 100 ml. of 2.5 *N* hydrochloric acid and 3.5 g. of tartaric acid and the Landolt tube *G* contains a column of glass beads

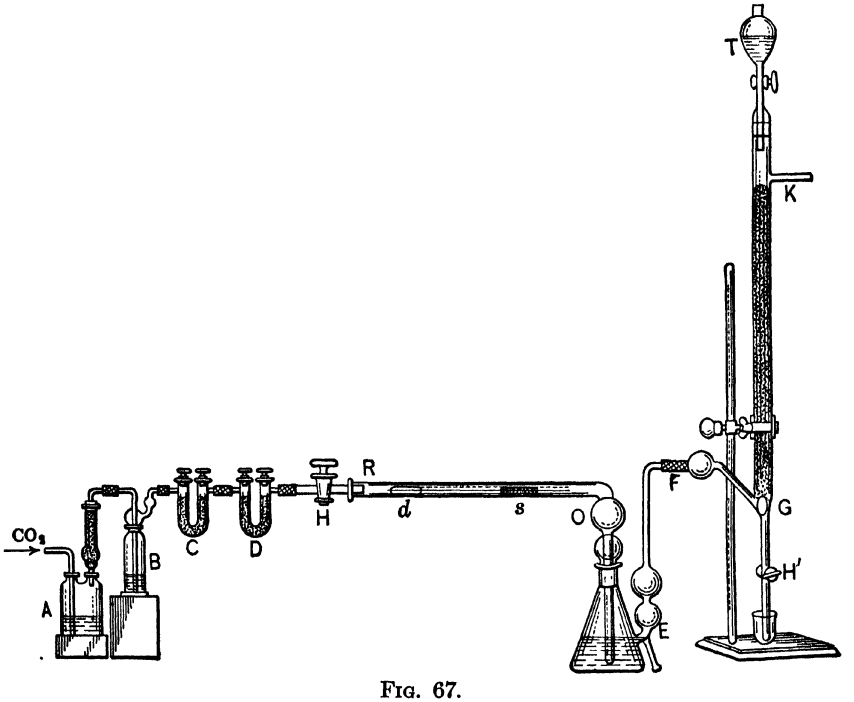


FIG. 67.

upon which hydrochloric and tartaric acid mixture trickles from the funnel *T* during the entire experiment. Conduct a slow, steady stream of chlorine through the apparatus without heating. Generate the chlorine in a Kipp apparatus by the action of hydrochloric acid upon bleaching powder in a Kipp generator. Pass the gas through the wash bottle *A* containing water, the bottle *B* containing sulfuric acid, and the tubes *C* and *D* containing pieces of calcite to remove traces of acid. The action of the chlorine upon the substance generates heat and the decomposition at once starts. The volatile chlorides to some extent reach the flask *E* but condense also in *O* and in the front end of

the tube outside the drying closet. By careful heating with a small flame, it is easy to drive the condensed chlorides into the receiver. Allow the contents of the tube to cool in the stream of chlorine and finally drive out the chlorine with carbon dioxide. Then remove the diffusion tube *d* and the boat. Loosen the connection with the Landolt tube and by blowing at *F* cause acid to flow into *O* several times. Then wash out the entire contents of the tubes into *E* with hydrochloric-tartaric acid mixture.

The Residue A

consists of silver, lead, and copper chlorides, almost all of the zinc, lead, considerable amounts of iron, and the gangue.

The Solution B

contains all of the sulfur as sulfuric acid, the bismuth as chloride, the arsenic and antimony as their pentoxide compounds, a part of the iron and zinc and often small amounts of lead.

Treatment of the Residue A

Heat this for some time with 6 *N* hydrochloric acid, finally dilute with water, allow to settle, and filter off the residue consisting of silver chloride and the gangue. Wash thoroughly with hot water to make sure that all lead chloride is removed, treat with ammonia on the filter and precipitate the silver from the ammoniacal filtrate by acidifying with hydrochloric acid, and determine as the chloride. Ignite the residue, insoluble in ammonia, wet in a platinum crucible and weigh.

Into the filtrate from the silver chloride, pass hydrogen sulfide until the solution is saturated. Filter off the precipitate of copper and lead sulfides and separate the lead from the copper according to p. 199. Combine the filtrate from the hydrogen sulfide precipitate with that obtained from Solution B after hydrogen sulfide has been passed into it.

Treatment of Solution B

Pass a stream of carbon dioxide through the solution for some time to remove the greater part of the excess of chlorine, and then saturate with hydrogen sulfide at the temperature of the water-bath after standing 12 hours. Filter off the precipitate of arsenic, antimony, mercury, and possibly bismuth sulfides. Separate the arsenic and antimony from the mercury and bismuth by means of ammonium sulfide as described on p. 219. From the ammonium sulfide solution precipitate the arsenic and antimony by acidifying with dilute hydrochloric

or sulfuric acid, filter off the precipitated sulfides and separate the arsenic from the antimony as described on p. 224 *et seq.*

The precipitate insoluble in ammonium sulfide usually consists almost entirely of mercuric sulfide and sulfur, in which case, wash it first with alcohol, then a few times with carbon bisulfide, then with alcohol again, dry at 110° C. and weigh. If bismuth is present, however, treat the mixture of the two sulfides with 6 *N* nitric acid. Boil, add an equal volume of water, filter off the residue and determine the bismuth in the filtrate according to p. 182, and the mercury as just described.

The filtrate from the hydrogen sulfide precipitate contains iron and zinc. Combine it with the corresponding filtrate from the Residue A, which likewise contains these metals. Precipitate by the addition of ammonia and ammonium sulfide, filter off, dissolve the precipitate in 2 *N* hydrochloric acid, oxidize the solution with nitric acid, and separate the iron from the zinc, preferably by the basic acetate method (see p. 153).

It is best to determine the sulfur in a separate portion by fusion with sodium carbonate and peroxide as described on p. 316.

The determination of the sulfur in an aliquot part of the Solution B is not to be recommended on account of the fact that the metals present are likely to contaminate the precipitate of barium sulfate.

(B) OXIDATION OF SULFUR IN THE WET WAY

For this purpose aqua regia, fuming nitric acid, bromine, hydrochloric acid and potassium chlorate, and, in some cases, ammoniacal hydrogen peroxide have been proposed.

Aqua regia is most frequently used in practice and in the proportion first recommended by J. Lefort,* viz., 3 volumes of nitric acid, *d.* 1.4, and 1 volume of hydrochloric acid, *d.* 1.2. As an example we will cite the

Determination of Sulfur in Pyrite, G. Lunge's Method

The sample should be finely ground, but it must be borne in mind that rapid grinding in the air may generate enough heat to cause the oxidation of some sulfur so that an appreciable amount escapes as dioxide. Of the fine powder, treat 0.5 g. with 10 ml. of a mixture consisting of 3 parts nitric acid, *d.* 1.42, and 1 part hydrochloric acid, *d.* 1.2, in a 300 ml. beaker which is covered with a watch-glass. At first allow the acid to act upon the pyrite in the cold, but finish by heating upon the water-bath. If sulfur separates, oxidize it with a

* *J. Pharm. de Chimie* [IV], **9**, 99, and *Z. anal. Chem.*, **9**, 81.

very little powdered potassium chlorate. Transfer the solution to a porcelain evaporating dish and evaporate to dryness on the water-bath. Treat the residue with 5 ml. of concentrated hydrochloric acid and again evaporate to dryness. Moisten the dry mass now with 1 ml. of concentrated hydrochloric acid and 100 ml. of hot water, filter through a small filter and wash the residue first with cold water and then with hot water. To the hot filtrate, if not more than 150 ml. in volume, add ammonia till the odor persists and then 30 ml. of 3 *N* ammonium hydroxide in excess to prevent the formation of any basic ferric sulfate. Keep at about 70° for 15 minutes. Filter off the ferric hydroxide precipitate and wash with hot water, each time churning up the precipitate, until a volume of about 400 ml. is reached. Neutralize the filtrate with hydrochloric acid, using methyl orange as indicator, and add 1 ml. of concentrated hydrochloric acid in excess. Heat just to boiling and add 100 ml. of boiling-hot, 0.2 *N* barium chloride solution while stirring vigorously.

Wash the barium sulfate precipitate 3 times by decantation with boiling water, then transfer to a filter and wash free from chlorides, ignite and weigh.

To test the ammonia precipitate for sulfur, transfer it from the filter into a beaker by means of a stream of water from the wash bottle and dissolve it by the addition of as little hydrochloric acid as possible. To the resulting solution add an excess of ammonia, filter and test the filtrate and washings as in the main analysis. Should any barium sulfate be obtained in this way, it should be filtered off and weighed with the main part of the barium sulfate precipitate.

Remark. — It is still better to filter the precipitate through a Munroe crucible. After washing, dry the precipitate as much as possible by suction, place the crucible within a larger porcelain or platinum crucible, heat gently, cool and weigh.

The above method gives excellent results, which as a rule agree closely with those obtained by the Fresenius method. If the pyrite, however, contained barium or any considerable amount of lead, some sulfate will always remain undissolved with the gangue. In such cases the Lunge method will give lower results but on the other hand it represents more nearly the quantity of sulfur in the pyrite which is available for the manufacture of sulfuric acid. In spite of the strong oxidizing power of the above mixture of nitric and hydrochloric acids, it is not sufficient to permit the determination of sulfur in roasted pyrite, on account of the danger of losing some sulfur as hydrogen sulfide. Such products should be fused with sodium carbonate and peroxide as previously described (p. 316).

In carrying out the Lunge method, often a little sulfur separates in dissolving the sample. It has been recommended to dissolve this sulfur by adding potassium chlorate but when this is done the results are likely to be high. To overcome this difficulty, Allen and Bishop recommend dissolving the pyrite in a mixture of bromine and carbon tetrachloride. The latter dissolves any sulfur that is liberated and the dissolved sulfur is easy to oxidize.

Determination of Sulfur in Pyrite. Method of Allen and Bishop*

Weigh 0.5495 g. of sample, ground to pass an 80-mesh sieve, into a tall beaker of 300-400 ml. capacity and add 6–8 ml. of a soln. of 2 vols. liquid bromine in 3 vols. of carbon tetrachloride. Cover the beaker and allow to stand 15 minutes at the room temperature with occasional gentle shaking. Add 10 ml. of concentrated nitric acid and digest in the same way for another 15 minutes. Heat at a temperature below 100° until all action has ceased and most of the excess bromine has been expelled. Raise the cover glass and evaporate to dryness. Cover the residue with 10 ml. of concentrated hydrochloric acid, again evaporate to dryness and heat the contents of the covered beaker for at least 30 minutes at 100°.

Moisten the residue with 1 ml. of concentrated hydrochloric acid and dilute with 50 ml. of water, washing the cover glass and the sides of the beaker. Heat until the ferric salt is all dissolved and allow to cool for 3 minutes.

Reduce the iron by adding 0.1 g. of powdered aluminium, shaking the contents of the covered beaker to bring the metal in contact with all parts of the solution. Sufficient aluminium should be added to reduce all of the iron to the ferrous condition but any considerable excess is to be avoided.

When the reduction of the iron is complete, as shown by the color of the solution, and the latter has cooled sufficiently so that there is no noticeable " misting " in the beaker, filter off the silica and the excess aluminium and wash with water until free from chloride. Dilute with cold water to a volume of 650 ml., add 5 ml. of 6 N hydrochloric acid and stir thoroughly. To the cold solution slowly introduce, while stirring, 50 ml. of cold 5 per cent barium chloride solution in single drops, at the rate of about 5 ml. per minute. Allow the precipitate of barium sulfate to settle at least 2 hours and preferably over night. Filter, wash with cold water till free from chloride, dry, ignite and weigh in the usual manner. The weight of the precipitate multiplied by 25 gives the percentage of sulfur.

Determination of Sulfur in Coal, Eschka Method†

If sulfur compounds are heated with a mixture of magnesium oxide and sodium carbonate, all of the sulfur can be converted into water-soluble sulfate. It is generally assumed that air is the oxidizing agent and the heating is usually accomplished in an open dish. Recently, however, the use of a porcelain or platinum crucible has been

* *J. Ind. Eng. Chem.* **11**, 46 (1919).

† *Chem. News* **21**, 261 (1870).

advocated and the results appear to be equally good, which indicates that the oxidation of the sulfur may be accomplished as a result of the reduction of the carbonate. The magnesium oxide prevents the mass from fusing and apparently also catalyzes the oxidation which is, however, not as rapid as when an oxidizing flux is used.

Prepare Eschka's ignition mixture by mixing two parts of light calcined magnesium oxide with one part of anhydrous sodium carbonate, both free from sulfur. Mix 1 g. of 60-mesh coal with 3 g. of the Eschka mixture on a sheet of glazed paper. Transfer to a porcelain, silica or platinum dish, or to a spacious crucible, and cover with about 1 g. of the Eschka mixture.

Heat slowly with an alcohol flame until most of the volatile matter has been driven off, then gradually raise the temperature and heat with the full flame of the burner for 30 minutes or more, stirring occasionally, until all of the black particles have been oxidized.

After the ignition, rinse the material into a 200-ml. beaker, add 100 ml. of hot water and digest on the steam bath for 30 minutes with occasional stirring. Filter and wash the insoluble residue thoroughly with hot water. The filtrate and washings should total about 250 ml. Add 20 ml. of saturated bromine water, stir, make slightly acid with hydrochloric acid and boil till the excess bromine is removed and the solution is colorless. To the boiling solution add dilute barium chloride solution (20 ml. of a 5 per cent solution) and allow to stand at least one hour before filtering. Ignite and weigh the barium sulfate.

(c) EXPULSION OF HYDROGEN SULFIDE FROM INSOLUBLE SULFIDES

(a) *The Iron Method**

In 1881, M. Gröger showed that by heating pyrite with iron out of contact with the air the former is quantitatively changed into ferrous sulfide,

$$FeS_2 + Fe = 2\,FeS,$$

and from the latter all of the sulfur will be given off as hydrogen sulfide on treatment with hydrochloric acid. The following method is suitable not only for the analysis of pyrite but for all other insoluble sulfides.

Procedure. — First of all heat the finely-powdered sulfide out of contact with the air with iron powder. In this way part of the sulfur is usually given up to the iron, and the compound itself is reduced to compounds which are acted upon by hydrochloric acid with evolution of hydrogen sulfide; the latter can be absorbed in ammoniacal hydrogen peroxide solution, as described on p. 311. Heat with the iron in a small glass crucible about 30 mm. long and 10 mm. in diameter

* *Ber.*, **24**, 1937 (1891).

(Fig. 65, *b*), which can be easily made from an ordinary piece of combustion tubing. Place about 3 g. of iron powder, that has been previously ignited in hydrogen, in the crucible, mix with it 0.3–0.5 g. of the sulfide, and cover the mixture with a thin layer of iron powder. Place the crucible in the opening of the piece of asbestos board *A* (Fig. 65, *b*) and upon it place the gas-delivery tube *B* which has been prepared from difficultly-fusible glass. Pass a stream of dry carbon dioxide* through the apparatus for a few minutes and gently heat the crucible with a small flame. Usually there is a distinct glowing visible, but no trace of the sulfur is lost by volatilization. As soon as the contents of the crucible have ceased to glow, raise the temperature until a dull-red heat is obtained, and keep the crucible at this temperature for ten minutes.

After cooling in the carbon dioxide, place the crucible together with its contents in the 400-ml. flask *K* and connect with the absorption vessels *V* and *P* as shown in the figure. The rest of the procedure is carried out as described on p. 311.

Remark. — Commercial iron powder always contains a small amount of sulfur, so that a blank experiment must be made with a weighed amount of the powder, and the same quantity of iron used for the experiment proper. Subtract the amount of sulfur found to be present in the iron from the amount found in the analysis.

The author was disappointed in not being able by this method to distinguish between the sulfur present in insoluble sulfides as sulfide and that present as sulfate (barium sulfate). If the amount of sulfate present is small, it is completely reduced to sulfide by this method, while if a large amount of sulfate is present, it is often only partially reduced. As, however, the amount of barium sulfate† present in insoluble sulfides is usually small, this method serves for the determination of practically all the sulfur.

(*b*) *The Tin Method*‡

Principle. — Almost all insoluble sulfides on being treated with metallic tin and concentrated hydrochloric acid give off their sulfur as hydrogen sulfide. Harding,§ who first studied this method, used tin and hydrobromic acid.

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* Prepare the carbon dioxide from marble and hydrochloric acid in a Kipp generator. To purify the gas pass it through a wash-bottle containing water, then through one containing potassium permanganate, then through a tube filled with pumice soaked in copper sulfate solution, and finally through a calcium chloride tube. Potassium permanganate and copper sulfate serve to remove traces of hydrogen sulfide that the carbon dioxide might contain.

† Only barium sulfate is reduced with difficulty, the sulfates of the heavy metals are easily reduced.

‡ *Ber.*, **25**, 2377.

§ *Ber.*, **14**, 2085.

Procedure. — Into the evolution tube (Fig. 68), which is 20 cm. long and 2.5 cm. wide, place a layer of finely-powdered tin (*g*) about 0.5 cm. thick. Upon this place the substance enclosed in tinfoil (*s*) and then a layer of granulated tin *Z* about 6 cm. deep. Pass a current of pure hydrogen through the apparatus for about 5 minutes, after which close the stop-cock and connect the tube with the receivers *P* and *V*, as shown in the figure. The flask *V* contains an ammoniacal solution of hydrogen peroxide, but *P* contains 2–3 ml. of water to remove any stannous chloride that may be carried over with the gas. Add concentrated hydrochloric acid through the drop-funnel until the tin is at the most half covered with the acid. Heat the contents of the tube slightly, preferably by placing it in a small paraffin bath. The capsule of tin soon dissolves, and the substance is seen to be floating in the acid. It dissolves after about 15 minutes, and the acid becomes perfectly clear. Continue heating until there is no more yellow coloration to be detected in the delivery-tube which dips into the receiver *V*. Then add more acid to the contents of the tube, until the tin is completely covered, and heat for half an hour longer, meanwhile heating the contents of *P* to boiling and passing a current of hydrogen through *a*. By this means all of the sulfur will be driven over into *V** and is there held in solution as ammonium sulfate and analyzed as described on p. 404.

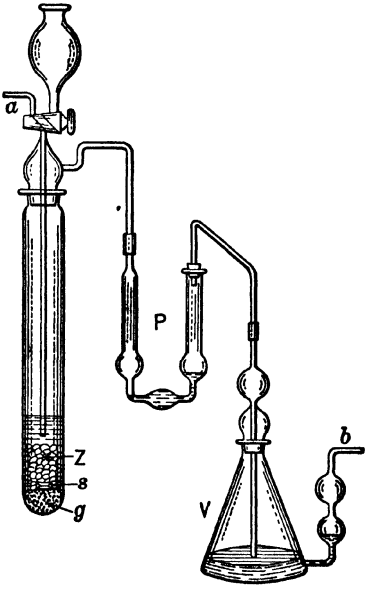


FIG. 68.

Remark. — This method affords an accurate means for determining the sulfur present in insoluble sulfides as sulfide in the presence of sulfate. Thus the amount of pyrite in clay-slate that contains gypsum can be determined by this method, although usually the treatment with aqua regia or fusion with soda and niter is used. By these last two methods, however, the *total* sulfur is determined. More accurate values for the *pyrite* present in such cases may be obtained by decomposition in a current of chlorine (see p. 317), in which case only the sulfide sulfur is determined.

* With large amounts of sulfur, one receiver is often insufficient. In such cases connect the tube *b* with a Péligot tube containing ammoniacal hydrogen peroxide as shown in Fig. 65, p. 311.

Finally, it may be mentioned that arsenic sulfide may be decomposed by the above method, although a longer time is required than is the case with pyrite, copper, chalcopyrite, galena, cinnabar, etc. Arsenopyrite, on the other hand, is either unacted upon or only decomposed with difficulty, while the iron method effects the decomposition with ease.

Determination of Sulfur in Non-electrolytes

To determine the amount of sulfur present in organic compounds, it is oxidized to sulfuric acid and determined as barium sulfate.

The oxidation is effected

(*a*) *In the Wet Way.*

(*b*) *In the Dry Way.*

(*a*) *Oxidation in the Wet Way* (*Carius*)

This operation is conducted in precisely the same manner as was described on p. 292 for the determination of halogens, except in this case there is no silver nitrate added to the contents of the tube. After the closed tube has been heated and opened, transfer its contents to a beaker, add hydrochloric acid and evaporate to a small volume in order to remove the nitric acid; dilute with water to a volume of about 200 ml., precipitate hot with a boiling solution of barium chloride and weigh as barium sulfate.

(*b*) *Oxidation in the Dry Way* (*Liebig*)

Melt a mixture of 8 parts of potassium hydroxide (free from sulfate) and 1 part of potassium nitrate in a large silver crucible with the addition of a little water. After cooling, add a weighed amount of the substance and heat the contents of the crucible again very gradually, frequently stirring the mixture with a silver wire until the organic substance is completely decomposed. Cool, dissolve the melt in water, make acid with hydrochloric acid and precipitate the sulfuric acid formed.

This method is particularly suited for the determination of sulfur present in difficultly volatile substances, *e.g.*, in wood-cements.

ACETIC ACID, $\begin{matrix} CH_3 \\ | \\ COOH \end{matrix}$. Mol. Wt. 60.04

Free acetic acid is always determined volumetrically. For the analysis of acetates, the substance is heated with phosphoric acid when the free acetic acid distils over and is then titrated (cf. Part II, Acidimetry). The carbon and hydrogen of the acetate can be determined by Elementary Analysis (which see).

CYANIC ACID, HOCN. Mol. Wt. 43.02

The only method for examining cyanates consists of determining the amount of carbon and nitrogen present by a combustion (see Elementary Analysis).

Determination of Cyanic Acid, Hydrocyanic Acid, and Carbonic Acid in a Mixture of their Potassium Salts

In one portion of the substance determine the carbonic acid by adding calcium chloride to the ammoniacal solution and weighing the ignited precipitate as calcium oxide.

In a second portion determine the cyanogen of the cyanide as silver cyanide by treating the aqueous solution with an excess of silver nitrate, acidifying with nitric acid and determining the weight of the silver cyanide as described on p. 301.

In a third portion determine the potassium by evaporating with sulfuric acid and weighing the residue of potassium sulfate as described on p. 57. If from the total amount of potassium present the amount present as potassium carbonate and potassium cyanide is deducted, the difference gives the amount of potassium combined with the cyanic acid.

HYPOPHOSPHOROUS ACID, H_3PO_2. Mol. Wt. 66.06

Forms: Mercurous Chloride, Hg_2Cl_2; Magnesium Pyrophosphate, $Mg_2P_2O_7$

(*a*) Determination as Mercurous Chloride

Treat the solution of the salt, which is slightly acid with hydrochloric acid, with an excess of mercuric chloride; by this means insoluble mercurous chloride is precipitated. After standing for 24 hours in a warm, dark place filter off the precipitate through a Gooch crucible, wash with water, dry at 110°, and from the weight of the mercurous chloride calculate the amount of hypophosphorous acid present as follows:

$$H_3PO_2 + 2\,H_2O + 4\,HgCl_2 = 2\,Hg_2Cl_2 + 4\,HCl + H_3PO_4$$

$$x = \frac{H_3PO_2 \cdot p}{2\,Hg_2Cl_2}$$

in which p is the weight of the Hg_2Cl_2 obtained in the analysis.

(*b*) Determination as Magnesium Pyrophosphate

First convert the hypophosphorous acid into phosphoric acid by adding 5 ml. of concentrated nitric acid to the aqueous solution of from 0.5–

1 g. of the substance in about 100 ml. of water,* evaporating on the water-bath to a small volume, adding a few drops of fuming nitric acid and again heating. After this, precipitate the phosphoric acid by magnesia mixture and ammonia and weigh the precipitate as magnesium pyrophosphate as described under Phosphoric Acid.

GROUP III

SULFUROUS, SELENOUS, TELLUROUS, PHOSPHOROUS, CARBONIC, OXALIC, IODIC, BORIC, MOLYBDIC, TARTARIC, META- AND PYROPHOSPHORIC ACIDS

SULFUROUS ACID, H_2SO_3. Mol. Wt. 82.08

Form: Barium Sulfate, $BaSO_4$

The sulfite, or free sulfurous acid, is first oxidized to sulfuric acid and then precipitated with barium chloride. The oxidation can be accomplished by means of chlorine, bromine, hydrogen peroxide, or potassium percarbonate.

Oxidation with Chlorine or Bromine

Allow chlorine water, or bromine water, to flow gradually into the aqueous solution of sulfurous acid, or of a sulfite; after the oxidation is complete, expel the excess of the reagent by boiling and precipitate the sulfuric acid with barium chloride.

Oxidation with Hydrogen Peroxide†

Treat the solution of sulfurous acid, or of a sulfite, with an excess of ammoniacal hydrogen peroxide, heat to boiling to remove the excess of the peroxide, make acid with hydrochloric acid and precipitate with barium chloride.

With potassium percarbonate a similar procedure is used. Treat the cold alkaline solution of the sulfite with solid potassium percarbonate, heat gently, and gradually raise the temperature till the boiling-point is reached. Then make acid with hydrochloric acid and precipitate with barium chloride.

Sulfurous acid may be determined very accurately by a volumetric analysis (cf. Part II, Iodimetry).

* If the hypophosphite were at once treated with nitric acid, metaphosphoric acid would be obtained; by the addition of water the ortho-salt is formed.

† The hydrogen peroxide should always be tested to see if it contains sulfuric acid; if it is found to be present, determine the amount and afterward use an accurately measured quantity for the oxidation. Deduct the amount of sulfuric acid from the peroxide from the total value found in the analysis.

Selenous and Tellurous Acids

The analysis of these acids was discussed under Selenium and Tellurium.

PHOSPHOROUS ACID, H_3PO_3. Mol. Wt. 82.06

Forms: Mercurous Chloride, Hg_2Cl_2, and Magnesium Pyrophosphate, $Mg_2P_2O_7$

This determination is effected exactly like that of hypophosphorous acid (cf. p. 327).

In this case, however, it is to be noted that 1 mole of Hg_2Cl_2 corresponds to 1 mole of H_3PO_3:

$$H_3PO_3 + 2\,HgCl_2 + H_2O = H_3PO_4 + 2\,HCl + Hg_2Cl_2.$$

Determination of Phosphorous and Hypophosphorous Acids

In this case an indirect analysis must be made. After oxidizing one portion of the substance to phosphoric acid, determine the total phosphorus as magnesium pyrophosphate; allow mercuric chloride to act upon a second portion and determine the weight of mercurous chloride formed. From these data the amount of each acid present can be calculated as follows:

Assume a solution containing the two acids is being analyzed. Let x denote the weight of hypophosphorous acid present in V ml. of the solution.

Let m, n, o, and v represent the following chemical factors:

$$m = \frac{Mg_2P_2O_7}{2\,H_3PO_2} = 1.686 \qquad n = \frac{Mg_2P_2O_7}{2\,H_3PO_3} = 1.357$$

$$o = \frac{2\,Hg_2Cl_2}{H_3PO_2} = 14.30 \qquad v = \frac{Hg_2Cl_2}{H_3PO_3} = 5.753$$

Then ox is the weight of mercurous chloride produced from the hypophosphorous acid and mx is the weight of magnesium pyrophosphate equivalent to the hypophosphorous acid. Further, let y represent the weight of phosphorous acid present in the same volume of the solution, vy the corresponding amount of mercurous chloride and ny that of magnesium pyrophosphate. The total amount of the mercurous chloride is q, and the total amount of magnesium pyrophosphate is p. Then

$$mx + ny = p$$
$$ox + vy = q$$

from which it follows

$$x = q\frac{n}{on - mv} - p\frac{v}{on - mv} = q \cdot 0.1399 - p \cdot 0.5933$$

and

$$y = p\frac{o}{on - mv} - q\frac{m}{on - mv} = p \cdot 1.474 - q \cdot 0.1738.$$

CARBONIC ACID, H_2CO_3. Mol. Wt. 62.02

Carbonic acid is determined gravimetrically as CO_2; it can also be determined by measuring the volume of the gas or by titrating with an acid to determine the amount required to decompose a carbonate.

1. Gravimetric Determination of Carbon Dioxide

This analysis may be accomplished in two ways. From the weighed substance, the carbon dioxide can be expelled and the loss in weight determined. Second, the carbon dioxide may be expelled from a weighed amount of the substance and then absorbed in a suitable apparatus; in this case the carbon dioxide is weighed directly.

A. DETERMINATION OF CARBONIC ACID BY DIFFERENCE

(*a*) *Determination in the Dry Way*

For the analysis of a carbonate, or a mixture of carbonates which contains no volatile constituent other than the carbon dioxide, weigh out 1 g. of the substance into a platinum crucible and gradually heat to a high temperature.* In case calcium, strontium, or magnesium is present a final heating over the blast-lamp or Méker is necessary, while with other carbonates the heat of a good Tirrill burner is sufficient; even the difficultly decomposable cadmium carbonate can be analyzed by this method. The carbonates of barium and the alkalies, on the other hand, do not lose their carbon dioxide by such ignition.

If the substance contains water besides carbon dioxide, then the sum of the water + carbon dioxide is determined by the loss on ignition, and the amount of carbon dioxide is determined in a second portion by (*b*).

(*b*) *Determination in the Wet Way*

Principle. — Place the weighed carbonate in an apparatus containing acid, but in such a way that the former does not at first come in contact with the latter. Then weigh the whole apparatus, and allow the acid to act upon the substance; carbon

* Carbonic acid cannot be determined by this method when the residual oxide suffers change, as, for example, in the case of $FeCO_3$ and $MnCO_3$ where an oxidation takes place.

dioxide is evolved and escapes from the apparatus. (Care must be taken that no moisture escapes with the gas.) By afterward weighing the apparatus and subtracting this weight from that first obtained, the weight of the carbon dioxide is ascertained.

Procedure. — This analysis is easily accomplished, and a large number of different forms of apparatus have been devised for the purpose. In this book, however, only one of these so-called *alkalimeters* will be described, namely, that of Mohr, which in an improved form is shown in Fig. 69, although it must be stated that many other forms (*e.g.*, those of Bunsen,* Shrötter, Geissler, Fresenius-Will, etc.) answer the purpose equally well.

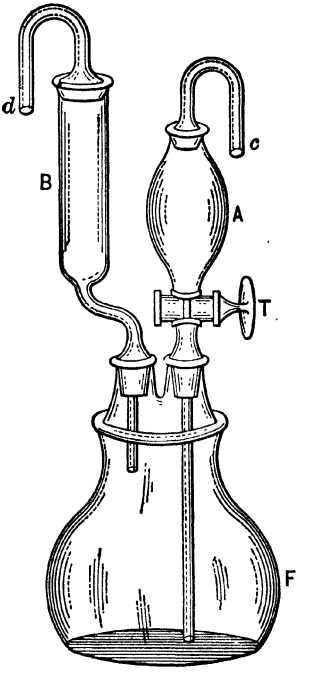


FIG. 69.

The alkalimeter consists of the small, wide-mouthed, flat-bottomed flask *F*, which has a ground-glass connection with the tubes *A* and *B*. At the bottom of *B* place a loose wad of cotton; insert a cylinder of glazed paper about 3 cm. wide into the neck of the tube, and through this cylinder pour small pieces of sifted calcium chloride.† Remove the paper cylinder after the tube is about three-quarters full of calcium chloride, and take care that none of the latter adheres to the glass above the filled portion. Place another wad of cotton in the tube, insert the top part, and close the tube temporarily at *d* by means of a piece of stirring-rod within rubber tubing. The tube should be kept closed when not in use to prevent the gradual absorption of moisture from the air. Fill two ordinary calcium chloride tubes in the same way about two-thirds full, but in this case place softened cork stoppers at the end of the tubes after the second wad of cotton. Through a hole in each stopper introduce

* In the German edition of this book, Bunsen's alkalimeter is described instead of Mohr's. The above apparatus has the advantage of having a stop-cock to separate the acid compartment from the flask, besides having a flat bottom, upon which it will rest unsupported. It is all made of very thin glass and is comparatively light.

† As commercial calcium chloride always contains a little free lime, some carbon dioxide will be absorbed by it and consequently low results obtained in the analysis, unless the calcium chloride is saturated with carbon dioxide before the analysis is made (see foot-note, p. 334).

a short piece of glass tubing with rounded ends, and shove the cork far into the tube with the help of a stirring-rod, leaving the outer 2 or 3 mm. empty. Fill this empty space in the tube with molten sealing-wax, so that a perfectly air-tight connection is made. Close these tubes, when not in use, by pieces of stirring-rod within rubber tubing.

Before beginning the determination the apparatus must be clean and dry. It is not advisable to dry the flask by washing with alcohol and ether, but it should be gently heated while a current of dry air is sucked through it. As aspirator an inverted wash-bottle may be used, from which the water is allowed to run out slowly through the shorter tube. During the aspiration the small calcium chloride tubes are connected with *c* and *d* respectively, so that no moisture can enter the flask.

When all is ready transfer 1–1.5 g. of the finely-powdered substance, from a weighing-tube, to the flask and add a little water.* Now fill the tube *A* two-thirds full with 2.5 *N* hydrochloric acid by means of a small funnel or thistle tube, and turn the stop-cock *T* so that none of the acid will run into the flask. Place the whole apparatus, as shown in Fig. 69, upon the balance-pan and accurately weigh. Remove from the balance, open the stop-cock *T* so that the acid in *A* slowly drops into the flask. As soon as the evolution of carbon dioxide begins to take place quietly, allow the apparatus to stand without watching for 30 minutes. At the end of this time all of the acid will have passed into the flask, and the decomposition will be nearly complete in most cases. It now remains to remove all carbon dioxide absorbed by the liquid and contained in the apparatus. This is effected by gently heating the solution by means of a small flame until the acid just begins to boil, meanwhile aspirating a current of dry air through *c* and out at *d*. Not more than three or four bubbles of air per second should be allowed to pass through the flask. As soon as the boiling begins, remove the flame and continue passing a slow current of air through the apparatus until it is cold. Then stopper and allow to stand near the balance for half an hour or more, after which weigh it again without the stoppers. The loss in weight represents the amount of carbon dioxide originally present in the substance as carbonate.

Remark. — This method affords excellent results in the estimation of large amounts of carbonic acid, but it is unreliable for the analysis of small amounts such as are

* This method is often used for the determination of the carbonic acid in baking-powders. Such substances are decomposed by water so that they should be kept dry until after the apparatus has been weighed.

present in cements, etc. In such cases the Fresenius-Classen or Lunge-Marchlewski method is better. (See below and p. 340.)

The objection to this method lies in the fact that owing to the size and weight of the apparatus, there is likely to be an error in making the two weighings.* On the other hand, it is somewhat easier to expel carbon dioxide from a solution than it is to absorb it quantitatively. Before each weighing, dry the outside of the apparatus by wiping with a piece of chamois or clean linen.

B. DIRECT DETERMINATION OF CARBON DIOXIDE

Here again the determination can be carried out both in the dry and wet ways.

(*a*) *Determination in the Dry Way*

Weigh out 1–2 g. of the substance into a porcelain boat, and shove the latter into the middle of a horizontally-held glass tube, about 20 cm. long and 1–1.5 cm. wide, and made of difficultly fusible glass. Both ends of the tube should be provided with calcium chloride tubes connected with it by means of tightly-fitting rubber stoppers. Through one of the calcium chloride tubes pass a slow stream of air (free from carbon dioxide)† and connect the other with two weighed soda-lime or ascarite tubes (cf. pp. 351, 352). Heat the substance gradually until it glows strongly, meanwhile passing a slow but steady current of air through the apparatus. When there is no further heat effect to be detected in the absorption tubes, allow the substance to cool in the current of air and subsequently weigh the tubes. The increase of weight represents the amount of carbon dioxide.

Remark. — This method can be employed for the analysis of all carbonates with the exception of those of barium and the alkalies,‡ though, of course, no other volatile acid can be present at the same time. Water is kept back by the calcium chloride tubes.

(*b*) *Determination in the Wet Way, Method of Fresenius-Classen*

The apparatus necessary for this determination is shown in Fig. 70. It consists of a decomposition-flask of about 400 ml. capacity provided with a condenser and connected with the drying-tubes *a*, *b*, and *c* and with the weighed soda-lime tubes

* There is some danger of losing a little hydrochloric-acid gas during the operation. To prevent this the calcium chloride may be replaced by pumice impregnated with anhydrous copper sulfate, or the carbonate may be decomposed by means of sulfuric acid.

† The air is passed through two wash-bottles containing caustic potash solution.

‡ Even the carbonates of the alkalies and of barium can be analyzed in this way if they are mixed with potassium bichromate.

d and *e*;* *f* is a protection tube with its left arm filled with calcium chloride and its right arm filled with soda-lime or ascarite. The first drying-tube, *a*, contains glass beads wet with concentrated sulfuric acid; *b* and *c* contain granular calcium chloride.†

Procedure. — Weigh out the substance into the dry flask, cover with a little water to prevent loss of the substance and pass a slow current of air (free from carbon dioxide) through the apparatus to remove any carbon dioxide that may be present in the flask or in the three drying-tubes. While the air is being led through the apparatus, carefully wipe dry the soda-lime tubes and weigh. Stop the current of air, connect the weighed tubes with *c* on the one hand and with *f* on the other, and allow a slow stream of 3 *N* hydrochloric acid to flow upon the substance from the funnel *T*, causing an immediate evolution of carbon

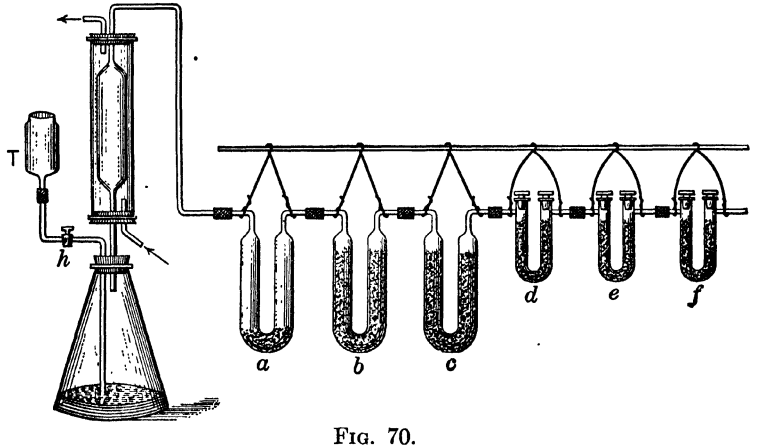


FIG. 70.

dioxide gas. Regulate the flow of acid so that not more than 3–4 bubbles per second of gas pass through *a*. When all of the acid has been added, slowly heat the contents of the flask to boiling and while the

* The right arm of the last soda-lime tube is one-third filled with calcium chloride in order to absorb the water set free by the absorption of the carbon dioxide by the soda-lime, $2\,NaOH + CO_2 = Na_2CO_3 + H_2O$.

† As commercial calcium chloride always contains lime which will absorb carbon dioxide, it must be saturated with this gas before the determination is made. For this purpose pass a dry current of the gas through the tubes for one or two minutes, then close the outer end of the tube by means of a glass rod within a piece of rubber tubing and keep the other end connected with the Kipp generator for 12 hours. At the end of that time remove the excess of carbon dioxide by passing air through the tubes for 20 minutes. The air is freed from carbon dioxide and dried by passing through two bottles containing concentrated caustic potash solution and then through a long tube filled with calcium chloride.

solution is boiling gently, pass a slow current of air through the apparatus so that not more than 2–3 bubbles per second pass through *a*. During the whole operation, allow cold water to flow through the condenser; in this way the water vapor is condensed and flows back into the flask instead of reaching the sulfuric acid in *a*; consequently the contents of the latter tube seldom have to be renewed. Almost all of the carbonic acid is absorbed in the first soda-lime tube, as may be ascertained by the heat effect there. The second tube, *e*, should remain perfectly cold provided not more than 0.5–1 g. of the carbonate was taken for the analysis. When all of the carbon dioxide has been absorbed the tube *d* quickly cools. As soon as this has taken place, remove the flame and pass air somewhat more rapidly through the apparatus for 20 minutes more. Then remove the soda-lime tubes, stopper, and allow to stand in the balance case for 20 minutes, to acquire the temperature of the balance; wipe them dry on the outside and weigh.

Remark. — The results obtained by this method are perfectly satisfactory. For the analysis of substances containing small amounts of carbonate, take from 3–10 g. for the analysis.

If the substance contains besides the carbonate a sulfide which is decomposable with acid, introduce between *a* and *b* a tube containing pumice impregnated with copper sulfate.* This serves to absorb all of the hydrogen sulfide evolved.

Sulfites interfere with this determination, but the difficulty can be overcome by first decomposing the carbonate with an excess of potassium dichromate solution and adding a little dilute sulfuric acid toward the end of the operation. †

The Fresenius-Classen method is suitable not only for the determination of carbon dioxide in solid substances, but also for the analysis of carbonates in solution provided little or no free carbonic acid is present. In case considerable amounts of the latter are to be estimated, as in the case of many mineral waters, the analysis is conducted as follows:

---

* Place 60 g. of pumice in pieces about the size of a pea in a porcelain dish and cover with a concentrated solution of 30–35 g. of copper sulfate. Evaporate the solution to dryness with constant stirring and allow the residue to remain in the hot closet at 150–160° for 4–5 hours. At this temperature the copper sulfate is partly dehydrated and in this condition it absorbs hydrogen sulfide more readily than when in the hydrous condition. It cannot be heated higher than the above temperature, as otherwise some sulfur dioxide is formed which would be absorbed by the soda-lime.

† E. R. Marle, *J. Chem. Soc.*, **95**, 1491 (1909).

As an example of the analysis of a commercial carbonate, let us consider the

Analysis of Commercial White Lead*

If the sample is in the form of a paste, or is a mixed paint, it is necessary to find the

Percentage of Pigment. — Weigh 15 g. of the paste into a weighed centrifuge tube. Add 20 ml. of an extraction mixture made by mixing 10 volumes of ethyl ether, 6 volumes of benzene, 4 volumes of methyl alcohol and 1 volume of acetone. Mix thoroughly with a stirring rod and wash off the rod with more of the extraction mixture, finally diluting to 60 ml. with the same. Place the tube in a container of a centrifuge, surround with water, balance with a similar tube on the opposite arm and whirl at a moderate speed until the precipitate has settled well. Decant off the clear liquid and repeat the treatment with two more 40 ml. portions of the extraction mixture and finally with 40 ml. of ethyl ether. After pouring off the clear ether, remove the rest by placing the tube in a beaker of water heated to 80°. Finally dry 2 hours at 110°, cool, weigh and calculate the percentage of pigment. Grind to a fine powder and pass through a No. 80 screen to remove skins. Preserve the dry sample in a glass-stoppered bottle.

Total Lead and Insoluble Impurity. — Moisten 1 g. of the pigment with water and dissolve in 25 ml. of 6 *N* nitric acid in a covered beaker. Heat until all carbon dioxide is expelled, dilute and filter off any dissolved impurity. Dry at 110° and compute the percentage of insoluble matter. Add to the filtrate 20 ml. of 18 *N* sulfuric acid, evaporate to fumes and determine the lead according to p. 176.

Metallic Lead. — Weigh 50 g. into a 400 ml. beaker, add a little water and 60 ml. of 40 per cent acetic acid, taking care to avoid loss by effervescence. Heat to boiling, fill the beaker with water, decant off the solution and digest the residue with 60 ml. of a mixture of 360 ml. of concentrated ammonium hydroxide, 1080 ml. of water and 2160 ml. of 80 per cent acetic acid. Boil, fill the beaker with water, decant and filter. Collect the residue on a watch-glass and float off everything but the metallic lead. Dry at 110° and weigh.

Carbon Dioxide. — Take 1 g. of the pigment and analyze as described on p. 334.

Acetic Acid. — Place 18 g. of pigment in a 500 ml. flask, add 40 ml. of sirupy phosphoric acid, 18 g. of zinc dust and 15 ml. of water. Distil through a Liebig condenser till only a small volume of liquid is left.

* This method given here is based on the Tentative Methods of the American Society of Testing Materials and Circular No. 84 of the U. S. Bureau of Standards.

With the condenser still in place, pass steam into the distilling flask until it is half full of condensed water, then distil again to a small volume. Repeat the steam treatment twice more. To the total distillate add 1 ml. of sirupy phosphoric acid and distil down to 20 ml. using a splash trap between the flask and the condenser. Introduce steam until 200 ml. of water condense in the distilling flask and again distil. To each 200 ml. of distillate add phenolphthalein indicator solution and titrate with 0.1 *N* sodium hydroxide. Keep on distilling, with intermediate treatment with steam, until 10 ml. of distillate require only 1 drop of 0.1 *N* alkali solution to color phenolphthalein. One ml. of 0.1 *N* caustic alkali solution reacts with 0.006004 g. of acetic acid or 0.005103 g. of acetic anhydride.

Determination of Total Amount of Carbonic Acid in Mineral Waters

Place 3–4 g. of freshly-burnt lime* and the same amount of crystallized calcium chloride† in each of from 4–6 Erlenmeyer flasks whose necks are of such a size that they will each fit the apparatus shown in Fig. 70. Close the flasks by means of tightly-fitting rubber stoppers and accurately weigh. Take a double-bored rubber stopper of such a size that it will fit into the neck of each of the above flasks and through one of the holes fit a short glass tube which reaches about 3 cm. above the stopper and the same distance below, and through the other hole insert a glass tube about 50 cm. long which likewise reaches about 3 cm. below the stopper. To fill the weighed flasks with the water to be analyzed, take them to the spring and fill one after another as follows: Replace the solid rubber stopper by the one fitted with the 2 tubes, hold the thumb over the shorter of the tubes, and dip the flask well below the surface of the water, but so that the longer tube still reaches into the air above. Now remove the thumb from the shorter tube; the spring-water will pass into the flask and the replaced air will escape through the long tube. As soon as the flask is almost full, again close

* To prepare this lime absolutely free from carbonate, place the lime in a tube of difficultly-fusible glass and heat in a small combustion furnace, meanwhile passing a current of dry air free from carbon dioxide over it. In this way 4 g. of commercial lime can be freed from carbonate in 30–45 minutes. That the carbon dioxide is actually removed can be shown at the end of that time by passing the escaping air through baryta water; there should be no turbidity. A blank experiment should always be made with this lime. If it is desired to use commercial lime for the determination, determine the amount of carbonate present and use an accurately weighed amount for the analysis.

† The addition of calcium chloride serves to decompose any alkali carbonate. This is not quantitatively decomposed by lime alone, particularly when magnesium carbonate is present.

the shorter tube with the thumb, remove the flask from the water, and once more quickly interchange the stoppers. To make sure that the solid stopper is not loosened while carrying the flask back to the laboratory, cover it with a piece of parchment paper, and tie it with string to the neck of the flask. Allow the flasks and contents to stand several days with frequent shaking. All the carbonic acid of the spring water will then have reacted with the lime and be precipitated as calcium carbonate. Allow the precipitate to settle and weigh. The gain in weight represents the weight of water taken. Quickly pour off the supernatant liquid through a plaited filter, quickly throw the filter and its contents into the decomposition flask, connect with the train shown in Fig. 70 and determine the carbon dioxide as in the previous method.

This method is capable of yielding excellent results provided the flasks can be filled as above described. Often, however, the spring is not easily accessible, so that the flasks must be filled by a different method and usually a small amount of carbonic acid is lost during the operation. A much more expeditious and accurate procedure which can be performed within one hour at the spring, consists in the determination of the total amount of carbonic acid present in mineral waters by measuring the volume of the gas.*

2. Gas-volumetric Determination of Carbonic Acid

(*a*) *Method of O. Pettersson*†

This excellent method, upon which the two following procedures are based, consists in evolving carbon dioxide from carbonates by the action of acid, collecting the gas over mercury and computing its weight from its volume. Pettersson's apparatus is shown in Fig. 71, and was used by him for the determination of the carbonic acid in sea-water and in carbonates, and also for the determination of carbon in iron and steel. The procedure for determining the carbonic acid in a water containing small amounts of free carbonic acid but considerable carbonate will suffice to show how the apparatus is used. Fill the decomposition-flask *K* with distilled water up to the mark just below the side-arm (the mark is not shown in the illustration). By weighing the flask both empty and with this amount of water, the volume of the flask when filled to the mark is obtained. Drop in a small piece of aluminium wire‡ and connect the flask with the rest of the apparatus as

* Cf. the modified method of Pettersson on p. 345.

† *Ber.*, **23**, 1402 (1890).

‡ 0.0142 g. aluminium evolves 20 ml. of moist hydrogen at 720 mm. and 15° C.

shown in the figure. All of the rubber tubing should be firmly fastened to the glass by means of wire. Close the cocks *a*, *b*, and *d*, open *c*, and remove the air in the measuring-tube by raising *M* until the mercury rises in the capillary up to the crossing point. After this close *c*, open *a*, lower *M*, and slowly open the screw-cock *d*. By this means the hydrochloric acid in *N* is introduced into the flask *K*. Allow the acid to run into the flask until the upper part of the apparatus is reached, then close *d* and *a*. Remove the air in the measuring-tube (which does not contain an appreciable amount of carbon dioxide) by opening *c* and raising *M*, after which again close *c*. Now once more open *a*, lower *M*, and heat the liquid in *K* by a flame.

A lively evolution of gas at once ensues. As soon as the measuring-tube is almost filled with the gas, close *a*, remove the flame from under *K*, raise *M* until the mercury within it stands level with that in the measuring-tube, and read its position in the latter. At the same time note the barometer reading and the temperature of the cold water which surrounds the measuring-tube. After this open *b* and raise *M*, whereby the gas passes into the Orsat tube *O* which contains caustic potash solution (1:2). As soon as the mercury has reached the juncture of the horizontal and vertical tubes, close *b* and allow the gas to remain in the Orsat tube for 3 minutes. Once more transfer the unabsorbed gas into the measuring-tube, taking care that none of the caustic potash solution comes with it (the latter should not quite reach the stop-cock *b*). After bringing the gas to the atmospheric pressure, read the volume of the gas, the thermometer and the barometer. As a rule, these readings of the barometer and thermometer remain constant, otherwise it is necessary to reduce the gas volumes in each case to 0° C. and 760 mm. pressure. The difference between the two volumes represents the amount of the carbonic acid gas. Remove the unabsorbed gas through *c* and repeat this whole operation of collecting the gas and

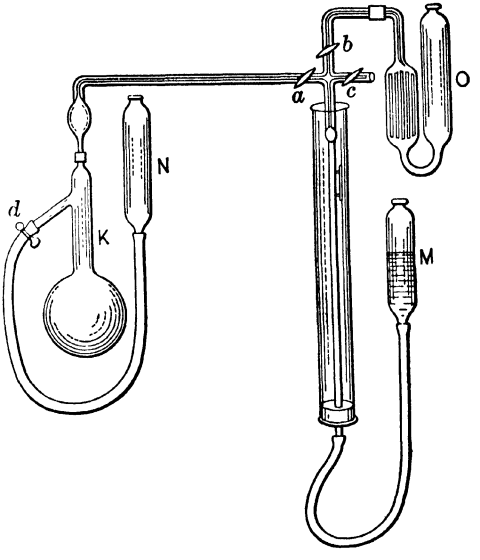


FIG. 71.

absorbing the carbon dioxide until finally no more gas is given off from the liquid in K.

If it is desired to determine the amount of carbonate in a solid substance, a smaller decomposition-flask should be used. Add the aluminium wire to the weighed substance and exhaust the apparatus by repeatedly lowering M, closing a, opening c, and then raising M. Finally allow the acid to act upon the substance and carry out the determination exactly as described above.

Computation of the Analysis. — Assume that from a g. of substance V ml. of carbon dioxide were obtained, which was measured moist at $t°$ C. and B. mm. pressure. First of all reduce the volume to 0° C. and 760 mm. pressure by the following formula:

$$V_0 = \frac{V\,(B - w) \cdot 273}{760\,(273 + t)}.$$

In this formula, w represents the tension of aqueous vapor expressed in millimeters of mercury.

Since the density of carbon dioxide is 1.529* referred to air as unity and 1 ml. of air at 0° and 760 mm. pressure weighs 0.001293 g.†, evidently

1 ml. CO_2 weighs $0.001293 \times 1.529 = 0.001977$ g. at 0° and 760 mm.

and V_0 ml. weigh $V \times 0.001977$ g. The percentage of CO_2 in the original substance is then

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2$$

Remark. — The addition of aluminium is absolutely necessary. By boiling an acid solution, carbonic acid is not completely expelled; this is only effected when a different gas simultaneously passes through the solution. Formerly it was customary to pass air through the apparatus, but Pettersson accomplished the same purpose by generating hydrogen within the liquid itself.

(*b*) *Method of Lunge and Marchlewski*‡

Lunge and Marchlewski carry out the determination according to the same principle as that of the above process; *i.e.*, by simultaneously evolving hydrogen (aluminium and hydrochloric acid), measuring the gas, and absorbing the carbon dioxide by means of caustic potash in an Orsat tube.

* Cf. Lord Rayleigh, *Proc. Roy. Soc.*, **62**, 204 (1897); Guye and Pintza, *Mém. soc. phys. hist. nat. Genève* 35, 569 (1908).

† Landolt-Börnstein, *Phys. chem. Tabellen.*

‡ *Zeitschr. angew. Chem.*, **1891**, 229.

The apparatus which they recommend is shown in Fig. 72, *b*. It consists of the 40-ml. decomposition-flask *N*, the 140-ml. measuring-

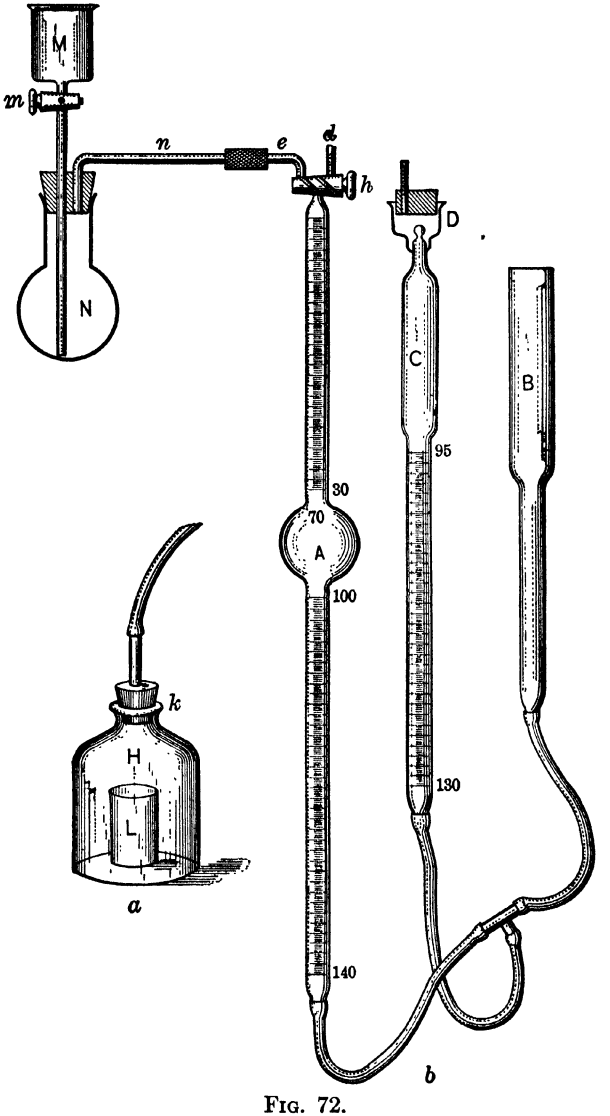


FIG. 72.

tube *A*, tne compensation-tube *C*, and the leveling-tube *B*; the three last are connected together as shown in the figure.

In the case of all gas-volumetric methods, the volume of the measured gas must be reduced to 0° C. and 760 mm. pressure, which ordinarily

requires a knowledge of the temperature and the barometric pressure. In this method the reduction is accomplished without paying any attention to the actual readings of the thermometer and barometer by means of the compensation-tube C, which contains a known amount of air, viz., that amount of air which in a dry condition assumes a volume of 100 ml. at 0° C. and 760 mm. pressure. If, therefore, this amount of air has a volume of V' at $t°$ and atmospheric pressure P' (with the mercury at the same level in B and C), we know that this volume of any gas would be equal to 100 ml. at 0° C. and 760 mm. pressure. By raising the leveling-tube B so high that V' ml. is compressed to 100 ml., we have accomplished the reduction in a mechanical way. If, however, there is a gas volume V'' in the measuring-tube A under the same pressure as that in the compensation-tube (this is the case when the mercury level is the same in A and C), we can reduce this volume to the standard conditions by simply raising B until the volume of the gas in C is just 100 ml., taking care that the mercury remains at the same height in the tubes A and C. The volume of the gas V_0'' in A corresponds, therefore, to the volume of this gas at 0° C. and 760 mm. pressure, for it has been compressed to the same degree as the gas in C. This is apparent when we remember that at a constant temperature the product of the pressure into the volume remains a constant for any gas.

In the compensation-tube we have the volume V' at atmospheric pressure P', and after compression the volume becomes $V_0' = 100$ ml. and the pressure is P_0, from which it follows:

$$1. \quad V'P' = V_0'P_0.$$

In the measuring-tube A, we have the volume V'' at the atmospheric pressure P', and after compression this volume becomes V_0'', and the pressure P_0, so that

$$2. \quad V'' \cdot P' = V_0''P_0.$$

By dividing equation 1 by equation 2 we have:

$$\frac{V' \cdot P'}{V'' \cdot P'} = \frac{V_0' \cdot P_0}{V_0'' \cdot P_0}$$

or

$$V' : V'' = V_0' : V_0''$$

and V_0'' is, therefore, the reduced gas volume that is desired.

Before using the apparatus for the determination, it is necessary to fill the compensation-tube with the correct amount of air; this is accomplished as follows:

First of all, calculate what would be the volume of 100 ml. of dry air measured at 0° C. and 760 mm. pressure when measured moist at the temperature of the laboratory and the prevailing barometric pressure. To illustrate, assume

$t = 17.5°$ C.; $B = 731$ mm.; $w = 14.9$ (tension of aqueous vapor), then

$$V = \frac{100 \times 760 \times 290.5}{273\,(731 - 14.9)} = 112.9 \text{ ml.}$$

In such a case introduce 112.9 ml. of air into the tube C by removing the stopper and lowering the leveling-tube until the mercury in the compensation-tube stands at exactly 112.9 ml. Add a drop of water by a pipet, immediately stopper the tube and make an air-tight seal by covering the latter with mercury. Then press down a rubber stopper containing a glass tube into D. After this the temperature and pressure may vary as much as it will; the reduced volume of the air in C will always be equal to 100 ml.

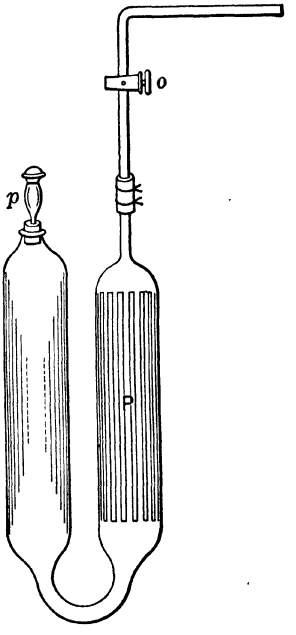


FIG. 73.

Procedure for the Analysis. — Weigh out about 0.08 g. of aluminium wire, *i.e.*, enough to furnish approximately 100 ml. of hydrogen, into the decomposition-flask. Add a sufficient weight of the substance to be analyzed so that about 30 ml. and no more of carbon dioxide will be generated, and connect the flask with the funnel tube M, and capillary n. Also make connection with the tube A after it has been completely filled with mercury by raising B. Exhaust the air from N by lowering B, opening h so that e is connected with A, then closing h by turning it 90°, and carefully raising B until the mercury stands at an equal height in A and B; after this turn h so that A is connected with the capillary d, and expel the air in A. After repeating this process 3–4 times until finally only 2–3 centimeters of air remain in A, lower B, add the necessary volume of 3 N hydrochloric acid to M, carefully open h, then m until 10 ml. of the acid have run into the flask N, when m is once more closed. The carbon dioxide evolution begins at once and the mercury level quickly falls in A. Heat the contents of the flask to boiling over a flame and maintain this temperature until all of

the aluminium has dissolved. During the whole operation the mercury level in B must be kept lower than that in A, In order to transfer the gas remaining in the flask N into the tube A, fill M with distilled water, slowly open m and allow the water to run into N until the stop-cock h is reached, then immediately close h. Compress the gas by raising the tube B until the mercury stands at the same height in A and C and the level in the latter tube is exactly at the 100-ml. mark. Read the volume of the gas. After this connect the capillary d with an Orsat tube filled with caustic potash (1:2) (Fig. 73), drive over the gas in A into the Orsat tube, allow to stand 3 minutes, and transfer the unabsorbed gas to A, where its volume at 0° C. and 760 mm. pressure is determined as before. The difference in the two readings represents the volume of the carbon dioxide, and the per cent can be computed according to the formula

$$\text{Per cent.}CO_2 = 0.1977 \cdot \frac{V}{a},$$

in which V is the amount of carbon dioxide absorbed in the Orsat tube and a represents the amount of substance taken for the analysis.

Remark. — This is the most exact of all methods for the determination of carbon dioxide in solid substances and is accomplished quickly. It is to be recommended where carbon dioxide determinations must be made daily, as, for example, in cement factories. It is necessary, however, to test the volume of the gas in the compensation-tube from time to time to make sure that it really corresponds to 100 ml. of air under the standard conditions of temperature and pressure.

For a single determination the author prefers to dispense with the compensation-tube. In this case, however, the collected gas must be kept surrounded by water at a definite temperature, as in the Pettersson method, and the temperature and pressure must be observed. It is also well to make these readings in the above-described procedure, to be sure that the volume in the compensation-tube has remained constant.

(c) *Method of Lunge and Rittener**

In the decomposition flask K, Fig. 74, place 0.14–0.15 g. of calcite, or a corresponding amount of any other carbonate, and fasten a small piece of aluminium wire, weighing about 0.015 g. to the neck of the flask. Allow about 1 ml. of water to flow through the funnel, T, and then connect the capillary with the dry Bunte buret. Close the stop-cock of the funnel T and open the two cocks of the Bunte buret. Connect the lower stop-cock, h_1, with the suction pump, and produce a partial vacuum in the buret by letting the pump run 2–3 minutes, after which close h_1. Now from the funnel T, allow 2.5 N hydrochloric acid to

* *Z. angew. Chem.*, 1906, 1849.

flow upon the substance until the latter is decomposed completely; then heat the liquid to boiling,* taking care that no water gets into the buret. Add acid from T until the aluminium wire is reached and heat the flask again. The hydrogen now evolved serves to expel the last traces of carbon dioxide from the flask. As soon as all the aluminium is dissolved, add hydrochloric acid through the funnel until the liquid reaches the stop-cock h, which is then closed at once. Now connect the lower end, a, of the buret by rubber tubing with the leveling tube N, which contains a saturated solution of common salt. By carefully opening the lower stop-cock h_1 allow the salt solution to rise in the buret until the liquid there stands at the same height as in the leveling tube, whereupon the stop-cock h_1 is closed. Allow the apparatus to stand for 20–25 minutes so that the temperature of the gas will be that of the surroundings and then, by suitably raising or lowering the leveling tube with h_1 open, read the buret, the thermometer and the barometer. Fill the funnel T of the buret with strong potassium hydroxide solution (1:2) and produce a partial vacuum in the buret, by lowering the leveling tube and opening the stop-cock h_1.

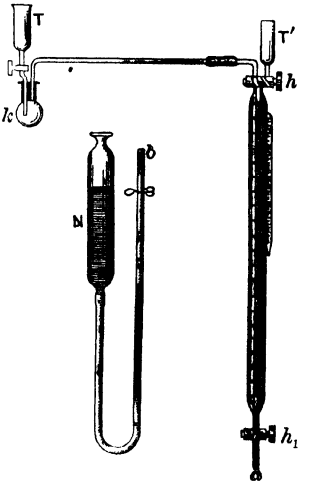


FIG. 74.

Allow the caustic potash solution to run into the buret by opening the upper stop-cock h, but closing it before the last few drops of liquid leave the funnel. Mix the contents of the buret by shaking. By repeating the operation it is easy to tell whether the absorption of carbon dioxide has been complete. Read the residual volume with the usual precautions and the difference between the two readings gives the volume of the carbon dioxide.†

Compute the weight of carbon dioxide exactly as described on p. 340, except that the vapor tension of the saturated salt solution only amounts to 80 per cent of the tension of pure water at the same temperature.

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* In the case of carbonates, such as magnesite, dolomite, or siderite, they are decomposed so slowly by cold, dilute acid that it may be added much more quickly than prescribed above.

† Provided the temperature and pressure are the same as before the absorption of the CO_2. If this is not the case, both volumes must be reduced to 0° and 760 mm. pressure before the difference is found.

Example: Weight of substance = a — Temperature = $t°$,
Volume of hydrogen + air + CO_2 = V_1 — Barometer = B mm.
Hydrogen + air = V_2 — Tension of aqueous vapor = w mm.
$CO_2 = V_1 - V_2$ — Tension of salt solution = $0.8w$ mm.

The volume reduced to 0° and 760 mm., is, therefore:

$$V_0 = \frac{(V_1 - V_2) \cdot (B - 0.8w)\, 273}{760\,(273 + t)},$$

and the percentage of CO_2 in the substance (see p. 340) is,

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2.$$

For the determination of carbon dioxide in mineral waters this apparatus is not suited; for this purpose the author has modified the Pettersson apparatus as shown in Fig. 75.

(*d*) *The Modified Method of Pettersson*

For decomposition-flasks, use 70–200 ml. Erlenmeyers (according to the supposed amount of carbonic acid) and etch the exact capacity of each flask upon it. To determine this, provide each flask with a tightly-fitting stopper of gray (not red) rubber containing one hole, through which the small tube R is introduced. Fuse together the bottom of R but near the bottom make a small hole.

Shove the tube R into the stopper until the small opening can be seen just below the bottom of the rubber stopper, and press the latter as far as possible into the Erlenmeyer flask full of water. By this means some of the water passes from the flask into the tube R. Then raise the latter as is shown in Fig. 75, *b*; in this way an air-tight seal is made.

Remove the water in R by filter-paper and weigh the flask and contents to the nearest centigram. By deducting from this the weight of the empty flask together with the rubber stopper and R, the weight of the water, *i.e.*, the volume of the flask, is obtained. By means of a piece of gummed paper fastened to the flask, note the position of the lower edge of the rubber stopper. Empty the flask, dry, and cover the neck of the flask as well as the paper strip with a thin coating of wax. Along the edge of the paper where the bottom of the rubber stopper came on the flask, cut a sharp line in the wax by means of a knife and write the capacity upon the wax with a pointed file. Etch these lines upon the flask by exposing them to the action of hydrofluoric acid for 2 minutes. Wash off the excess of the latter, dry the flask, melt the wax and wipe off with filter-paper. The flask is now ready to be used for the analysis.

Place about 0.04 g. of aluminium in the flask, and fill it by dipping into the spring. When this is not possible, place a piece of rubber tubing in the bottle containing the water to be analyzed, so that it reaches to the bottom, and siphon the water into the flask for 2–3 minutes. After this, close the filled flask by the rubber stopper with the tube *R* so that the bottom of the stopper reaches just to the mark again. Raise the tube *R* (Fig. 75, *b*) and wash out the spring-water within the tube by a stream of distilled water from a wash-bottle.* Then connect the flask with the bulb-tube *P* (of about 40 ml. capacity), which in turn is connected with the measuring-tube *B*. Place the latter in a condenser through which a stream of ordinary water constantly flows. Now connect the reservoir *N'* with the flask as shown in the figure and close the screw-cock *H*. All rubber connections must be tightly fastened with wire.

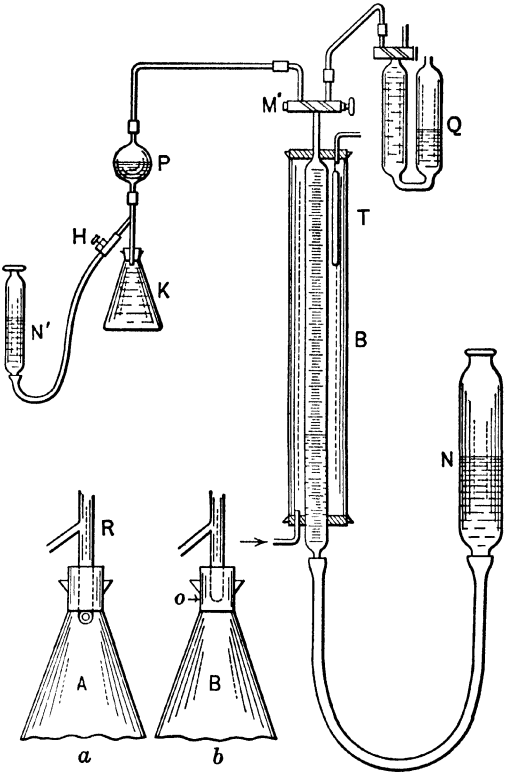


FIG. 75.

Exhaust the bulb *P* by lowering *N* so that the air passes into *B*, from whence it is driven into the Orsat tube *O* by turning the stop-cock *M* and raising *N*. Repeat this operation 4 times. Then remove the air from the Orsat tube by suction through the right-hand capillary and change the stop-cock to its original position as shown in the figure. Now press down the tube *R* into the flask so that the small opening reaches below the lower surface of the stopper.

Usually carbon dioxide is immediately evolved and the mercury in *B* at once begins to sink slowly. Hasten the evolution of the gas by

* With water containing much carbonic acid, cool the flask and its contents by ice in order to prevent the glass breaking.

gently heating the contents of the flask. As soon as the measuring-tube is almost entirely filled with gas, remove the flame, close *M*, and bring the contents of *B* under atmospheric pressure by raising *N* until the mercury in the two tubes is at the same height, and read its position in *B*. Take the temperature of the water surrounding *B*, read the barometer,* drive the gas over into the Orsat tube and allow it to remain there. Repeat this boiling, measuring, and driving over of the gas until only a slight gas evolution can be made to take place. In this way all the free carbon dioxide and a part of that present as bicarbonate is driven off, while that present as normal carbonate together with the rest of the bicarbonate remains in the flask; the liquid in the latter is usually turbid at this point owing to the precipitation of alkaline-earth carbonates. Now fill the reservoir *N'* with 4 *N* hydrochloric acid (1:2) and remove the air from the rubber tubing by raising *N'* high and pinching the tubing with the fingers. Place the leveling-tube *N* in a low position, open *H*, and allow a little acid to run into *K*, after which *H* is again closed. As soon as the acid reaches the contents of *K*, a lively evolution of carbon dioxide ensues, which is afterward hastened by gentle warming. When the measuring-tube *B* is nearly filled, read its contents and drive over into the Orsat tube as before. Repeat the addition of the acid, etc., until finally the liquid in *K* clears up and the aluminium begins to evolve a steady stream of hydrogen, then heat the contents of the flask to boiling, but take care that none of the liquid in the flask is carried over with the escaping gas. As soon as the aluminium has completely dissolved, lower *N*, open *H* so that the flask is filled with the hydrochloric acid solution and the last portions of the gas are carried over into the measuring-tube *B*. As soon as the acid has reached the stop-cock *M*, close it, and after reading the volume of the gas as before, transfer it to the Orsat tube. After remaining there 3 minutes bring back the unabsorbed gas to *B* and subtract its volume from the total amount of gas which has been expelled from the water that was analyzed. This difference represents the volume of the carbon dioxide gas. By correctly adjusting the current of water flowing through the condenser, the temperature at which the gas is measured will remain constant during the entire experiment.

From the volume of the absorbed carbon dioxide the per cent present is computed as was shown under the Pettersson method.

Determination of Carbonic Acid in the Air

See Part II, Acidimetry.

* If this analysis is made at the spring, it is necessary to have a sensitive aneroid barometer at hand.

Determination of Carbonic Acid in the Presence of Other Volatile Substances

(a) Determination of Carbonic Acid in the Presence of Chlorine

If it is desired to determine the amount of carbonate present in commercial chloride of lime, chlorine will be evolved with the carbonic acid on treatment of the solid substance with hydrochloric acid, so that neither the direct nor the indirect method will give correct results. The determination can easily be effected by the following procedure:

Decompose the chloride of lime with hydrochloric acid and pass the evolved gases ($CO_2 + Cl_2$) into an ammoniacal solution containing calcium chloride.* After standing several hours in a warm place, quickly filter off the precipitate, wash with water, and determine the carbonate in the precipitated calcium carbonate by one of the usual methods.

Remark. — On conducting the mixture of chlorine and carbon dioxide into the ammoniacal solution of calcium chloride, the chlorine is changed into ammonium chloride with evolution of nitrogen, $8\,NH_3 + 3\,Cl_2 = 6\,NH_4Cl + N_2$, while the carbon dioxide is absorbed by the ammonia, forming ammonium carbonate; the latter is precipitated by the calcium chloride as calcium carbonate.

(b) Determination of Carbon Dioxide in the Presence of Alkali Sulfides, Sulfites, or Thiosulfates

Treat the solution to be analyzed with an excess of a solution of hydrogen peroxide containing potassium hydroxide, but free from carbonate. Boil to destroy the excess of the hydrogen peroxide, concentrate, and determine the carbonate preferably by the Fresenius-Classen method (p. 333).

DETERMINATION OF CARBON

(1) *In Iron and Steel.*
(2) *In Organic Compounds.*

1. Determination of Carbon in Iron and Steel

Carbon occurs in iron and steel as carbide, as a solid solution of carbide in iron, as graphite and as temper carbon. Iron carbide, Fe_3C, is often called cementite. The properties of iron and steel depend not only upon the chemical composition of the material but also upon the treatment which has been given to it. Thus a steel with a given per-

* Dissolve 50 g. of crystallized calcium chloride in 250 ml. of water, add 500 ml. of concentrated ammonia water, and allow the mixture to stand at least 4 weeks before using.

centage of carbon may be very hard if it has been cooled quickly from say 1000°, or it may be much softer if it has been annealed. By polishing a piece of metal and etching the surface, it is possible to estimate by microscopical examination the percentage of carbon present, the heat treatment which has been given to the specimen and whether the material is homogeneous. In testing steel and other alloys the work of the chemist should go hand in hand with that of the metallographer as either is likely to be led astray without the other.*

In the chemical analysis of iron and steel the total carbon is usually obtained by combustion. In this country, this is usually done in the dry way with an electric furnace. In some parts of Europe a wet combustion, or oxidation by a mixture of chromic and sulfuric acids is preferred. The first method to be described is that recommended by the Bureau of Standards at Washington. It was formerly considered desirable to remove the iron by volatilization in a stream of chlorine (Wöhler) or by treating the metal with a solution of double chloride of copper and potassium (Berzelius-Richter), but at a temperature of 1100° it is possible to get complete oxidation of the sample without removing the iron and the procedure is thus shortened.

The combined carbon is sometimes determined quickly by matching the color of the solution obtained by dissolving the steel in nitric acid but the color is not strictly proportional to the carbon content and a hardened steel gives a different color than an annealed one with the same carbon content. If speed is required, it is possible to determine carbon by combustion in less than 10 minutes so that there is no longer any excuse for carrying out the colorimetric determination except in small steel works with limited laboratory equipment.

(*a*) Determination of Carbon by Direct Combustion in Oxygen

Combustion tube and furnace. — The combustion should take place in a platinum, glazed porcelain, or silica combustion tube, which is so arranged that no compounds of carbon other than those obtained from the burning sample can possibly contaminate the current of gases flowing through it. The temperature of the portion of the tube occupied by the sample should be maintained between 1050 and 1100° and the furnace should preferably be of the electric resistance type (Fig. 76).

Boats and lining. — Platinum, nickel, alundum, or clay boats may be used (see Fig. 77), provided that the nickel, alundum, and clay boats are first proven to give no blank or a constant one of not over

* Cf. *Examination of Iron, Steel and Brass*, W. T. Hall and R. S. Williams.

0.0005 g. The lining or bedding material for the sample may be alundum, chrome brick, emery, or sand, provided the combined blank of boat and lining is constant and not over 0.0005 g. To prevent injuring the combustion tube a shield of pure sheet nickel should encase the boat when in the tube.

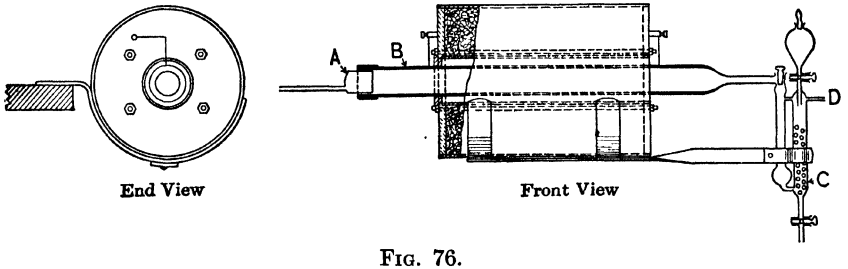


FIG. 76.

Absorption tubes. — The glass absorption tubes (Fig. 78 or Fig. 70) should be so constructed as to provide for filling as follows: The soda-lime, or ascarite (soda asbestos) in the absorption tubes should be 12-mesh or smaller and so arranged as to provide a column at least 5 cm.

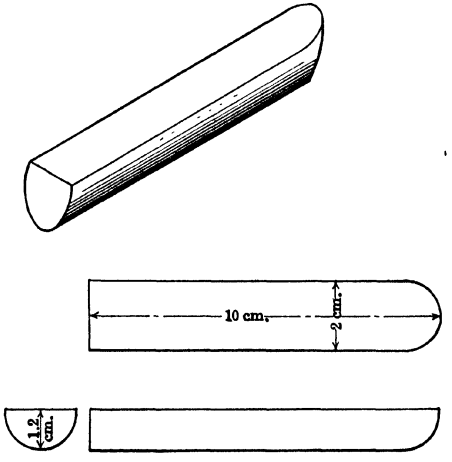


FIG. 77.

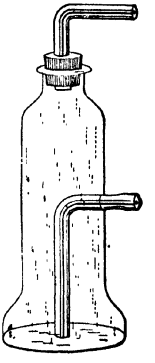


FIG. 78.

long and 1 cm. in diameter. The column of phosphorus pentoxide on top of the soda-lime should be at least 3 cm. long and 0.5 cm. in diameter. The absorption tube should be provided with suitably lubricated glass stop-cocks to close both inlet and outlet for the gases. When filled it should not weigh over 200 g. It should not be moistened with any liquid between weighings and, for amounts of carbon over 0.6 per cent,

it should stand 20 minutes by the balance case before weighing. It should always be weighed filled with oxygen and against a counterpoise. The absorption tube should be followed by a phosphorus pentoxide guard tube and a bubble tube containing a saturated solution of barium hydroxide as an " exhaustion indicator."

Procedure. — Connect the absorption tube with the cocks closed to the post train, the guard tube, and the " exhaustion indicator." Place 1–3 g. of weighed sample freed from oil (cf. p. 220) in a furrow in the bedding material in the boat so that the particles are in intimate contact. Introduce the boat into the hot combustion tube, close the tube, open the absorption tube, and turn on the current of oxygen. The rate of flow of the oxygen should be between 200 and 400 ml. per minute and should continue for 10 minutes. Then close the absorption tube, turn off the oxygen, and place the absorption tube by the balance. Remove the boat from the tube and examine the oxide of iron for complete fusion. If the fusion has not been complete repeat the determination.

The absorption tube and counterpoise, before being placed on the balance, should both be momentarily opened to the air to bring the pressure inside to that of the atmosphere. The increase in weight of the tube multiplied by 27.3 and divided by the weight of the sample in grams is equal to the percentage of carbon.

Note. In the case of alloy steels it is advisable to heat the chips to dull redness before turning on the oxygen and to employ a temperature of at least 1100° C.

The combustion train recommended by Stetser and Norton* is shown in Fig. 79. *A* and *B* are 8-liter aspirator bottles, *B* is filled with oxygen through the reducing valve *N*; the upper bottle is graduated for each 250 ml. The pressure of water from *A* forces oxygen into the furnace and the volume used is measured by the fall of water in *A*. C is a glass stop-cock to be closed when filling *B* with oxygen. *D* is an empty safety bottle. Bottle *E* is one-third filled with concentrated sulfuric acid and *F* contains ascarite. *J* contains 80-mesh zinc and *K* a little concentrated sulfuric acid. *M* is the absorption bulb with ascarite which is a dehydrating agent itself so that no phosphorus pentoxide is required. Two of the ascarite bulbs should be filled and one used as a tare in weighing the other. A pair of the bulbs should accomplish about 140 combustions.

The directions of Stetser and Norton emphasize the following points which were not mentioned in the above procedure.

1. First test the apparatus to see if it is tight; with *C* open and *K* closed the pressure from *A* should not cause gas to bubble through *E*

* *Iron Age*, **102**, No. 8.

and K after a few minutes. Then close C and slowly open the stopcock on K. Fill B with water, open the gas regulator valve and force the water from B into A. When A is full of water, close the regulator and the train is ready for combustion.

2. For the combustion of 1 g. of steel, about 300 ml. of oxygen are required. Allow about 500 ml. for the combustion and an equal vol-

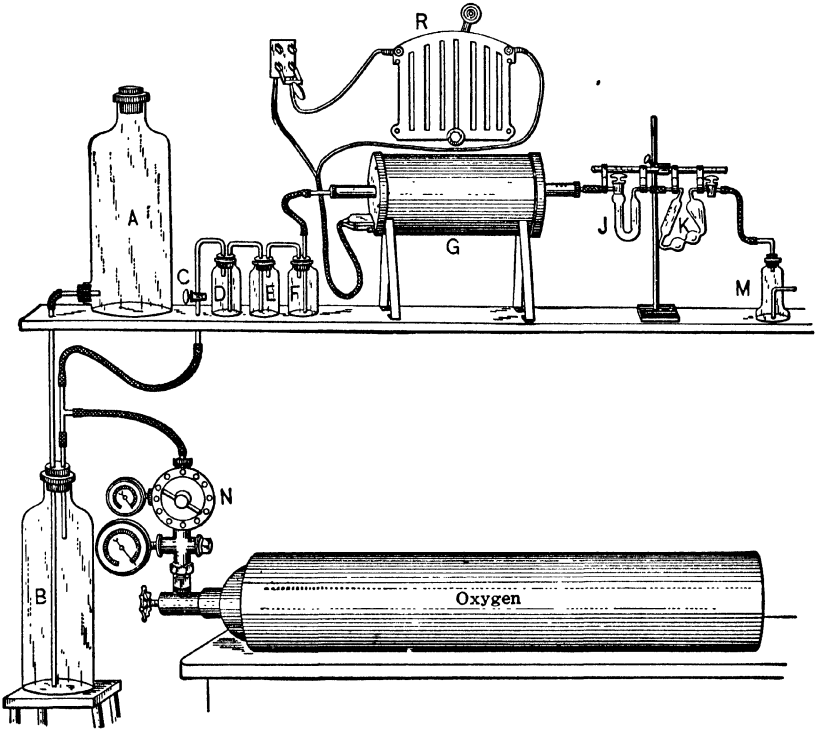


FIG. 79.

ume to sweep out the carbon dioxide into the absorption tube. The gas will flow rapidly through the liquid in E when the sample starts to burn and will slacken when the combustion is finished. Place ignited asbestos in the front end of the tube.

3. A freshly-filled absorption bulb should be run on the train for an hour and then weighed. Pass 2 liters more of oxygen through the hot furnace and again weigh. The bulb should show less than 1 mg. change in weight. It is well to check the efficiency of the apparatus by occasionally running a standard steel which can be obtained from the Bureau of Standards at Washington, D. C.

Methods of Cain and Maxwell*

Instead of absorbing the carbon dioxide in an absorption bulb containing soda-lime, ascarite or strong potassium hydroxide solution (in the latter case a Geissler bulb should be used) Cain and Maxwell recommend using a 10-bulb Meyer tube filled with barium hydroxide solution (25 g. $Ba(OH)_2.8\ H_2O$ per liter). Enough of the alkali should be used in an analysis to fill each small bulb of the absorption tube and half of the larger exit bulb.

During the combustion of the iron or steel, keep gas flowing through the Meyer bulbs. This requires a rapid stream of oxygen when the steel is burning. By placing a capillary tube in the rubber stopper at the front end of the furnace, the rapid escape of gas from the furnace is hindered. This cuts down the flow of gas automatically when the combustion is over. At no time should more than 200 ml. per minute of oxygen enter the combustion tube.

At the end of 5 minutes, the combustion should be complete. Disconnect the Meyer bulb and the furnace is ready for another combustion.

Pour off the contents of the Meyer bulb into a Büchner funnel fitted to a suction flask and containing two 7-cm. filter papers, one on top of the other. Wash out the tube 3 times with distilled water that has been boiled and cooled in a flask stoppered with a soda-lime tube in the stopper, so that no carbon dioxide can be absorbed from the air. Then wash the filter 4 times more, taking care that the top of the funnel is washed each time.

To the rinsed Meyer tube, add from a buret about 5 ml. of 0.1 *N* hydrochloric acid more than is necessary to dissolve all of the barium carbonate precipitate. Transfer the acid from the Meyer tube to a wide-mouthed flask into which also place the filter papers containing a part of the precipitate. Rinse out the Meyer bulb with 2 portions of boiled water. It is then ready to be filled for another determination.

Heat the flask containing the acid until all of the barium carbonate has dissolved, cool and titrate with the 0.1 *N* acid using methyl orange as an indicator. (See Acidimetry).

Cain and Maxwell have also worked out an electric resistance method which is still more rapid.† The apparatus is shown in Fig. 80.

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* Bureau of Standards, *Technologic Paper No.* 33, J. Ind. Eng. Chem., **10**, 520 (1918); **11**, 852 (1919).

† J. Ind. Eng. Chem., **11**, 852, Bureau of Standards, *Technologic Paper, No.* 141. The necessary equipment can be obtained from the Arthur H. Thomas Co. of Philadelphia.

The absorption apparatus is essentially a Meyer bulb capable of holding 200 ml. of barium hydroxide solution when filled to the mark. The entrance bulb is modified so that a sensitive thermometer and a pair of platinized electrodes can be introduced. By means of a galvanometer and a specially constructed bridge, the electric resistance of the solution can be determined with the aid of an ordinary 60 or 25 cycle alternating current. A nomographic chart has been worked out

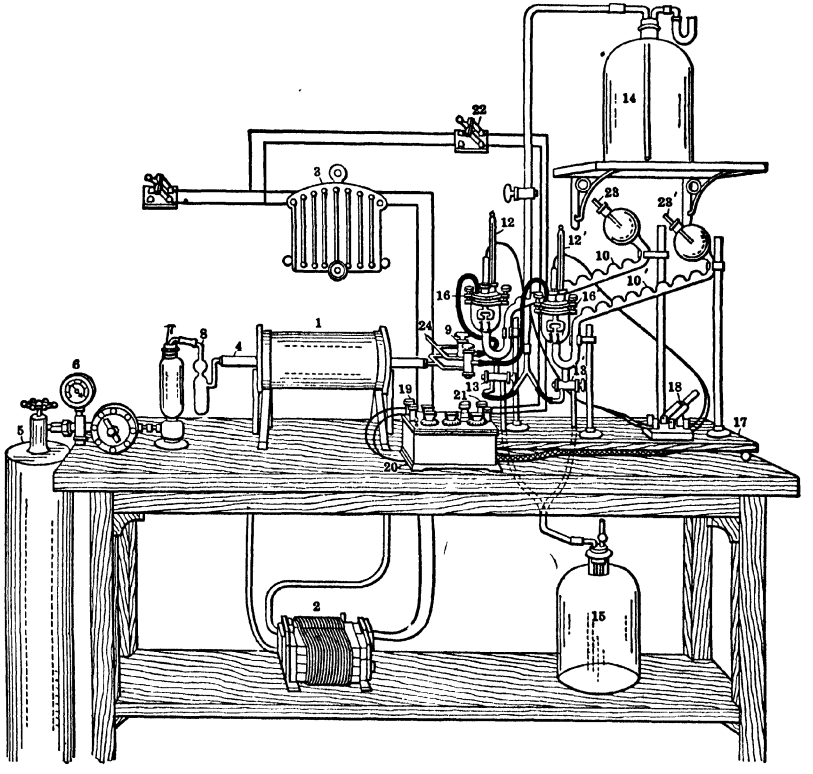


FIG. 80.

so that the concentration of the barium hydroxide solution can be read in terms of per cent carbon as soon as the electric resistance and temperature of the barium hydroxide are known. Thus the difference between the two readings, with a 2-g. sample used for analysis, gives the percentage of carbon present. In carrying out a series of analyses at the Bureau of Standards the average time per analysis was 5 minutes.

Determination of Graphite

Dissolve 1 g. of cast iron in 50 ml. of 6 *N* nitric acid in a 300-ml. beaker and heat gently until there is no further evolution of gas. By this means the carbide carbon is dissolved while the graphite is not attacked. Filter the solution through an ignited asbestos filter and wash the residue with hot water, then with a hot solution of potassium hydroxide (*d.* 1.1), followed by hot water, dilute hydrochloric acid, and finally with hot water again until free from chloride. After drying at 110°, transfer the asbestos and graphite to a combustion-tube and burn the carbon in a current of pure oxygen as described on page 352.

(*b*) Determination of Carbon by Wet Combustion

The Chrome-Sulfuric Acid Method

In this method the borings, which should be as fine as possible and free from grease, are treated with a mixture of chromic and sulfuric acids and heated to boiling. Thereby, the iron goes into solution and the carbon is oxidized to carbon dioxide. In spite of a large excess of chromic acid, however, some carbon is likely to escape in the form of hydrocarbons and carbon monoxide, unless precautions are taken. To prevent such losses, Särnström* recommended leading the escaping vapors over copper oxide in a combustion tube,† 80 cm. long, which is heated in a combustion furnace. Many experiments have shown that the method of Särnström gives exact results, although objection has been raised to the long combustion tube that is required.

Corleis has succeeded in simplifying the method by showing that a very short combustion tube, filled with copper oxide and heated by a single Bunsen flame, suffices if the sample is covered with a coating of copper during the treatment with chromic and sulfuric acids. In fact the use of the combustion tube is unnecessary in an ordinary steel analysis, because only 2 per cent of the total amount of carbon present is lost in this case. In the analysis of ferro-manganese, and similar alloys, however, the use of the hot tube is to be recommended.

Ledebur‡ even found that the results obtained with irons rich in graphite were a little too high on account of the formation of some sulfur dioxide, but this error can be overcome by passing the gases through chromium trioxide just before they enter the combustion tube.

The apparatus required is shown in Fig. 81 and consists of a Corleis decomposition flask *A* with condenser.

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* Särnström, *Berg- und Hüttenm. Ztg.*, **1885**, 52, and Corleis, *Stahl u. Eisen*, **1894**, 581. With ferromanganese the loss amounts to 22.5 per cent of the total carbon, with steel 9 per cent. With ferromanganese the escaping gases contain, besides carbon dioxide and traces of heavy hydrocarbons, 18 per cent methane, 76 per cent hydrogen, 3 per cent oxygen, and 2 per cent carbon monoxide.

† A small tube of glass, quartz or porcelain filled with copper oxide or platinized asbestos.

‡ *Leitfaden für Eisenhütten-Laborat.*

The flask is connected, as shown in the drawing, on one side with a soda-lime tower, *W*, at the bottom of which is placed a little concentrated caustic potash solution, and on the other side with a system of tubes. The tube *B* is about 10 cm. long and contains chromium trioxide between 2 asbestos plugs. The tube *C* is 15 cm. long, is made of difficultly fusible glass, and filled with granular cupric oxide. It is placed in a little box made of asbestos paper. The tubes *a*, *b*, *c*, *d*, *e*, and *f* are filled exactly as described on p. 333. Tubes *a*, *b*, and *c* are drying tubes, the first containing glass beads wet with concentrated sulfuric acid, the other two containing calcium chloride; *d* and *e* are glass-stoppered soda-lime tubes, the upper third of the right-hand arm of each containing calcium chloride. The tube *f* is a safety tube which is not weighed, but is used to avoid any chance of carbon dioxide or moisture entering the weighed tubes from the air.

Reagents. — 1. A saturated solution of ordinary chromic acid containing some sulfate. It is not advisable to use chemically-pure chromic acid for this purpose, for the latter often contains organic substances.

2. A solution of copper sulfate made by dissolving 200 g. of the salt in 1 liter of water.

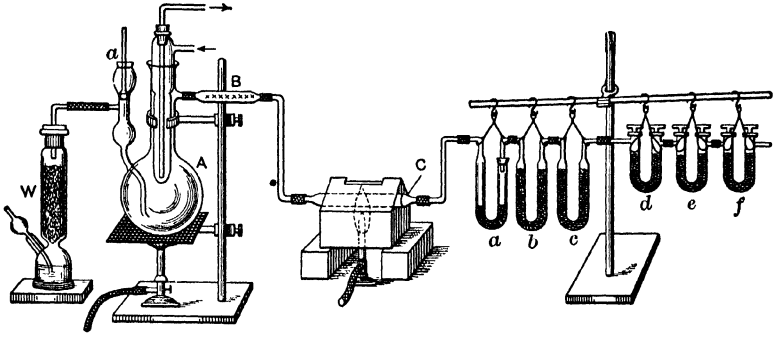


FIG. 81.

Procedure. — Remove the ground-glass stopper *a*, and through the opening pour 25 ml. of chromic acid solution, 150 ml. of copper sulfate solution and 200 ml. of concentrated sulfuric acid into the flask, *A*, and mix. Heat the mixture in the flask to boiling and keep at this temperature for 10 minutes. Then remove the flame and pass a current of air free from carbon dioxide through the apparatus for 10 minutes at the rate of about 3 bubbles per second. Connect the flask with the tube *B*, the red-hot copper oxide tube, and with the U tubes,* while continuing the current of air for 5 minutes more. Remove the soda-lime tubes *d* and *e*, close and allow to stand 10 minutes in the balance room. Open for a moment, quickly close, wipe dry with a piece of chamois skin, allow to stand 5 minutes in the balance-case, and then weigh.

* Corleis used phosphorus pentoxide for a drying agent, but calcium chloride is satisfactory.

By means of this preliminary boiling, traces of organic matter contained in the apparatus are removed.

After weighing the soda-lime tubes, connect them again with the apparatus, open the decomposition-flask, and quickly drop in 0.5–5 g. of the weighed substance, according to the amount of carbon present,* from a weighed glass-stoppered weighing tube, which is subsequently weighed again to determine the amount of sample. Immediately close the flask and heat the copper oxide tube to glowing, after which slowly heat the contents of the flask so that after from 15–20 minutes the liquid begins to boil. Keep the solution boiling for 1 or 2 hours while passing a slow current of air through the apparatus. Then remove the flame, and pass about 2 liters more of air through the apparatus. Then remove the soda-lime tubes and weigh as before.

Since the use of the copper sulfate solution prevents the loss of more than about 2 per cent of the total amount of carbon present, it is evident that the combustion-tube can be dispensed with for technical purposes.

(*c*) Combustion of Carbon in the Wet Way and Measuring the Volume of the Carbon Dioxide

This operation is best carried out by means of the Lunge-Marchlewski method The apparatus necessary is shown in Fig. 72, p. 341. In this case, however, the decomposition-flask is larger and there should be a ground-glass connection between the flask and a condenser. Furthermore, a funnel-tube is fused into the neck of the flask, and runs along the side of the flask on the inside ending in a quite fine point near its bottom. The upper end of the condenser is connected with the measuring-tube by means of a capillary tube about 36 cm. long, ground to fit the condenser-tube.

Reagents. — 1. A saturated, neutral solution of copper sulfate.
2. A chromic acid solution (100 g. CrO_3 in 100 ml. of water).
3. Sulfuric acid, *d.* 1.65 and saturated with chromic acid.
4. Sulfuric acid, *d.* 1.71, also saturated with chromic acid.
5. Pure sulfuric acid, *d.* 1.10.
6. Commercial hydrogen peroxide solution.

Procedure. — The amount of iron or steel to be weighed out and the necessary quantities of the reagents are shown in the following table:

Per Cent C.	Weigh Out Grams	ml. Copper Sulphate Solution	ml. Chromic Acid Solution	ml. Acid *d.* 1.65	ml. Acid *d.* 1.71	ml. Acid *d.* 1.10	ml. H_2O_2
Over 1.5	0.4–0.5	5	5	135	.....	30	1
0.8–1.5	1	10	10	130	.....	25	2
0.5–0.8	2	20	20	130	.....	5	2
0.25–0.5	3	50	45	.....	75	5	2
Less than 0.25	5	50	50	.....	70	5	2

* For cast iron 0.5 g. suffices but for steel from 1–2 g. and for wrought iron 5 g. should be used.

Treat the substance with the copper sulfate solution in the decomposition-flask at the ordinary temperature. Allow malleable iron to stand for at least 1 hour, but cast iron requires at least 6 hours. Connect the flask with the measuring-tube, which is filled with mercury, and exhaust the air in the flask as was described on p. 343. After this is accomplished, place the leveling-tube in a low position and add the proper amount of the chromic acid solution through the funnel, followed first by the proper amount of the stronger acid and then by that of the weaker acid, after which quickly close the stop-cock in the funnel. The communication between the measuring-tube and the flask remains open. With the leveling-tube remaining in its low position heat the contents of the flask to gentle boiling, and boil for 1 hour. Then remove the flame. Now, in order to remove the last traces of carbon dioxide from the solution, add the prescribed amount of hydrogen peroxide to the contents of the flask and fill the flask with hot water until all of the gas is driven over into the measuring-tube. Then close the stop-cock *b*, reduce the gas to the volume corresponding to 0° C. and 760 mm. pressure as described on p. 342 and read this volume. Then drive over the gas into the Orsat tube and determine the volume of the unabsorbed gas as before. The difference between the two readings represents the amount of carbon dioxide measured under the standard conditions of temperature and pressure. If this is multiplied by the factor 0.0005392 the amount of carbon present will be obtained.

After the analysis has been completed, a blank determination must be made, using the same amounts of each reagent, in order to determine small amounts of organic matter which are invariably present in them. The amount of carbon dioxide found under these conditions must be subtracted from that obtained in the analysis proper.

*Method of Hempel**

Hempel objects to the above procedure on the ground that by dissolving the iron in the mixture of chromic and sulfuric acids some hydrocarbon is likely to escape oxidation. He found that by dissolving iron in chromic-sulfuric acid under diminished pressure in the presence of mercury all of the carbon would be readily oxidized to its dioxide. Fig. 82 represents the apparatus used.

Reagents Required

1. Chromic acid solution. 100 g. of chromic acid dissolved in 300 ml. of water and 30 g. of sulfuric acid, *d.* 1.704. The resulting solution has a density of 1.2.

* *Verhandlg. d. Vereins z. Beförd d. Gewerbefleisses*, 1893.

2. Sulfuric acid. Mix 1000 ml. of concentrated sulfuric acid with 500 ml. of water and 10 g. of chromic acid and heat for an hour in a large flask upon a sand-bath to completely destroy any dust, etc., that may be present. Then take away the flame and slowly conduct a current of air through the solution to remove any carbon dioxide that may have been formed. After cooling, dilute the solution with water until it has a density of 1.704.

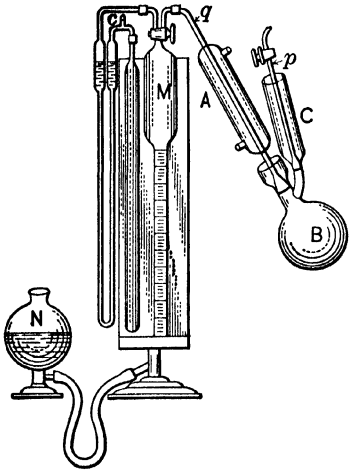


FIG. 82.

Procedure. — Place about 0.5 g. of the iron or steel in the decomposition-flask *B*, add about 2.3 g. of mercury by means of a small pipet, and connect the apparatus together as is shown in the drawing.

By raising the leveling-bulb *N*, fill the measuring-tube *M* with mercury, close the stop-cock, and connect the apparatus at *p* with a suction-pump, by means of which exhaust the air in the flask *B* as completely as possible. To make sure that the ground-glass connection between the flask and the condenser is perfectly air-tight, pour a little water into the cup there. Into the funnel *C* place 30 ml. of chromic acid solution, close the stop-cock at *p*, and by carefully lifting the latter a little allow the chromic acid to run into the flask, and at once heat to boiling over a small flame. After boiling for half an hour, add 120 ml. of sulfuric acid through *C*, open the stop-cock at *M* for the first time and boil the contents of the flask for half an hour longer. (At the start only carbon dioxide is generated, in proportion to the temperature of the solution, but toward the end of the operation there is a fairly lively evolution of oxygen.) Remove the flame, and carry over the gas in the flask into *M* by pouring water into *C* and lifting the tube *d* until the gas in the flask is entirely expelled. Read the total volume of the gas, and then absorb the carbon dioxide in a Hempel's potash pipet and determine the volume of the unabsorbed gas. The difference represents the amount of carbon dioxide formed by the oxidation. From this the amount of carbon present can be computed.

The measuring of the gas in this apparatus will be described more in detail in Part III, Gas Analysis.

Other methods for the determination of the volume of the carbon

dioxide formed from the carbon in iron or steel are those of J. Wiborgh,* Otto Pettersson and August Smitt.†

For certain alloy steels and materials hard to oxidize such as ferro-silicon, ferro-chrome or tungsten steel, the following method is recommended:

Wöhler's Volatilization of Ferric Chloride Process‡

Principle. — The sample of iron or steel is heated in a stream of pure chlorine gas whereby iron, silicon, phosphorus, and sulfur are volatilized while the carbon remains behind in the presence of small amounts of non-volatile chlorides. The silicon present as silica, due to inclosed slag, is not affected by the treatment. The residue is filtered through asbestos, the chlorides washed out by water, and the carbon burned to dioxide either in the wet or in the dry way.

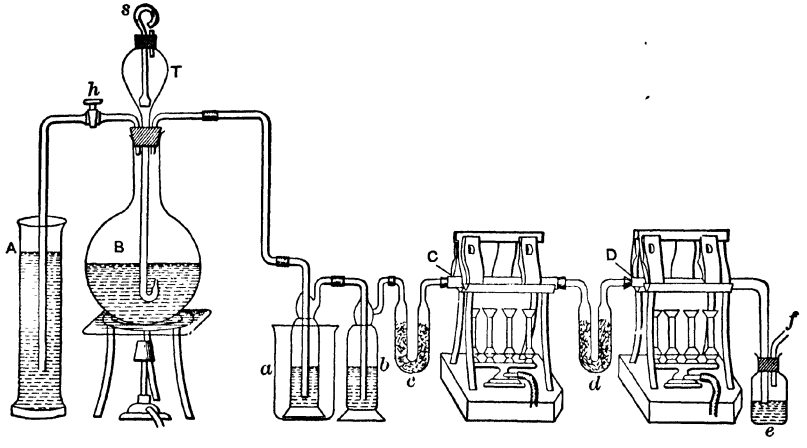


FIG. 83.

The principal requisite for the success of the process is *pure* chlorine. This must not contain oxygen, water, nor carbon dioxide, because these substances all tend to convert a part of the carbon into carbon monoxide, whereby low results are obtained in the carbon determination.

Procedure. — The specimen is subjected to the action of chlorine in an apparatus like that shown in Fig. 83.

B is the liter flask in which the chlorine is generated; it contains about 200 g. of pyrolusite and 500 ml. of concentrated hydrochloric acid. Heat the contents of the flask over a very low flame and in this way evolve a continuous stream of chlorine. When the current begins

* *Zeit. anal. Chem.*, **29**, 198 (1890).

† *Ibid.*, **32**, 385 (1893).

‡ *Z. anal. Chem.*, **8**, 401 (1869), cf. A. Ledebur, *Leitfaden für Eisenhütten Laboratorien.*

to slacken, add more hydrochloric acid through a Bulk's* dropping funnel.† To regulate the current of gas, connect the flask with the right-angled tube, *h*, which is provided with a stop-cock and leads to a cylinder, *A*, containing caustic soda solution. If the stream of chlorine becomes too strong, open the stop-cock a little so that the excess of chlorine is absorbed by the sodium hydroxide. The chlorine is purified by means of the tubes *a*, *b*, *c*, *C*, and *d*; *a* contains water, *b* concentrated sulfuric acid, *c* glass beads, or pumice, moistened with sulfuric acid. *C* is a tube 40 cm. long and 1 cm. wide, made of difficultly-fusible glass. It contains a layer, 15 cm. long, of coarse charcoal which has previously been well ignited and cooled in a desiccator. The charcoal is placed in the tube between two loose plugs of ignited asbestos. Heat the tube to dark redness in a small combustion furnace. If the chlorine gas contains small amounts of oxygen (air) or carbon dioxide, these are changed, on coming in contact with the hot charcoal, to carbon monoxide, which is unaffected by the carbon in the iron or steel. Remove the last traces of moisture by passing the gas through the tube *d* containing glass beads moistened with concentrated sulfuric acid.

Next pass the chlorine into the combustion tube *D*. This is about 40 cm. long by 1.5 cm. wide, is bent into a right angle and leads into concentrated sulfuric acid in the flask *e*. The sulfuric acid serves as a seal and prevents air from getting into the tube.

Sprinkle the substance, which should be as fine as possible, as a thin layer‡ upon a previously-ignited porcelain boat. Of ferro-chrome take about 0.5 g., and of ferro-silicon about 1 g. Shove the boat into the combustion tube and start the evolution of chlorine as described above. Do not heat the tube until after about twenty minutes, when the air will have all been expelled; then begin heating very gradually, lighting the burners one at a time from right to left. The formation and volatilization of the ferric chloride takes place at a relatively low temperature.

As soon as no more brown vapors escape from the tube, gradually raise the temperature until the tube begins to get red; then allow the residue in the tube to cool in the stream of chlorine.

Remove the boat from the combustion tube, and, in the case of ferro-silicon, rinse the contents with cold water into a beaker. From the

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* *Z. anal. Chem.*, **16**, 467 (1892).

† The flow of the acid is regulated by raising the tube *S*. Instead of *S* a glass rod covered with rubber tubing may be used.

‡ This is especially important in the case of ferro-chrome, because otherwise the metal will become covered with a coating of non-volatile chromic chloride which prevents it from being acted upon by the chlorine.

beaker wash the insoluble residue into an asbestos filter prepared as follows: In the funnel *R*, Fig. 84, which is about 1 cm. wide and 5 cm. long, place a little glass wool, and upon this pour a suspension of ignited asbestos fibers in water until, with the aid of light suction, the filtrate comes through perfectly free from asbestos fibers. Wash the residue on such a filter with cold water until no chloride can be detected in the filtrate.

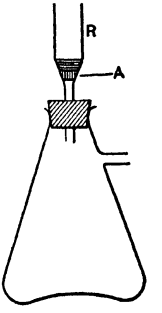


FIG. 84.

The carbonaceous residue can be oxidized in the apparatus shown in Fig. 81, p. 357, but in this case the flask *A* should contain 5 ml. of a saturated, aqueous solution of chromic acid, and 60 ml. of sulfuric acid, *d.* 1.71 which is likewise saturated with chromic acid.

In the analysis of ferro-chrome, there is always some insoluble chromic chloride in the boat which cannot be removed by washing. In this case, therefore, heat the substance after the ignition in chlorine, in an atmosphere of hydrogen, whereby the insoluble chromic chloride is converted into soluble chromous chloride. The contents of the boat are then treated exactly as described above.

Determination of Carbon by the Berzelius-Richter Method

A number of methods have been proposed for dissolving away the iron and leaving the carbon behind in the form of an insoluble residue. For this purpose a solution of potassium-cupric chloride containing 300 g. of the double salt ($2\,KCl.CuCl_2.2\,H_2O$) and 75 ml. of concentrated hydrochloric acid to the liter has proved most satisfactory. Before using, filter the solution through ignited asbestos and preserve in a glass-stoppered bottle. The solution of the borings takes place very slowly unless the solution is stirred, which is best accomplished by means of a mechanical stirrer. Warming the solution also helps, but it should never be heated above 60°–70°. The following reactions take place:

$$Fe + CuCl_2 = FeCl_2 + Cu,$$
$$Cu + CuCl_2 = Cu_2Cl_2.$$

The presence of potassium chloride aids the solution of the copper, probably on account of the formation of a double salt.

The residue is filtered on an asbestos filter, dried and burned in oxygen or in the Corleis flask. It may also be used for the determination of sulfur (see *Meinicke Method*, p. 313).

Determination of Carbon and Hydrogen in Organic Substances, according to Liebig

(*Elementary Analysis*)

Principle. — The organic substance is burned in air or in oxygen and the products of the combustion are passed over glowing copper oxide, which oxidizes all of the carbon to carbon dioxide and the hydrogen to water. The latter is collected in a weighed calcium chloride tube or sulfuric acid worm, the former in a weighed vessel which contains either caustic potash solution, soda-lime of 2 per cent moisture content and phosphorus pentoxide, or ascarite (soda-asbestos).

The combustion is performed

(*a*) *In an open tube.*

(*b*) *In a closed tube.*

(*a*) *Combustion in an Open Tube*

Most combustions take place in a tube open at both ends and usually a gas-heated furnace and a glass tube are used. The progress of the combustion can be watched through the glass and a long horizontal column of copper oxide insures the complete combustion of the carbon. It is possible in many cases to use an electric furnace and carry out the combustion much more rapidly than heretofore. With the electric furnace, it is easier to get a constant temperature sufficient to burn the substance completely and with soda-lime of the best grade or with ascarite there is less danger of carbon results being too low. With the Geissler bulb and caustic potash solution, the rapid passage of gas causes volatilization of some of the water too fast to be absorbed by a short drying tube attached to the absorption bulb.

Pregl has shown that it is possible to simplify the process greatly by taking a smaller weight of substance and using a miniature apparatus. This requires a more sensitive balance than is ordinarily used. Pregl's argument that it is easier to get a perfect combustion with a small quantity of substance than with a larger quantity and that it is possible to realize the necessary refinement in weighing, is a perfectly sound one and many chemists are enthusiastic about the results obtained with the so-called *micro* apparatus. Pregl finds that the technique is easier for a beginner to master. For combustion in the old-fashioned way there are the following

Requirements. — (1) An open tube made of difficultly-fusible glass which is from 12–15 mm. wide. The length of the tube depends upon that of the combustion-furnace; it must be 10 cm. longer than the furnace. (2) 350 g. of coarse and 50 g. of fine copper oxide. (3) A drying apparatus (Fig. 85, on the left). (4) A calcium chloride tube (Fig. 86). (5) A Geissler potash bulb (Fig. 87), or two soda-lime

tubes (see p. 334, *d* and *e*) or an ascarite bulb (Fig. 78, p. 351). (6) A screw-cock. (7) Dry rubber tubing. (8) Two plates of asbestos board to protect the rubber stoppers in the two ends of the tube from the heat of the furnace.

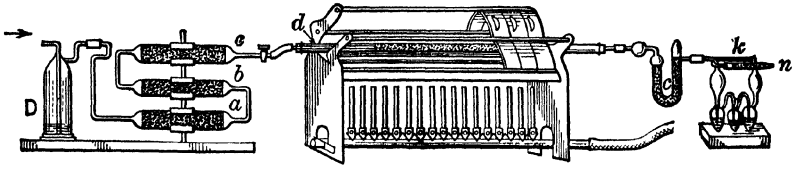


FIG. 85.

Procedure for the Combustion of Organic Substances Free from Nitrogen, Halogen, Sulfur, and Metals

Preparation and Combustion

1. *Fill the calcium chloride tube* (Fig. 86) from the left side as described on p. 334, close with a plug of glass-wool and fuse together the end of the tube, as shown in the figure.* It is more practical to use a calcium chloride tube fitted with ground-glass stoppers. After filling the tube, saturate with carbon dioxide, as described on p. 334, in the foot-note.

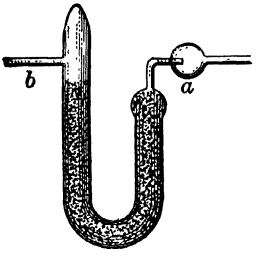


FIG. 86.

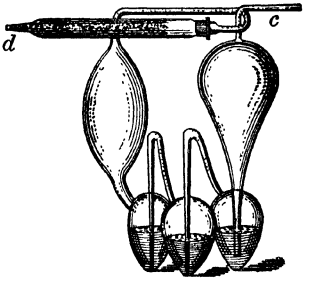


FIG. 87.

Rub the outside of the tube with a piece of chamois skin, and stopper the two ends with short pieces of rubber tubing each containing a piece of stirring-rod. Allow the tube to stand in the balance-case for 15 minutes and then weigh without the stoppers.

2. *Fill the Geissler bulb* (Fig. 87) with caustic potash solution (2 parts solid KOH in 3 parts of water) as follows: Replace the small soda-lime tube *d* by a piece of rubber tubing, dip *c* into the solution of caustic potash, and fill the bulbs two-thirds full by sucking through

* Or the tube is stoppered and an air-tight seal made by covering it neatly with sealing-wax.

the rubber tubing. Then clean the end of the tube *c* with a piece of filter-paper, again connect the tube *d* (its right half is filled with soda-lime and the outer half with calcium chloride), close the two ends with pieces of rubber tubing each containing a piece of stirring-rod with rounded ends. Wipe the apparatus with chamois and weigh *without* the stoppers, taking the same precautions as with the weighing of the large calcium chloride tube.

3. *The drying apparatus* (Fig. 85, on the left), which serves to free the air and oxygen used for the combustion from carbon dioxide and water vapor, consists of a wash-bottle, *D*, containing concentrated caustic potash solution, the soda-lime tube *a*, and the 2 calcium chloride tubes *b* and *c*.

4. *The Combustion-tube* (Fig. 88), both ends of which are rounded by heating in the blast-lamp; after cooling, wash the tube, dry, and fill as follows: First place a short roll, *k*, of copper gauze at the right-hand end of the tube so that 5–6 cm. of the latter are left empty. This roll serves as a plug and must, therefore, fit tightly in the tube. Next



FIG. 88.

add a layer of coarse copper oxide, *K*, about 45 cm. long, and after this place another plug of copper gauze, *k'*. Finally insert another roll of copper gauze, *d*, about 10 cm. long and large enough to fill the tube loosely, so that a space of about 10 cm. is left on the right and about 5 cm. on the left. Place the tube in the combustion-furnace, so that about 5 cm. extend beyond the furnace at each end, as shown in Fig. 85. Close the left end of the tube with a tightly-fitting rubber stopper through which a glass tube passes, and connect with the drying apparatus by means of a short piece of rubber tubing. (The tube should be provided with a glass stop-cock, as is shown in Fig. 88, *a*, but which is lacking in Fig. 85.) The right end of the tube is left open for the time being.

Pass a slow current of oxygen* through the apparatus and light the furnace. At first turn the flame low and heat the whole tube equally. Gradually raise the temperature, until, with the tiles covering the tube, the copper oxide is at a dull-red heat.

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* The oxygen must be free from hydrogen. Commercial oxygen often contains the latter, in which case it is necessary to pass the gas through a "preheating" furnace before using it.

Usually some water condenses in the right-hand end of the tube; expel this by carefully holding a hot tile under the tube. When all the water is removed, and the presence of oxygen can be detected at the right end of the tube (by its igniting a glowing splinter), close this end of the tube with a rubber stopper connected to an open calcium chloride tube. Now turn down the burners and discontinue the oxygen current. Extinguish all of the flames after some time except those under the right half of the tube.

While the tube is cooling, weigh the calcium chloride tube and the potash bulb (or soda-lime tubes) replacing the stoppers immediately after the weighing and weigh 0.15–0.2 g. of the substance into a porcelain boat.

If the substance is a difficultly-volatile oil weigh it from a small glass tube open at one end. If it is readily volatile, blow a bulb into a small capillary tube; weigh this, heat the bulb, and introduce the capillary into the liquid to be analyzed, so that the liquid rises in the bulb as it cools. Then turn the bulb so that the capillary lies in a horizontal position, heat slightly to expel a little liquid that adheres to the sides of the tube, melt the end together, and again weigh the tube. Take care that there is no liquid in the capillary. Everything is now ready for the combustion. Remove the stopper from the left (and now cold) end of the combustion-tube, remove the long copper roll by means of a piece of wire with a hook in the end of it, place the boat with the substance in it in the tube and the copper roll right after it. Make connection with the drying apparatus on the left and with the absorption-tubes on the right, as is shown in Fig. 85. In case the substance is a liquid, place the bulb containing it so that its capillary is pointed towards the left, and in the case of a volatile liquid break off the end of the capillary with a file just before introducing it into the combustion-tube. Close the stop-cock between the tube and the drying apparatus, connect the latter with an air-gasometer, and open wide the stop-cock in the drying apparatus and that between the drying apparatus and the combustion-tube just enough to permit 2, or at the most 3, bubbles of gas per second to pass through the apparatus. Light the two outer burners on the left and heat the copper oxide spiral *d* (the copper was changed to the oxide by the ignition in oxygen) just to redness. Gradually heat the tube from right to left, taking care that the gas evolution is never greater than 4 bubbles per second through the potash bulb; this can be easily regulated by means of the stop-cock or by turning the gas-burners. When the contents of the entire tube have been brought to redness, with the tiles in place, and the boat is empty, the combustion is usually complete. It is well, however, to pass oxy-

gen through the hot tube until the gas can be detected at the right-hand end of the combustion train (a glowing splinter ignites at *n*).* Then turn down the flames and pass a current of air through the apparatus until the oxygen is completely expelled. A little water always collects in the front (right) end of the tube, and this must be driven over into the calcium chloride tube by holding a hot tile under it. Now remove the calcium chloride tube and the potash bulbs, wipe off with a piece of chamois skin, allow to stand in the balance-room for 20 minutes, and weigh without the stoppers. The gain in weight represents the amount of water and carbon dioxide respectively, and from this the amount of hydrogen and carbon can be calculated.

Remark. — The combustion may be accomplished as described for the determination of carbon in steel but with the following precautions: —

1. Place plugs of copper gauze and a layer of copper oxide in the front end of the furnace as described above but use less copper oxide because of the shorter furnace. Before the combustion heat in oxygen to convert the copper to copper oxide, as described above, and to burn any dust in the tube.
2. Do not use more than about 0.1 g. of substance and cover it with about 2 g. of copper oxide powder. Use a slower stream of oxygen as only about 12 ml. are required for complete combustion.
3. Have the combustion-tube well cooled before introducing the boat with the substance and heat the front end of the tube first by moving the tube so that the part containing the boat is outside the furnace. When the front end of the tube is hot, place the tube in its normal position.
4. Use the absorption train as described above, without the zinc used in steel analysis, but substitute a Midvale or Fleming tube filled with good quality soda-lime or ascarite as described on p. 351.

Determination of Carbon and Hydrogen in Nitrogenous Organic Substances

By the combustion of many organic substances containing nitrogen, especially nitroso- and nitro-compounds, oxides of nitrogen are formed which are partly absorbed in the calcium chloride tube and partly in the potash bulb, so that if such substances were analyzed according to the previous process, both the carbon and hydrogen results will be too high. If, however, a reduced copper spiral is introduced in the front (right) end of the combustion-tube, this serves to reduce the oxides of nitrogen to nitrogen itself, and, as the latter is not absorbed, correct results will be obtained.

Prepare the copper spiral by rolling together a piece of copper gauze about 10 cm. wide, making it as large as will conveniently pass into

* To prevent moisture from getting into this tube from the air, it is well to connect it with an unweighed calcium chloride tube.

the combustion-tube. Heat the spiral till it glows by holding it in a large gas flame, and while still hot drop it into a test-tube containing one or two cubic centimeters of methyl alcohol. The alcohol quickly boils away, but some of it is oxidized to aldehyde by the hot copper oxide, and the latter is reduced completely to bright metallic copper. Take out the spiral with a pair of crucible tongs and dry by quickly passing it through a flame a few times, and while still warm introduce it into the front end of the combustion-tube, which has been previously burned out as described in the previous analysis.

To carry out the combustion, close the stop-cock between the combustion-tube and the drying apparatus (Fig. 85), insert the substance into the tube, and first heat the copper oxide spiral at *d* and then the reduced spiral at the other end of the tube. Then beginning at *k* (Fig. 88), light one burner after another, until finally the entire contents of the tube are heated to dull redness and no more bubbles escape through the potash bulb. Now for the first time open the stop-cock somewhat and pass oxygen through the tube until it can be detected at *n*, by a test with a glowing splinter. Then gradually turn down the flames, replace the oxygen by air, and complete the analysis as in the previous case.

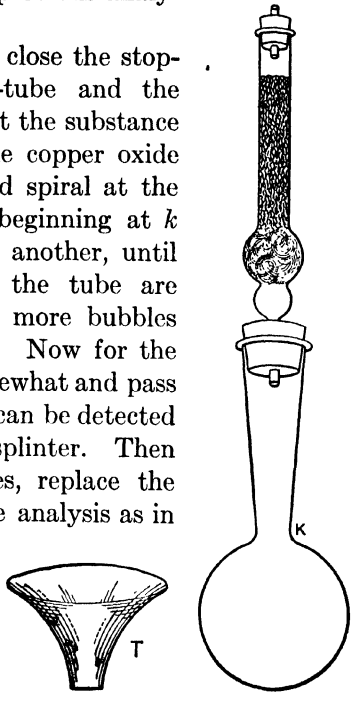


FIG. 89. FIG. 90. FIG. 91.

Substances hard to burn are treated somewhat differently. First of all fill the back end of the combustion-tube (Fig. 85) with the aid of the funnel *T* (Fig. 89), with fine, granular, but not pulverized, copper oxide, and ignite this in a stream of oxygen. Replace the oxygen by air and allow the tube to cool until it can be held in the hand. Next transfer the fine, granular copper oxide to the small flask *K*, Fig. 90, and close the flask by inserting a tin-foil covered cork, fitted with a calcium chloride tube. While the copper oxide in the flask is becoming perfectly cold, weigh the substance to be analyzed into the glass-stoppered mixing tube *M*, Fig. 91. Transfer from one-sixth to one-fifth of the copper oxide in the flask to the mixing tube, stopper and shake the contents well, whereby the substance becomes intimately mixed

with the copper oxide to which it adheres. Transfer the mixture back to the combustion-tube, and shake the mixing-tube repeatedly with small portions of the remaining copper oxide in the flask until finally it can be assumed that all of the substance has been transferred to the combustion-tube. Then carry out the combustion in the usual manner.*

Combustion of Organic Substances Containing Halogens

The analysis is conducted exactly the same as in the case of nitrogenous substances, except instead of a reduced copper spiral one of silver is used to keep back any halogen. The silver spiral should not be heated to redness, but only to about 180–200°. In case a silver spiral is not at hand, use a long copper spiral, its end reaching outside the furnace.

Combustion of Organic Substances Containing Sulfur

Sulfur compounds cannot be burned in a tube containing copper oxide, for the sulfur dioxide escapes and is partly absorbed by the water in the calcium chloride tube and partly in the potash bulb, so that absolutely worthless results are obtained. Instead of the long layer of copper oxide, use one of ignited lead chromate. The latter oxidizes the sulfur dioxide to sulfur trioxide, forming difficultly-volatile lead sulfate which remains in the tube. When lead chromate is used, the combustion must take place at a lower temperature than with copper oxide, for the former melts easily, and by adhering to the glass is likely to cause the tube to break.

Combustion of Organic Substances Containing Metals

If the substance contains alkalies, alkaline earths, or cadmium, a part of the carbon will remain in the tube as carbonate. In this case mix the substance in the boat with a mixture of 10 parts of powdered lead chromate and 1 part of potassium chromate, and conduct the combustion as when sulfur is present.

Dumas' Method for Determining Nitrogen in Organic Substances

This determination should really be discussed under Part III, but it will be described here on account of its being an analysis by combustion.

Principle. — The substance is burned in a combustion-tube, free from air, which contains copper oxide and copper spirals exactly as in the determination of the hydrogen and carbon in substances containing nitrogen, but in this case the nitrogen evolved is *measured.*

* For another method of conducting a combustion in an open tube, consult M. Dennstedt, *Z. anal. Chem.*, **40**, 611 (1903).

Procedure. — This determination may be carried out in either a closed or open tube.

(*a*) *Determination in a Closed Tube*

The necessary apparatus is shown in Fig. 92. The combustion-tube is closed at one end and is about 75 cm. long. It contains at *M* a layer of magnesite or of manganese carbonate 15 cm. long, in pieces about the size of a pea, followed by a loose plug of ignited asbestos and then a 10-cm. layer of coarse copper oxide, *S*. Add the substance at *a* in a

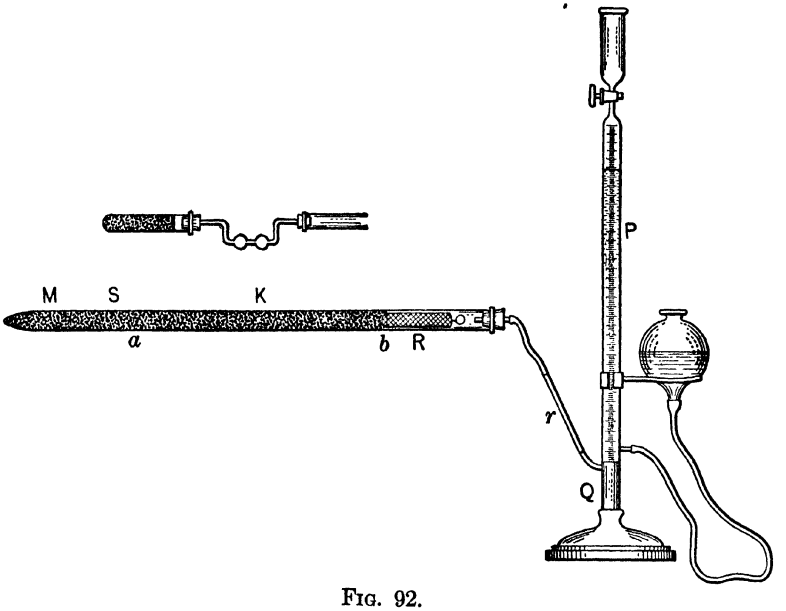


FIG. 92.

boat and mix with powdered copper oxide by means of a spiral wire (cf. p. 369), then add a layer of coarse copper oxide* about 40 cm. long and finally the reduced copper spiral (prepared as described on p. 369). Place the tube in a combustion-furnace and connect as shown in the figure with an azotometer,† which contains mercury to a little above the lower end of *r*, and a liberal amount of caustic potash solution (300 g. KOH dissolved in a liter of water).

Begin the analysis (with the leveling-bulb low and the stop-cock of the azotometer open) by heating the left half of the magnesite layer,

* The copper oxide must be previously ignited, as described on p. 369.

† H. Schiff, *Ber.*, **13**, 885.

whereby the air in the tube is expelled by the carbon dioxide and passes through the azotometer. From time to time make a test to see whether the air has all been expelled. Raise the leveling-bulb, and close the stop-cock with the azotometer tube completely filled. If all the air has been replaced by carbon dioxide gas, the bubbles of gas will all be absorbed by the caustic alkali. When this is the case put out the flame under *M*. Heat the tube first at *R* and light the burners one after another toward the left until about three-quarters of the layer of coarse copper oxide is heated to a dull redness. Then heat the tube at *S* and continue the process as in an ordinary combustion until the whole tube (with the exception of the part where the magnesite is found) is heated to a uniform temperature and finally no more nitrogen is evolved.

The heating must be accomplished so that there will be a slow but steady evolution of nitrogen. When the combustion is complete, heat the magnesite layer once more and expel all nitrogen remaining in the tube. As soon as the volume of the gas in the azotometer remains constant, measure the nitrogen.

For this purpose remove the azotometer together with the connecting piece of rubber tubing from the combustion-tube and close the tubing by means of a pinch-cock. Set the apparatus aside for at least 30 minutes at a place where a uniform temperature prevails, then raise the leveling-tube until the solution in it stands at exactly the same height as that in the tube. Read the volume of nitrogen, the thermometer and the barometer.

The weight of the nitrogen present is computed as follows:

If *a* g. of the substance were used for the analysis and *V* ml. of nitrogen were obtained at *t*° and *B* mm. barometric pressure. In order to obtain the weight of the nitrogen, its volume must be first reduced to 0° and 760 mm. pressure. If the gas had been measured over pure water the formula

$$V_0 = \frac{V\,(B_0 - w)\cdot 273}{760\,(273 + t)}$$

would hold in which B_0 represents the observed barometer reading reduced to a temperature of 0° and w is the tension of water vapor measured in millimeters of mercury. The nitrogen, however, was not measured over pure water but over a solution of potassium hydroxide and the vapor tension of this solution is less than that of pure water. In fact, with potassium hydroxide of the concentration used, the diminution of the vapor tension as compared with pure water almost exactly compensates the correction which would be applied in reducing

the barometer reading to 0°. Consequently the following formula holds with sufficient accuracy:

$$V_0 = \frac{V\,(B - w) \cdot 273}{760\,(273 + t)}.$$

As 1 ml. of nitrogen at 0° and 760 mm. has been found to weigh 0.0012506 g.,* then V_0 ml. of nitrogen will weigh

$$0.0012506 \times V_0 \text{ g.}$$

and the substance contains $\frac{0.12506 \cdot V_0}{a}$ per cent of nitrogen.

If the value of V_0 is inserted in this last equation, and the constant values are united, it becomes

$$x = 0.04493 \frac{V\,(B - w)}{(273 + t) \cdot a} = \text{per cent N.}$$

(b) Determination of Nitrogen in an Open Tube

The determination is carried out in practically the same way as before, except that in this case the carbon dioxide is generated outside of the tube. If the combustion-tube of Fig. 92 is imagined cut off at M and connected by means of the two-bulbed tube with a long test-tube, as shown in the upper part of the figure, the apparatus necessary for this determination will be seen.

The long test-tube contains sodium bicarbonate, and it is covered with a piece of copper gauze in order that it may be heated more uniformly.

At S is a long copper oxide spiral, this is followed by a copper boat containing the substance mixed with powdered copper oxide, then the long layer of coarse copper oxide, and finally the reduced copper spiral. After the connection with the azotometer has been made, heat the tube containing the sodium bicarbonate and remove the air from the combustion-tube by means of the carbon dioxide evolved. The greater part of the water that is simultaneously set free collects in the two-bulbed tube. Otherwise the procedure is exactly the same as in the former case.

Remark. — The advantage of this method over the former lies in the fact that the combustion-tube can be used for a large number of nitrogen determinations without refilling it each time.

With difficultly-combustible substances the author prefers to work with the closed tube, for in this way it is possible to get a very intimate mixture of the substance with the powdered copper oxide.

* Cf. Nitrogen under Gas Analysis.

OXALIC ACID, $H_2C_2O_4.2\,H_2O$. Mol. Wt. 126.06

Forms Calcium Oxide, CaO, and Carbon Dioxide, CO_2

Determination as Calcium Oxide

Treat the neutral solution of an alkali oxalate with a few drops of acetic acid, heat to boiling, and precipitate with boiling calcium chloride solution. After standing twelve hours filter off the precipitate, wash with hot water, ignite wet in a platinum crucible, and from the weight of the calcium oxide calculate the amount of oxalic acid as follows:

Let a = wt. of substance, p the weight of CaO from the CaC_2O_4 precipitate, then $\frac{224.6\,p}{a}$ = per cent $H_2C_2O_4.2\,H_2O$.

Determination as Carbon Dioxide

Principle. — The method is based upon the fact that oxalic acid on being heated with manganese dioxide and dilute sulfuric acid is oxidized quantitatively to carbon dioxide:

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + 2\,CO_2.$$

Procedure. — Treat a weighed amount of the oxalate with one and a half times as much manganese dioxide (free from carbonate) either in the apparatus shown on p. 331 (Fig. 69), or in that of Fresenius-Classen (Fig. 70, p. 334). The procedure is exactly the same as was described for the determination of carbon dioxide. If p g. of carbon dioxide were found, this corresponds to

$$p \cdot 1.431 = \text{g. Oxalic Acid, } H_2C_2O_4.2\,H_2O.$$

Remark. — Both methods give good results, but oxalic acid can be much more conveniently determined by a volumetric process (see Part II, Volumetric Analysis).

BORIC ACID, H_3BO_3. Mol. Wt. 61.92

Determination as Boron Trioxide, B_2O_3, by the Method of Rosenbladt-Gooch*

Principle. — Alkali and alkaline-earth borates, on being distilled with absolute methyl alcohol (free from acetone) and acetic acid, give up all their boron in the form of methyl borate, a liquid which boils at 65°. If the methyl borate is brought into contact with a weighed amount of lime in the presence of water, it is completely saponified:

$$B(OCH_3)_3 + 3\,H_2O = 3\,CH_3OH + B(OH)_3.$$

* *Z. anal. Chem.*, **27**, 18, 364 (1887).

The boric acid set free combines with the lime to form calcium borate. If the paste of water and lime is evaporated to dryness, the gain in weight, therefore, represents the amount of B_2O_3.

Procedure. — Ignite about 1 g. of the purest lime* obtainable to constant weight over the blast-lamp, and transfer as much of it as possible to the dry Erlenmeyer flask (Fig. 93) which serves as a receiver. Place the crucible, with some of the lime adhering to it, in a desiccator and set aside for the present.

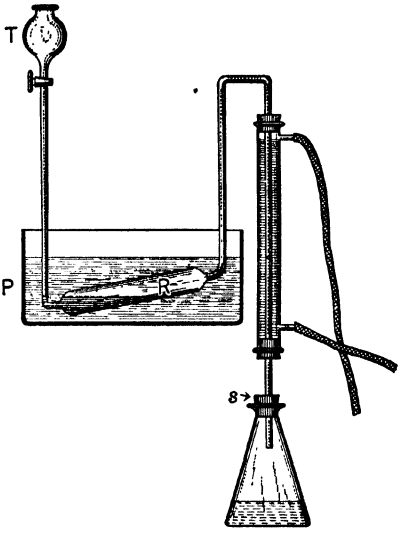


FIG. 93.

Slake the lime in the flask by carefully adding about 10 ml. of water. Connect the flask with the distillation-flask as shown in the figure.†

Treat the aqueous solution of the alkali borate (containing not more than 0.2 g. B_2O_3) with a few drops of either litmus or lacmoid solution, and add hydrochloric acid drop by drop until the solution turns red. Then add 1 drop of dilute sodium hydroxide and a few drops of acetic acid.‡ Add the faintly acid solution by means of the funnel *T* to the pipet-shaped retort, *R*, of about 200 ml. capacity. Rinse out the funnel 3 times with 3 ml. portions of water and close the stop-cock. Distil off the liquid by placing *R* in a paraffin bath at not over 140°, and collect the distillate in the Erlenmeyer flask containing the lime. When all of the liquid has distilled over, lower the paraffin bath and, after *R* has cooled somewhat, add 10 ml. of methyl alcohol (free from acetone) through the funnel and again distil off the liquid in *R*. Repeat this process 3 times. Then add 2–3 ml. of water to the retort, a few

* Instead of lime, Gooch and Jones use 4–7 g. of sodium tungstate fused with about 0.5 g. WO_3 in a platinum crucible to expel any carbonic acid. The fused mass is cooled and weighed.

† To permit the escape of air from the flask, make a cut in the side of the cork stopper, at *s*.

‡ It is absolutely necessary to neutralize the greater part of the alkali with hydrochloric acid and then the last of it with acetic acid. If the alkali were all neutralized with acetic acid, little or none of the boric acid would pass over into the receiver during the subsequent distillation with alcohol.

drops of acetic acid until the liquid becomes distinctly red again,* and repeat the distillation with 10 ml. of methyl alcohol 3 times more. At the end of this time all of the boric acid will be found in the receiver. When the distillation is over, the retort should be removed from the paraffin bath, by lowering the latter. If this is not done, the retort is likely to break when the paraffin solidifies. Shake the stoppered flask thoroughly and allow to stand for an hour or two to make sure that all of the methyl borate is saponified. Then pour the contents of the receiver into a 200 ml. platinum dish and evaporate on the water-bath to dryness at as low a temperature as possible. During this process the alcohol must not be allowed to boil under any circumstances. Then, in order to remove the small amount of lime that remained adhering to the sides of the flask, add a few drops of dilute nitric acid to the receiver, and, by carefully inclining the flask, wet its entire inner surface with the acid, after which wash the contents into the platinum dish and evaporate to dryness again. This time the water in the bath may boil, as there is now no danger of losing the boric acid, the alcohol being all removed by the first evaporation. Gently ignite the residue in the dish over a small flame to destroy the calcium acetate that was formed by the excess of acetic acid added. Allow to cool and transfer by means of a little water to the crucible in which it was originally weighed. Dissolve the dark-colored lime remaining on the sides of the dish in a little nitric or acetic acid and wash into the crucible. Evaporate the contents of the crucible to dryness on the water-bath and, with the cover upon it, ignite the crucible at first gently and finally more strongly until a constant weight is obtained. The increase in weight represents the amount of B_2O_3.

Remark. — This method affords faultless results, even in the presence of considerable amounts of other salts. Free halogen hydride or sulfuric acid must not be present, for these acids form esters with the methyl alcohol and distil over with boric acid, with which they would be weighed. Instead of using lime in the receiver, the methyl borate can be distilled into a dilute solution of ammonium carbonate, and the latter evaporated with slaked lime in a platinum dish immediately after the distillation. The author, however, prefers the above method.

If one possesses a large platinum crucible (with a capacity of from 80–100 ml.), the first evaporation can take place in this and it is then advisable to place the crucible within a ring-shaped copper or tin tube through which steam passes (Fig. 25, p. 47). In this way the calcium acetate does not creep up over the sides of the dish, and there is no danger of any bumping.

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* By the repeated distillation, the contents of the retort become alkaline, as shown by the blue color of the solution.

Determination of Boric Acid in Silicates, Enamel, etc.

Fuse the finely-powdered substance with 4 times as much sodium carbonate, extract the melt with water and evaporate the aqueous solution containing the boric acid* to a small volume, make acid with acetic acid, and, without regard to any separation of silica, transfer the solution to the Gooch retort and analyze as above directed.

Remark. — This determination can be performed in the presence of fluorine provided acetic and not nitric acid is used to set free the boric acid; but, for that matter, it is in no case advisable to use nitric acid and it is not permissible when chlorides are present.

Determination of Boric Acid in Mineral Waters

If the water contains considerable boric acid (0.1 g. or more of B_2O_3 in a liter), evaporate a weighed amount (from 200–300 ml.) to a small volume,† filter off the precipitated calcium and magnesium carbonates, concentrate the filtrate, make slightly acid with acetic acid, and analyze as described on p. 375.

If the water contains only a little boric acid, as is true in most cases, a large amount must be taken for the determination. Evaporate 10–15 liters in a large porcelain dish to about 1 liter,† filter off the deposited salts (these never contain any borate), wash thoroughly with hot water, and evaporate the filtrate and washings on the water-bath until a moist residue is obtained. If this residue does not amount to more than 5 or 6 g. redissolve it in water, make acid with acetic acid, transfer to the Gooch retort, and distil as described on p. 375. Usually a larger residue is obtained, such that it cannot be conveniently analyzed directly, in which case the boric acid is extracted from it. For this purpose make the residue acid with a little hydrochloric acid, thoroughly stir with absolute alcohol, and by means of more of the latter transfer it to a flask, cork up, and allow to stand 12 hours with frequent shaking. The boric acid will then be found in the alcoholic solution. Filter off the residue, wash with 96 per cent alcohol, dilute largely with water, add 1 g. of sodium hydroxide, distil off the alcohol (see Remark below), and evaporate the liquid until a moist residue is obtained. Make this again acid with hydrochloric acid and repeat the above extraction with alcohol, and subsequent distillation of the alcohol, after the addition of water and 1 g. of sodium hydroxide. If the residue

* Sometimes the insoluble residue contains appreciable amounts of boric acid. In the method given under Volumetric Analysis, this fact will be taken into consideration.

† If the water reacts alkaline, evaporate it at once; otherwise add enough sodium carbonate solution to make it alkaline.

now obtained is not too large, ignite gently to destroy the organic matter; after extracting with water, filter off the carbonaceous residue and make the filtrate acid with hydrochloric acid. Then add sodium hydroxide till barely alkaline and just enough acetic acid to make the solution react acid again. Analyze the solution thus prepared as described on p. 375.

Remark. — Unless a large amount of water and the sodium hydroxide are added, some of the boric acid will be volatilized with the alcohol. It is always best to test the alcoholic distillate for boric acid as follows: extract a few pieces of turmeric root with alcohol, place 2–3 drops of the yellow solution in a porcelain dish, add the alcoholic solution to be tested for boric acid and a few drops of acetic acid. Dilute with water and evaporate to dryness on the water-bath. According to F. Henz, if as much as 0.001 mg. of boric acid is present, a faint but distinct coloration will be evident, while the presence of 0.02 mg. will cause a strong reddish-brown coloration, which on being treated with sodium hydroxide is turned to the characteristic blue-black color.

If boric acid is found in the alcoholic distillate, it must be again treated with water and sodium hydroxide, and the alcohol once more distilled off.

MOLYBDIC ACID, H_2MoO_4. Mol. Wt. 162.02

The determination of molybdic acid has already been considered on p. 263.

TARTARIC ACID, $H_2C_4H_4O_6$. Mol. Wt. 150.07

The composition of free tartaric acid as well as that of the tartrates is determined by an elementary analysis, see p. 364 *et seq.*

META- AND PYROPHOSPHORIC ACIDS

These acids are changed to phosphoric acid and determined as described on p. 379.

IODIC ACID, HIO_3. Mol. Wt. 175.93

Form: Silver Iodide, AgI

For the determination of iodic acid as silver iodide, make the solution of the alkali iodate acid with sulfuric acid, and add sulfurous acid until the solution, which at first becomes yellow on account of the separation of iodine, is again colorless. After this add an excess of silver nitrate and a considerable amount of nitric acid. Heat the solution to boiling and determine the precipitated silver iodide as described on p. 296.

It is not permissible to change the iodate to iodide by ignition, for the decomposition takes place at a temperature above that at which

the iodide itself begins to volatilize. The transformation is, therefore, not quantitative. This is especially true of sodium iodate, which is only changed to iodide upon heating to a white heat. Potassium and silver iodates are much more readily decomposed, but even then some iodide is lost. Both iodic and periodic acids may be more accurately determined by a volumetric process (see Part II, Iodimetry).

For the determination of the metal present in an iodate, first change it to the chloride by repeated evaporation with concentrated hydrochloric acid:

$$KIO_3 + 6\,HCl = KCl + 3\,H_2O + 2\,Cl_2 + ICl.$$

GROUP IV

PHOSPHORIC, ARSENIC, ARSENIOUS, THIOSULFURIC, CHROMIC, VANADIC, AND PERIODIC ACIDS

PHOSPHORIC ACID, H_3PO_4. Mol. Wt. 98.06

Forms: Magnesium Pyrophosphate, $Mg_2P_2O_7$; Ammonium Phosphomolybdate, $(NH_4)_3PO_4 \cdot 12\,MoO_3$; Phosphomolybdic Anhydride, $P_2O_5 \cdot 24\,MoO_3$

1. Determination as Magnesium Pyrophosphate, according to B. Schmitz

Formerly it was the usual practice to precipitate phosphoric acid in the cold with "magnesia mixture" and ammonia, but according to the experiments of Neubauer* and of Gooch† it is evident that it is very difficult to obtain a pure precipitate of magnesium ammonium phosphate in this way; sometimes it is contaminated with $Mg_3(PO_4)_2$ and sometimes with $Mg(NH_4)_4(PO_4)_2$. If, however, the precipitation takes place in a hot solution, as recommended by Schmitz,‡ Järvinen,§ and Jörgensen,|| a very pure, coarsely crystalline precipitate of $Mg(NH_4)PO_4 \cdot 6\,H_2O$ is obtained.

Procedure. — To the neutral solution of alkali phosphate add a little hydrochloric acid, a considerable excess of "magnesia mixture,"¶ and 10–20 ml. of a saturated solution of ammonium chloride. After heating the mixture to boiling, slowly add 1.5 *N* ammonia, while constantly stirring, until a precipitate begins to form, and then regulate

* H. Neubauer, *Z. angew. Chem.*, **1896**, 439.

† F. A. Gooch, *Z. anorg. Chem.*, **20**, 135.

‡ B. Schmitz, *Z. anal. Chem.*, **45**, 512 (1906).

§ K. K. Järvinen, *Z. anal. Chem.*, **43**, 279 (1904), **44**, 333 (1905).

|| G. Jörgensen, *Z. anal. Chem.*, **45**, 278 (1906).

¶ The "magnesia mixture" is prepared, according to Schmitz, by dissolving 55 g. of crystallized magnesium chloride and 105 g. of ammonium chloride in water, adding a little hydrochloric acid and diluting to a volume of one liter.

the addition of the ammonia so that about 4 drops are added in a minute. If a milky turbidity appears, it must be redissolved in hydrochloric acid. It is important that the precipitate which first forms shall be crystalline. As the precipitate increases in amount, the addition of the ammonia may be quickened, until finally the liquid smells of ammonia, after blowing away the vapors on top of the liquid. Then allow the solution to cool, add one-fifth of its volume of concentrated ammonia, and at the end of 10 minutes more it is ready to filter. Wash the precipitate 3 times by decantation with 1.5 *N* ammonia, then transfer to a filter and wash free from chloride. Dry, ignite and weigh as described on p. 78. It is best to use a Munroe crucible and an electric oven.

If the weight of the precipitate is p, then the corresponding weights of H_3PO_4 and P_2O_5 are

$$\frac{2\,H_3PO_4 \cdot p}{Mg_2P_2O_7} = \text{weight } H_3PO_4 \quad \text{and} \quad \frac{P_2O_5 \cdot p}{Mg_2P_2O_7} = \text{weight } P_2O_5.$$

Solution and Reprecipitation of the Ignited Magnesium Pyrophosphate

If it is desired to dissolve the ignited precipitate and to reprecipitate the phosphoric acid, place the crucible, together with its cover, in a beaker, add enough water to cover the crucible, and then an excess of concentrated hydrochloric acid. Cover the beaker with a watch-glass and heat its contents on the water-bath, with occasional stirring. When the precipitate has dissolved, continue the heating for 3–4 hours longer to make sure that the pyrophosphoric acid is completely changed to orthophosphoric acid. This change is always complete at the end of this time if the weight of the magnesium pyrophosphate was not over 0.2 g. The time necessary to effect this transformation is proportional to the amount of acid used.

After the liquid has been sufficiently heated, remove the crucible and its cover, and to the solution add 2–5 ml. of magnesia mixture, and precipitate, as described above, with 1.5 *N* ammonia, etc.

The method described on p. 379 for the precipitation of phosphoric acid is not applicable when the substance contains alkaline earths or heavy metals. In such cases the phosphoric acid should be precipitated first as ammonium phosphomolybdate and the phosphoric acid in this precipitate determined by one of the following methods.

2. Determination of Phosphoric Acid as Magnesium Pyrophosphate after Previous Precipitation as Ammonium Phosphomolybdate

This method, first proposed by Sonnenschein, has experienced, in the course of time, a great many modifications, and of these, that of

Woy* will be described, for it is one of the quickest and most accurate. It may be mentioned that the molybdate method is always applicable when the phosphoric acid is present as orthophosphate.

Titanium, zirconium, quinquevalent vanadium and quinquevalent arsenic interfere, all precipitating with the phosphorus. Titanium and quinquevalent vanadium also prevent complete precipitation. Cain and Tucker† have shown that the interference of vanadium can be prevented by reducing to the quadrivalent condition and precipitating at 20° and by precipitating at this low temperature the interference of arsenic is overcome.

Principle. — If a solution containing phosphoric acid, in the presence of ammonium nitrate and sufficient nitric acid, is treated with a slight excess of ammonium molybdate and heated just to the boiling-point, all of the phosphoric acid is immediately precipitated as yellow ammonium phosphomolybdate. According to Hundeshagen, the precipitate possesses the following composition:

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 2\ HNO_3 \cdot H_2O,$$

and always contains, when sufficient molybdic acid is present, 24 moles of MoO_3 to 1 mole of P_2O_5. The precipitate is usually impure but a fairly pure precipitate can be obtained by dissolving it, after decanting off the supernatant liquid, in ammonia, adding little more ammonium molybdate, and reprecipitating by the addition of nitric acid at 30–40°.

It must also be noted that the solution may contain neither silicic acid nor organic substances‡ and only a small amount of chloride (best none at all), but there must be considerable free nitric acid present; 1 g. of P_2O_5 requires 11.6 g. of HNO_3, but as much as 35.5 g. of the latter acid does no harm.§ The precipitate will dissolve somewhat if more nitric acid than the above quantity is used, but the addition of ammonium molybdate decreases the solubility of the precipitate in nitric acid; 1 g. of ammonium molybdate makes 55.7 g. of nitric acid inactive. The presence of ammonium nitrate not only facilitates the formation of the precipitate, but its presence is absolutely necessary, although about 5 per cent is sufficient.

Solutions Required

1. A 3 per cent solution of ammonium molybdate obtained by dissolving 120 g. of commercial ammonium molybdate, $(NH_4)_6Mo_7O_{24} + 4\ H_2O$, in 4 liters of water (1 ml. of this solution will precipitate 0.001 g. P_2O_5).

* *Chem. Zeit.*, **21**, 442.

† *J. Ind. Eng. Chem.* **5**, 647 (1913).

‡ According to Hundeshagen (*Z. anal. Chem.*, **28**, 164) and Eggertz (*J. prak. Chem.*, **79**, 496) the presence of tartaric and oxalic acids hinders the formation of the yellow precipitate, and in some cases prevents it entirely. According to Hans v. Jüptner (*Oesterr. Z. Berg- u. Hüttenw.*, **1894**, 471) this is not the case; he even recommends that tartaric acid be added for the determination of phosphorus in iron, on the ground that it prevents the precipitate being contaminated with molybdic acid and ferric oxide.

§ These figures are taken from experimental data furnished by Hundeshagen. They do not refer to the above formula given the yellow precipitate.

2. A solution of ammonium nitrate, obtained by dissolving 340 g. of ammonium nitrate in 1 liter of water.

3. Nitric acid, *d.* 1. 153 (containing 25 per cent HNO_3).

4. As wash liquid, 200 g. ammonium nitrate and 160 ml. of nitric acid dissolved in 4 liters of water.

Procedure. — In all cases take 50 ml. of the solution, containing at the most 0.1 g. P_2O_5. If the solution contains more than this amount of phosphoric acid, use an aliquot part for the analysis.

Place the 50 ml. of neutral or slightly acid (HNO_3) solution in a 400-ml. beaker and to precipitate 0.1 g. of P_2O_5 add 30 ml. of ammonium nitrate solution and 10–20 ml. of nitric acid. Heat the solution until bubbles begin to rise. At the same time heat the required amount of ammonium molybdate solution (in this case 120 ml.*) until it begins to boil, and then transfer to a separatory funnel and allow it to run in a thin stream into the middle of the phosphate solution, which is rotated while the molybdate solution is being added. The yellow ammonium phosphomolybdate is at once thrown down and the separation is quantitative. Keep the contents of the beaker in motion for about one minute more and then allow to stand for 15 minutes. Then decant the clear liquid through a filter, wash the precipitate once by decantation with 50 ml. of the wash liquid and then dissolve in 10 ml. of 4.5 *N* ammonia. To this solution add 20 ml. of the ammonium nitrate solution, 30 ml. of water, and 1 ml. of ammonium molybdate. Heat as before, until bubbles begin to rise, and precipitate the phosphoric acid by the addition of 20 ml. of hot nitric acid, added drop by drop through the same funnel that was used for the molybdate solution, the solution being rotated as before. The precipitate is immediately formed and is now pure. After standing 10 minutes filter it off and dissolve in warm 1.5 *N* ammonia. To the ammoniacal solution add hydrochloric acid until the yellow precipitate produced dissolves only slowly on being mixed with the solution. Now, according to Schmitz,† add an excess of an acid solution of " magnesia mixture " and heat the solution to boiling. Introduce a few drops of phenolphthalein indicator solution, and add 1.5 *N* ammonia solution rapidly from a buret, while stirring the solution,

* AMOUNTS OF REAGENTS REQUIRED

Amount of P_2O_5 Present in Grams	Ammonium Molybdate	Ammonium Nitrate	Nitric Acid
0.1	120 ml.	30 ml.	19 ml.
0.01	15 "	20 "	10 "
0.005	15 "	20 "	10 "
0.002	10 "	15 "	5 "
0.001	10 "	15 "	5 "

† *Loc. cit.*

until the liquid becomes slightly red in color. Allow to cool and then add one-fifth of its volume of concentrated ammonia. After four hours, the precipitate of magnesium ammonium phosphate is ready to filter.

3. Direct Determination of Phosphoric Acid as Ammonium Phosphomolybdate (Finkener)*

The precipitate produced as described under 1, having the composition,

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 2\ HNO_3 \cdot H_2O,$$

is transformed by heating at 160–180° C. into pure ammonium phosphomolybdate of the composition $(NH_4)_3PO_4 \cdot 12\ MoO_3$. Theoretically this substance contains 3.784 per cent of P_2O_5.

If, therefore, the weight of yellow precipitate (dried until its weight is constant) is multiplied by 0.03784, the actual amount of P_2O_5 present should be obtained. The results obtained by Finkener, however, were accurate only when the factor 0.03794† was used. Hundeshagen,‡ on the other hand, found that the factor 0.03753 should be used, and this has been confirmed by experiments performed in the author's laboratory.

Procedure. — Precipitate the phosphoric acid twice, according to the directions of Woy (p. 382), with ammonium molybdate; filter the precipitate into a Gooch crucible, wash with the prescribed mixture until no further brown coloration is produced in the filtrate upon adding $K_4[Fe(CN)_6]$, and dry in a current of air at 160° in a Paul's drying oven, until a constant weight is obtained. If the precipitate should become slightly greenish, add a small crystal of ammonium nitrate and one of ammonium carbonate and again heat the contents of the crucible, whereby the precipitate will at once assume a homogeneous yellow color.

Remark. — The results of Hundeshagen and Steffan show that this method gives very exact results. Steffan worked precisely according to the directions of Finkener, precipitating the phosphoric acid in the cold with a $33\frac{1}{3}$ per cent solution of ammonium molybdate and filtering after standing 24 hours. It is, however, not necessary, as Hundeshagen has shown, to work with such a concentrated solution of ammonium molybdate; the precipitation from a hot solution with a 3 per cent molybdate solution yields just as accurate results and the solution does not have to stand so long before filtering. Even when iron is present this method gives good results, so that it is to be recommended for the determination of phosphorus in iron and steel.

4. Determination of Phosphoric Acid as Phosphomolybdic Anhydride (Woy)

Gently ignite the precipitate, produced in the same way as before, until a greenish-black residue remains of the composition $24\ MoO_3 \cdot$

* *Ber.*, **11** (1878), 1640.

† *Loc. cit.*

‡ *Z. anal. Chem.*, **32**, 144 (1893).

P_2O_5, with 3.946 per cent of P_2O_5. Perform the ignition as follows: Upon the bottom of a nickel crucible place a disk of ignited asbestos about 2 mm. thick, or the porcelain plate of a Gooch crucible may be used. Upon this place the Gooch crucible containing the precipitate, cover with a watch-glass and heat at first gently and finally until the bottom of the nickel crucible is at a dull-red heat. When the precipitate has become of a homogeneous, bluish-black color, allow to cool in a desiccator and weigh.

This method is rapid and gives good results in the presence of iron and aluminium.

Determination of Phosphorus in Iron, Steel and Bronze*

Procedure. — **Cast Iron.** — Dissolve 1–3 g. of sample in a covered casserole in 30 ml. of 7.5 *N* nitric acid. When the iron is all in solution, add 10 ml. of 6 *N* hydrochloric acid, evaporate to dryness and bake on the hot plate for 15 minutes. Cool, drench the residue with concentrated hydrochloric acid, dilute to 50 ml. and heat until all the salts are in solution. Filter without delay, wash the residue with 0.6 *N* hydrochloric acid and evaporate the filtrate to sirupy consistency. Meanwhile ignite the above residue in a platinum crucible, cool and heat with 10 drops of concentrated hydrochloric acid and 2 ml. of hydrofluoric acid. Evaporate just to dryness, add 5 ml. of concentrated hydrochloric acid and add to the main solution that is being evaporated.

When the solution is of sirupy consistency, transfer to a 300 ml. Erlenmeyer flask by alternate rinsing with 7.5 *N* nitric acid and hot water, using not more than 30 ml. of the former and 70 ml. of the latter. Heat to boiling and digest for 10 minutes.

Precipitation. — To the boiling solution, add 100 ml. of ammonium molybdate solution†, shake 10 minutes and allow to stand at least 4 hours. If an appreciable amount of vanadium is present, carry out the precipitation at 20° in a solution which has just been treated with 2–3 ml. of 10 per cent ferrous sulfate solution and a few drops of sulfurous acid to reduce quinquevalent vanadium. Decant off the solution through a filter, keeping as much of the precipitate as possible back in the flask and wash with not more than 50 ml. of cold 1 per cent nitric acid. Dissolve the precipitate in 24 ml. of 6 *N* ammonium hydroxide to which 2 g. of citric acid has been added. Pour the solvent through

* G. E. F. Lundell, *Ind. Eng. Chem.*, **15**, 171 (1923).

† Stir 100 g. of pure MoO_3 into 400 ml. of cold distilled water and add 80 ml. of concentrated ammonium hydroxide. Filter and pour while stirring into one liter of 6 *N* nitric acid. Add 50 mg. of microcomic salt and allow to stand 24 hours before using. Do not prepare over a week's supply of the acid reagent at a time.

the filter that contained some of the phosphomolybdate and catch the solution in the flask containing the bulk of the precipitate. Finally wash the filter several times with 0.6 *N* hydrochloric acid. If the ammoniacal filtrate is not clear, heat it to boiling, filter through the same filter and wash with hot water. In this case, and whenever appreciable quantities of elements like titanium, zirconium and tin are present, preserve this filter paper and treat it together with the filter referred to in the following directions.

Make the ammoniacal solution acid with hydrochloric acid, add 20 ml. of magnesia mixture and precipitate magnesium ammonium phosphate as described on p. 382. Allow the precipitate to stand 4 hours. Filter, keeping the precipitate back in the flask as much as possible. Dissolve the precipitate on the filter with 28 ml. of 6 *N* hydrochloric acid, catching the solution in the flask containing the bulk of the precipitate. Wash the filter thoroughly with 0.6 *N* hydrochloric acid. In case titanium, zirconium or tin is present, ignite this filter and the one previously set aside, in a platinum crucible, fuse with a little sodium carbonate extract with water and add the aqueous extract to the hydrochloric acid solution of the first magnesium ammonium phosphate precipitate.

Transfer the solution to a 200-ml. beaker. If considerable arsenic is present precipitate with hydrogen sulfide, washing the arsenic sulfide precipitate with dilute hydrochloric acid saturated with hydrogen sulfide. Boil off the excess of hydrogen sulfide and reduce to 50–75 ml. If only a little arsenic is present, add 0.6–1 g. of ammonium bromide and evaporate the solution to a volume of 5–10 ml.; the arsenic will volatilize as arsenic trichloride.

To the solution free from arsenic, and at a volume of 50–75 ml., add 0.1–0.2 g. of citric acid, 2–3 ml. of magnesia mixture and again precipitate magnesium ammonium phosphate.

Ignite and weigh the magnesium pyrophosphate as described on p. 78.

Plain Carbon Steel. — Dissolve 1–3 g. in 30 ml. of 7.5 *N* nitric acid. When the steel has all dissolved, boil and slowly add a saturated solution of potassium permanganate until oxides of manganese are precipitated. Clear the solution by cautious addition of 10 per cent ferrous sulfate solution, boil gently for 10 minutes and treat with ammonium molybdate as above described.

Alloy Steels. — Treat *chromium* steels in the same way but if any residue is obtained on dissolving in nitric acid, continue heating until it dissolves, adding sulfuric acid if necessary. Treat a high *silicon* steel like cast iron. If *titanium* or *zirconium* is present to any extent,

a phosphate may precipitate during the boiling prescribed for plain carbon steels. Filter off the precipitate, fuse the residue with sodium carbonate and add the aqueous extract of the melt to the main solution. *Tungsten* steel does not dissolve in nitric acid. Dissolve 1–3 g. in a mixture of 20 ml. concentrated nitric acid and 60 ml. of concentrated hydrochloric acid in a covered casserole. Heat gently and evaporate to dryness. Remove the cover glass and bake till all the acid is expelled. Cool, and add 30 ml. of concentrated hydrochloric acid. Heat until the iron all dissolves, dilute to 100 ml., filter and wash the residue of tungstic acid with *N* hydrochloric acid. Evaporate the filtrate to a sirup and meanwhile dissolve the tungstic acid in hot 2 *N* ammonium hydroxide, finally washing the paper with dilute hydrochloric acid. Make the ammoniacal solution faintly acid, add 1 g. of alum and then add ammonium hydroxide in slight excess. Filter off the aluminium hydroxide and phosphate, dissolve in hot hydrochloric acid and add the solution to the main solution which is being evaporated. Dilute the sirup as described for the analysis of cast iron.

Bronze. — Dissolve 1–3 g. in a 300-ml. Erlenmeyer flask with a mixture of 15 ml. concentrated nitric acid and 5 ml. of concentrated hydrochloric acid. Add 15 ml. of hot water to the aqua regia solution, digest at 85° for 10 minutes, dilute to 50 ml. and precipitate with molybdate as above. If the antimony and tin content is high it may be desirable to remove all nitric acid by repeated evaporation with hydrochloric acid, precipitate the copper, tin, lead and antimony in the diluted solution with zinc, add ferric chloride and ammonia and dissolve the precipitate in hydrochloric acid. Treat this solution with molybdate as above.

The Basic Acetate Method of Blair

This method is capable of giving good results. It depends upon the precipitation of phosphoric acid as ferric phosphate, dissolving the precipitate in hydrochloric acid and precipitating magnesium ammonium phosphate in the presence of citrate ions which prevent the precipitation of ferric ions by ammonia.

Procedure. — Dissolve the sample as described in the preceding method and after the removal of the silica, in the case of cast iron, add ammonia until a slight permanent precipitate is formed. Add 200 ml. of saturated sulfurous acid and heat until the solution is nearly colorless, due to reduction of the irons. Add 10 ml. of concentrated hydrochloric acid and remove the excess of sulfur dioxide by a stream of carbon dioxide into the hot solution. Cool, add 2 ml. of bromine to oxidize enough iron to combine with all of the phosphorus as ferric phosphate. Add ammonium hydroxide, drop by drop, until a distinct

red or brown precipitate is formed which turns green with another drop of ammonium hydroxide.

If before this occurs the precipitate does not appear decidedly red in color, add a few drops of hydrochloric acid and 2 ml. more of bromine water, and repeat the addition of ammonia until the red and then the permanent green precipitate is obtained. Add 6 *N* acetic acid, drop by drop, until the green precipitate dissolves and the remaining precipitate is quite red in color. Add about 1 ml. of acid in excess and boil the solution for one minute. All the phosphoric acid is then precipitated as white ferric phosphate and the excess of *ferric iron* as red basic acetate. The greater part of the iron remains in solution as ferrous salt. Filter the solution promptly through a large filter and wash once with hot water.

Dissolve the precipitate adhering to the sides of the beaker in hot 6 *N* hydrochloric acid and 10 ml. of bromine water. Pour the solution upon the filter containing the precipitate and receive the filtrate in a small beaker using more acid if necessary, wash with hot water and evaporate the solution nearly to dryness to remove the excess of hydrochloric acid, add 5 ml. of a 50 per cent citric acid solution and precipitate magnesium ammonium phosphate as described on p. 379.

Determination of Phosphoric Acid in Silicates

In the analysis of silicates (see p. 423) the phosphoric acid is found in the precipitate produced by ammonia in the filtrate from the silica together with iron and aluminium hydroxides. It is analyzed according to p. 112.

Determination of Phosphoric Acid in Mineral Waters

To 5–6 liters of the water add a little hydrochloric acid and evaporate to dryness; moisten the residue with concentrated hydrochloric acid, take up with water, and filter off the silicic acid. To the filtrate add a slight excess of ammonia; the phosphoric acid is usually completely thrown down in the form of phosphate of iron, aluminium, or alkaline earth. Dissolve the filtered and washed precipitate in nitric acid and determine the phosphoric acid according to one of the molybdate methods (pp. 380–384).

Remark. — If the mineral water does not contain much iron, aluminium, or alkaline-earth metal, but is rich in phosphoric acid and the alkalies, the precipitate produced by ammonia will not contain all of the phosphoric acid. In such a case evaporate the hydrochloric acid solution from the silica several times to dryness with nitric acid. dissolve the residue in as little nitric acid as possible, and determine the phosphoric acid by one of the molybdate methods.

Recovery of Molybdenum Residue (H. Bornträger)*

Into a large, wide-mouthed flask place 250 ml. of strong ammonia and add the acid molybdenum filtrates to this. Either immediately or after standing some time, a crystalline deposit of nearly pure molybdic acid is formed. When the flask is nearly full, make the solution nearly neutral, allow the precipitate to settle, and decant off the upper liquid containing only a small amount of molybdenum. Pour the residue upon a suction plate, wash once with water (not more, or the molybdic acid will dissolve) and suck as dry as possible. Dissolve the precipitate by warming with as little ammonia as possible, leaving behind a residue of iron and aluminium hydroxides, magnesia, and silicic acid. Filter these off and dilute the solution with distilled water until at 17° C. it has a density of 1.11 = 14° Bé. It then contains 150 g. of ammonium molybdate in a liter. If this solution is diluted with 4 times as much water a 3½ per cent solution will be obtained.

Determination of Phosphorus in Organic Substances

The substance is decomposed by the method of Carius. By the action of the nitric acid in the closed tube the phosphorus is oxidized to phosphoric acid and this is determined as usual.

Separation of Phosphoric Acid from the Metals

1. Separation from the Metals of Groups I and II

Hydrogen sulfide is conducted into the hydrochloric acid solution,† by which means all the members of these groups are precipitated as sulfides while the phosphoric acid remains in solution.

2. Separation from the Metals of Group III

(*a*) The phosphoric acid is first precipitated as ammonium phosphomolybdate according to p. 382. In order to determine the metals, evaporate the solution containing molybdenum, but free from phosphoric acid, with sulfuric acid to a sirupy consistency, and carefully heat over a free flame until the nitric acid is expelled. After cooling, moisten the residue with hydrochloric acid and take up in water. Place the solution in a pressure-flask, saturate with hydrogen sulfide, stopper the flask, and heat for some time on the water-bath, when the molyb-

* *Z. anal. Chem.*, **33**, 341 (1894).

† When silver is present it is precipitated as silver chloride, filtered off, and the filtrate treated with hydrogen sulfide.

denum is precipitated in large flocks. After cooling, slowly open the pressure-flask and filter off the molybdenum sulfide. Analyze the filtrate, now free from phosphoric acid and molybdenum, for the metals as described on pp. 91 to 171.

(*b*) Separate the phosphoric acid as before, make the filtrate slightly ammoniacal and saturate with hydrogen sulfide. After standing for some time the solution becomes reddish yellow in color, when the precipitate is filtered off. The metals of this group will be found in the precipitate while the molybdenum is in the filtrate in the form of its sulfo-salt.

Remark. — If nickel is present, some of it will remain in the filtrate with the molybdenum on account of the solubility of nickel sulfide in ammonium sulfide, so that method (*a*) will then give more accurate results. Vanadium (and tungsten) will also go with the molybdenum.

3. Separation of Phosphoric Acid from Iron, Cobalt, Manganese, and Zinc

In case the solution contains iron in the ferric form, acidify with hydrochloric acid, saturate with hydrogen sulfide, and for each gram of the mixed oxides add 3 g. of tartaric acid; make the solution slightly ammoniacal and allow to stand overnight in a stoppered flask. The precipitate contains the metals as sulfides free from phosphoric acid. Filter, wash with water containing ammonium sulfide, dissolve in acid, and analyze according to pp. 94 to 171.

4. Separation from Chromic Acid

If the solution contains free alkali or alkali carbonate, make acid with nitric acid, then slightly alkaline with ammonia and precipitate the phosphoric acid with " magnesia mixture " as described on p. 379.

5. Separation from Calcium, Strontium, Barium, Magnesium, and the Alkalies

Add ammonium carbonate to the hydrochloric acid solution until a slight permanent turbidity* is produced, and dissolve this with a few drops of hydrochloric acid. Then add ferric chloride drop by drop until the liquid above the yellowish-white precipitate of ferric phosphate becomes distinctly brown in color. Dilute the solution with water to a volume of 300–400 ml., boil for one minute, filter and wash

* If only alkalies are present there will be no turbidity; add the ammonium carbonate until the solution is neutral.

with water containing ammonium acetate. In the filtrate are the alkaline earths and alkalies, which, after expelling the ammonium salts by igniting the residue obtained after evaporating to dryness, are determined in the usual way (see pp. 55 to 90).

Determination of Phosphoric Anhydride in Apatite

Weigh out 0.2 g. of the powdered mineral and heat with 15 ml. of 6 *N* nitric acid in a covered casserole. Evaporate to dryness on the water bath and heat 15 minutes at 130° to dehydrate silica. Digest the residue with 25 ml. of 6 *N* nitric acid and heat a few minutes to dissolve the soluble material. Filter and wash with small portions of hot water, receiving the filtrate and washings in a 400-ml. beaker. Continue to wash until 5 ml. of the filtrate will give no precipitate of calcium phosphate when neutralized with ammonia. If a precipitate is obtained pour the test back into the filtrate. Carefully neutralize with ammonium hydroxide till a slight permanent precipitate is obtained and redissolve this in a little nitric acid. The volume of the solution should not exceed 100 ml. at this point.

Heat the solution to 70°, and precipitate with ammonium molybdate solution as directed on p. 382, finally igniting the magnesium ammonium phosphate precipitate and weighing as pyrophosphate.

THIOSULFURIC ACID, $H_2S_2O_3$. Mol. Wt. 114.14

Form: Barium Sulfate, $BaSO_4$

Treat the aqueous solution of the alkali thiosulfate with an ammoniacal solution of hydrogen peroxide, or with ammoniacal percarbonate solution, heat for some time on the water-bath, and then boil to destroy the excess of the reagent. Make the solution acid with hydrochloric acid and precipitate the sulfuric acid formed by the above treatment as barium sulfate. Two moles of $BaSO_4$ correspond to 1 mole of $H_2S_2O_3$.

A much better procedure for the estimation of thiosulfuric acid will be discussed under Iodimetry, Part II.

The remaining acids of this group, arsenious, arsenic, vanadic, and chromic, have been discussed under the respective metals; periodic acid is analyzed precisely in the same way as iodic acid.

GROUP V

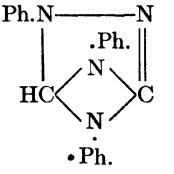
NITRIC, CHLORIC, AND PERCHLORIC ACIDS

NITRIC ACID, HNO_3. Mol. Wt. 63.02

Forms: Nitron Nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, Nitrogen Pentoxide, N_2O_5; Ammonia, NH_3; Nitric Oxide, NO, and Volumetrically

1. Determination of Nitric Acid as Nitron Nitrate*

The base diphenylendoanilohydrotriazole, $C_{20}H_{16}N_4$,



called *nitron* for short, forms a fairly insoluble, crystalline nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, which can be used for the separation and quantitative estimation of this acid. To prepare the reagent, nitron acetate, dissolve 10 g. of nitron in 100 ml. of 0.1 *N* acetic acid. It keeps fairly well in a dark bottle.

Procedure. — Take substance equivalent to not more than 0.1 g. of nitric acid, and dissolve in 80–100 ml. of water containing 1 ml. of glacial acetic acid. Heat the solution nearly to boiling and add at one time 10–12 ml. of nitron acetate solution. Allow the precipitate to stand 24 hours in a dark place, then filter into a Gooch or Munroe crucible and drain as completely as possible from the pale yellow mother-liquor. Wash with 50 ml. of saturated nitron, added in small portions, and drain the precipitate well after each washing. Dry at 110° for 2 hours. The precipitate contains 16.79 per cent of NO_3.

Remarks. — The method gives good results in the presence of sulfate and iodate ions. If large quantities of chloride are present a correction should be applied, as determined by an analysis with pure nitric acid and the same weight of chloride.

In 100 ml. of very dilute acid, approximately the following weights of nitron salts dissolve: — 0.0099 g. of nitrate, 0.008 g. of perchlorate, 0.017 g. of iodide, 0.04 g. of thiocyanate, 0.06 g. of chromate, 0.12 g. of chlorate, 0.19 g. of nitrite, 0.61 g. of bromide.

The results of the nitric acid determination are a little high rather than low, owing to occlusion of a little precipitant.

Besides the acids represented by the above difficultly-soluble salts, ferro- and ferricyanic, picric, and oxalic acids interfere with the determination. Hydrobromic acid can be decomposed by adding chlorine water, drop by drop, to the boiling solu-

* M. Busch, *Ber.*, **38**, 861 (1905); A. Gutbier, *Z. angew. Chem.*, **1905**, 494.

tion until the yellow color of bromine disappears, hydriodic acid by adding an excess of potassium iodate to the neutral solution and boiling off the iodine. Nitrous acid can be removed by dropping powdered hydrazine sulfate into the concentrated solution and chromic acid by reduction with hydrazine sulfate.

2. Determination of Nitric Acid as Nitrogen Pentoxide*

This method is based upon the fact that when an intimate mixture of a dry nitrate is heated with an excess of silica, nitrogen pentoxide is evolved and the amount is determined by the loss in weight.

$$2\,NaNO_3 + SiO_2 = Na_2SiO_3 + N_2O_5.$$

This method cannot be used when there is any other volatile substance present, which is usually the case.

3. Determination of Nitric Acid as Ammonia†

The usual method for the determination of nitric acid is to reduce it in alkaline solution to ammonia. by means of aluminium, zinc, or, best, Devarda's alloy (cf. Vol. I):

$$NO_3^- + 4\,Zn + 7\,OH^- \rightarrow 4\,ZnO_2^= + NH_3 \uparrow + 2\,H_2O.$$

After the reduction, the solution is distilled into a known quantity of acid and the excess of the acid found by titration, or the ammonia can be determined as ammonium chloroplatinate or as platinum (cf. pp. 71–72, *b* and *c*).

Procedure. — Place about 0.5 g. of the nitrate in a 500 ml. Erlenmeyer flask (Fig. 94) and dissolve in 110 ml. of water. To this solution add 5 ml. of alcohol, 50 ml. of caustic potash (*d* 1.3), and 2–2.5 g. of powdered Devarda's alloy. Or, instead of Devarda's alloy, use 5 g. of well-washed zinc and 2 g. of ferrous sulfate. Instead of the caustic potash solution, 80 ml. of saturated sodium hydroxide solution can be substituted. At once connect the flask with the distillation apparatus shown in the figure. The left arm of the 250 ml. Péligot tube, *A*, is connected by a curved tube with the middle bulb, so that a spurting back of the liquid is avoided. The delivery-tube (of potash glass) connecting the flask *K* with the tube *A* is about 1 cm. in diameter and is provided with a small opening at *o*, inside the flask, to prevent spurting of condensed liquid over into *A*. Place 20 ml. of 0.5 *N* sulfuric acid in *A* and dilute so that the solution just reaches to each of the bulbs on the side. Place 5 ml. of the acid in *B*, with a few drops of methyl orange indicator solution, and dilute in the same way. Connect

* Reich, *Z. Chem.*, **1**, 86 (1862).

† Devarda, *Z. anal. Chem.*, **33**, 113 (1894), Pannertz, *Z. anal Chem.*, **39**, 318 (1900).

the tubes A and B by means of a T tube, of which the upper end is closed by a pinch-cock upon a piece of rubber tubing, so that a piece of red litmus paper may be introduced here in case it is desired to see if NH_3 is escaping.

When all is ready, gently heat the contents of the flask K to start the reaction, then remove the flame and allow the reaction to proceed by itself. After an hour this will be shown to be complete by the cessation of the hydrogen evolution. Then slowly heat the liquid in K to boiling, and keep at this temperature until about half of the liquid has distilled over into A; this requires about half an hour. During the last 10 minutes pass a slow current of air through the tube r.

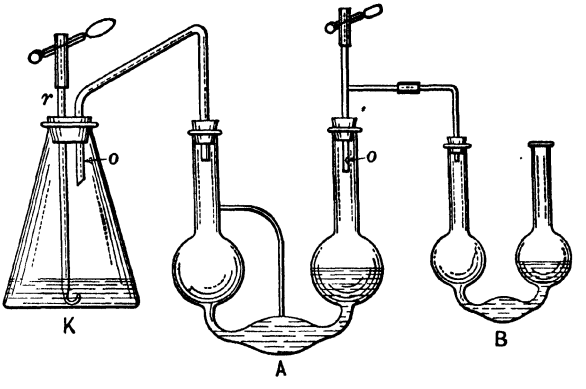


FIG. 94.

If the distillation has been correctly performed, all of the ammonia will now be found in A; no trace should reach B, and the red litmus paper in the T-tube should show no tinge of blue.

When the distillation is finished, open the pinch-cock at r and remove the flame. Add a little methyl orange to A whereby the liquid is colored red, pour the contents of B into A and rinse out B with water that is added to A. Finally titrate the excess of the sulfuric acid with 0.5 N caustic alkali solution until a yellow end-point is obtained. The amount of nitric acid is computed as follows:

If t ml. of 0.5 N base are used in the titration of a g. of substance, then $\frac{(25 - t) \times 3.151}{a}$ = per cent HNO_3 or $\frac{(25 - t) \times 2.700}{a}$ = per cent N_2O_5.

Determination of Nitric Acid as Nitric Oxide

*Method of Schlösing and Grandeau, modified by Tiemann and Schulze**

Principle. — If a nitrate is heated with ferrous chloride and hydrochloric acid, the nitric acid is reduced to nitric oxide:

$$NaNO_3 + 3\,FeCl_2 + 4\,HCl = NaCl + 3\,FeCl_3 + 2\,H_2O + NO.$$

From the volume of the nitric oxide its weight can be calculated.

* *Z. anal. Chem.*, **9**, 401 (1870), and *Ber.*, **6**, 1041 (1873).

The method of Schlösing in its original form* was not much used on account of the apparatus required; but after being modified by Grandeau† it has become one of the best methods for the determination of nitric acid.

The apparatus necessary is shown in Fig. 95 and consists of a 150-ml. flask *K* fitted with a double-bored rubber stopper. Through one of the holes pass the tube *b*, which reaches into the flask just to the lower surface of the stopper; through the other hole pass the tube *a*,‡ ending in a restriction about 1 mm. wide and reaching 1½ cm. below the stopper. Connect the tube *b* by means of a piece of rubber tubing 5 cm. long, and provided with a pinch-cock, with a second tube whose lower end reaches up into the measuring-tube and is covered with rubber tubing as is shown in the figure. In the same way connect the tube *a* with a straight tube.

Solutions required. — 1. A nitrate solution of known strength; dissolve 2.022 g. of recrystallized potassium nitrate, dried at 160°, in one liter of water. Fifty ml. of this solution evolve at 0° and 760 mm. pressure 22.39 ml. of NO.

2. Ferrous chloride solution. Dissolve 20 g. of iron (nails) in 100 ml. of concentrated hydrochloric acid.

3. Six normal hydrochloric acid, *d.* 1.1.

Procedure. — Pour 10 ml. of water into *K* and mark its upper level on the outside of the flask with a colored pencil, then add 40 ml. more and mark its position.

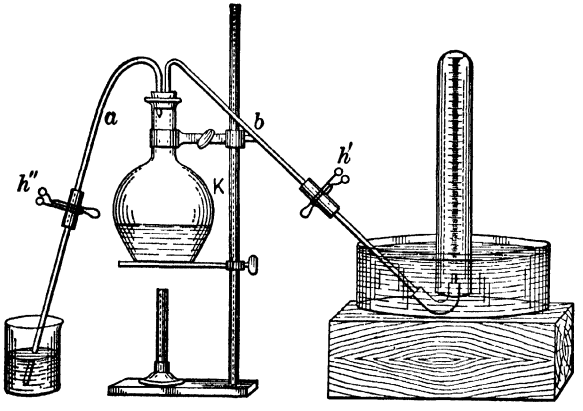


FIG. 95.

Now pour out the water and add from a pipet exactly 50 ml. of the standard nitrate solution to *K*, insert the stopper with the delivery tubing in place and open the pinch-cocks *h'* and *h''*. Heat the contents of the flask to boiling with a free flame until no more bubbles of air escape from the lower end of *b* into the bath containing boiled water. To make sure that the air is all expelled from the apparatus, pinch the rubber tubing at *h'* with the thumb and finger; if no air is present, the liquid will quickly rise in *b*, exerting a noticeable pressure. Then close the pinch-cock *h'* and continue the boiling until the 50 ml. has been reduced to a volume of 10 ml.; then remove the flame and close

* *Annal. chim. et phys.*, [3], **40**, 479 (1853).

† Grandeau, *Analyse chimique appliquée à l'agriculture.*

‡ Grandeau used a separatory funnel instead of the tube *a*; the latter was proposed by Tiemann and Schulze.

the pinch-cock h''. The lower end of a, which dips into distilled water, is immediately filled up to the pinch-cock. The vapors in the flask condense, forming a vacuum, as shown by the closing together of the rubber tubing at h' and h''.

Pour 30 ml. of the ferrous chloride solution into a beaker and mark the upper level on the outside with a colored pencil, add 20 ml. more and note the position in the beaker again. Place the lower end of the tube a in the ferrous chloride solution so that it reaches below the lower mark on the beaker, and, by opening h'', allow 20 ml. of the solution to pass into the flask K. Then replace the beaker containing the ferrous chloride with one containing boiled water. The tube a should not extend vertically into the water, but should be inclined as much as possible. The specifically heavier ferrous chloride solution in the tube passes into the water, while the latter takes its place. When the lower end of a has become filled with pure water in this way, dip it into a beaker containing 6 N hydrochloric acid and allow about 20 ml. of the acid to flow into K, and finally add 3–4 ml. of water to replace the acid in a. Now fill a 50-ml. measuring-cylinder with boiled water, place over the lower end of b as shown in the figure, and heat the contents of the flask K 15 minutes on the water-bath,* then boil with a free flame. As soon as the compressed rubber tubing begins to expand open h', but at the same time pinch the rubber tubing between the thumb and finger. When the liquid no longer rises in b, remove the hand from the rubber tubing and allow the nitric oxide to collect slowly in the measuring-tube. After half of the liquid has evaporated there is no further evolution of nitric oxide to be noticed, although the brown color of the solution shows that the gas has not been completely expelled. To accomplish this, remove the flame, close h', and allow the liquid in K to cool. By means of the vacuum thus produced the remainder of the nitric oxide is expelled from the solution. Repeat the boiling once more, with the same precautions, until the lower mark is reached. Remove the flame, close h', and place the measuring-tube containing the nitric oxide in a cylinder containing pure water at the temperature of the room. To prevent the tube containing the gas from sinking, encase its upper end in a large cork so that it floats on the water. After standing 15–20 minutes raise the tube, by means of the cork, until the level of the liquid within stands at the same height as that in the cylinder without, and read the volume of the gas. At the same time take the temperature of the water and note the barometer reading.

* The heating on the water-bath is necessary, as otherwise a little nitric acid will distil over and not be reduced. A. Wegelin, *Inaug. Dissert.* Zürich, 1907.

If the temperature was $t°$, the barometer reading B millimeters, and w the tension of aqueous vapor at $t°$, then the corresponding volume at 0° and 760 mm. pressure is

$$V_0 = \frac{V\,(B - w)\,273}{760\,(273 + t)}.$$

Now 50 ml. of the standard potassium nitrate solution contain 0.1011 g. of KNO_3 corresponding to 0.05401 g. of N_2O_5, so that the volume V_0 of the nitric oxide corresponds to 0.05401 g. of N_2O_5. Repeat the

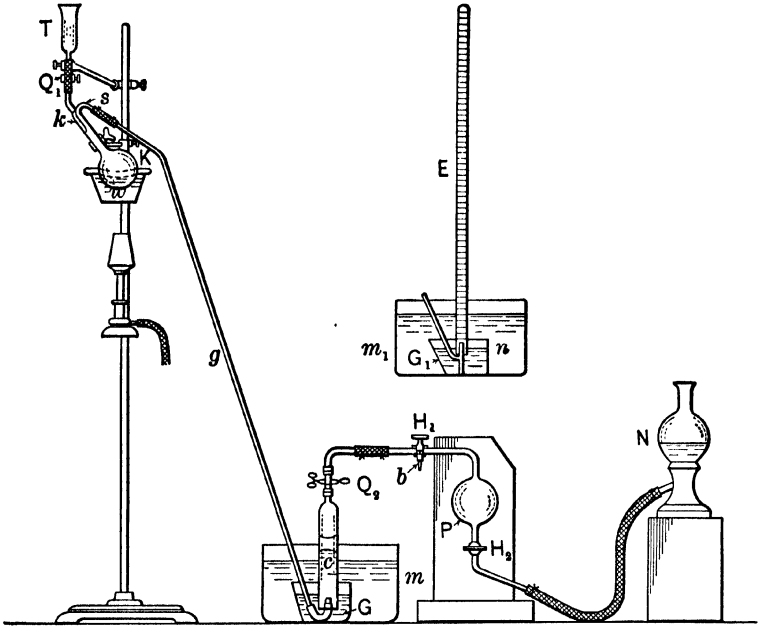


FIG. 96.

experiment several times and use the mean value. It is not permissible to assume that 0.1011 g. of KNO_3 will furnish exactly 22.39 ml. of nitric oxide as a little always remains in the flask.

Now carry out the same procedure with 50 ml. of the solution of the unknown nitrate, which should be prepared so that the amount of nitric oxide evolved will be about the same as that from 50 ml. of the standard solution.

Good results are obtained by this method but the rubber stoppers are attached quite badly and analyses are sometimes spoiled by not opening the pinch-cock h' at just the right time. These difficulties

have been overcome by Wegelin* in the apparatus shown in Fig. 96. The decomposition flask K has a capacity of about 120 ml. Its neck is about 9 cm. long and into it are fused glass tubes k and s connecting the flask with the funnel T and the delivery tubing G. The results are a little too high by this method so that it is advisable to carry out the standardization with about the same quantity of nitrate as taken for actual analysis.

Modified Procedure. — Through the funnel T pour the concentrated solution of the weighed nitrate and rinse out the funnel with 50 ml. of water. Close the stop-cock a, and boil the liquid in K. Have the 75 cm. long tube g in place, dipping under mercury in the small dish G but do not have the tube C over the end of the tubing. After half the liquid in K has boiled away, remove the flame and allow mercury to suck up into the tube g. Mark the height of the mercury; if it does not fall during 15 minutes, the apparatus is tight. Again heat the liquid in K to boiling and when steam escapes, at the bottom of g, open the stop-cock Q_1 and drive out all air from the tubing k. Boil, with Q_1 open, until the liquid in K is reduced to 10 ml. as shown by the mark etched on the flask. Then close Q_1 and allow the liquid in K to cool a little. Pour 20 ml. of standard ferrous chloride solution into T and cause it to flow into K by carefully opening the stop-cock but taking care not to let any air in. Rinse out T with 80 ml. of 6 N hydrochloric acid and place the cylinder C, filled with mercury, over the end of the tubing g. Heat the contents of K 20 minutes, with the water-bath W in place, and then boil with a free flame until the volume of liquid is reduced to 10 ml. Remove the flame and transfer the gas in C into the Drehschmidt pipet, P, by lowering the leveling bulb N, and opening H_1 and Q_2. Also introduce 0.5 ml. of 33 per cent caustic potash solution through the tip of the stop-cock H_1. This serves to absorb hydrochloric acid gas. After a little while, transfer the gas to a gas buret and measure it over mercury or over water.

It is also permissible to collect the gas over water. In that case have the 75 cm. tube g end in a 6–7 cm. T-tube G_1 open at both ends. Fill the dish n with mercury till level with the upper end of the T-tube and place n in the dish m_1 containing water.

Determination of Nitric Acid in a Drinking-water

Evaporate 100–300 ml. of the water to 40–50 ml. in a porcelain dish, add a few drops of methyl orange indicator solution, and dilute hydro-

* *Doctorate Thesis*, Zürich, 1907.

chloric acid, free from nitrate, until the solution is pink. Now add sodium carbonate solution until the liquid is barely alkaline and wash the contents of the flask into the decomposition-flask *K*, Fig. 95, and analyze as described on p. 394, but collect the gas over 10 per cent sodium hydroxide solution, to make sure that the carbonic acid is completely absorbed.

After the experiment with the water to be analyzed, repeat with an amount of the standard solution sufficient to evolve about the same quantity of nitric oxide.

Remark. — In drinking-water the neutralization of the evaporated sample is not absolutely necessary, except in the case of alkaline mineral waters; in that case the introduction of the hydrochloric acid would otherwise cause such a violent evolution of carbon dioxide that the flask might crack.

CHLORIC ACID, $HClO_3$. Mol. Wt. 84.47

Forms: Silver Chloride, AgCl, besides volumetric and gasometric methods

To determine chloric acid as silver chloride it must previously be reduced to chloride by means of ferrous sulfate or zinc.

Reduction by means of Ferrous Sulfate

Dissolve 0.3 g. of the salt in 100 ml. of water, add 50 ml. of a 10 per cent solution of crystallized ferrous sulfate, heat with constant stirring till the solution begins to boil, and keep at this temperature for 15 minutes. After cooling, add nitric acid until the deposited basic ferric salt is dissolved, precipitate the chloride by means of silver nitrate and weigh after the usual treatment.

One gram of silver chloride corresponds to 0.8550 g. $KClO_3$.

Reduction by Zinc

Although chlorates are reduced in neutral solution by means of zinc or Devarda's alloy, it is not advisable to effect the reduction in this way for quantitative purposes. The same end is reached more expeditiously by adding zinc-dust to an acetic acid solution. Treat the dilute chlorate solution with acetic acid until it reacts distinctly acid, add an excess of powdered zinc, and boil the solution for 1 hour. After cooling, add nitric acid in sufficient quantity to dissolve all of the excess of zinc, filter if necessary, and determine the chloride as silver salt (p. 288).

Remark. — Both of the above methods afford exact results, but the former is to be preferred, for it requires less time.

Chlorates are not decomposed quantitatively into chlorides by ignition in open vessels or in a current of carbon dioxide. Some chlorine and a little alkali is always lost, so that even when the residue is evaporated with hydrochloric acid, too low results are obtained.

According to the two following methods, the decomposition of alkali chlorate into chloride is quantitative.

(*a*) *By Evaporation with Hydrochloric Acid*

Cover 0.3 g. of chlorate in a weighed porcelain crucible with 1.5 *N* hydrochloric acid. Place a watch-glass upon the crucible, and heat the contents on the water-bath until the evolution of chlorine ceases. Rinse off the lower surface of the watch-glass, and evaporate the contents of the crucible to dryness on the water-bath. Replace the cover and gently ignite over a free flame until the decrepitation ceases. After cooling in a desiccator, again weigh the crucible.

(*b*) *By Ignition with Ammonium Chloride*

Mix the alkali chlorate in a porcelain crucible with 3 times as much pure ammonium chloride, cover with a watch-glass, heat over a free flame, keep in constant motion until the ammonium chloride is completely removed, and weigh the residual alkali chloride.

PERCHLORIC ACID, $HClO_4$. Mol. Wt. 100.47

Form: Silver Chloride, AgCl

Perchlorates cannot be reduced to chloride by means of ferrous sulfate, zinc, or by repeated evaporation with concentrated hydrochloric acid.* On ignition, some chlorine and alkali chloride and probably a little perchloric acid are lost, so that an error amounting to as much as 1 per cent may be expected. On the other hand, Winteler has shown that perchlorates may be changed to chlorides by heating with concentrated nitric acid and silver nitrate in a closed tube (see Carius' method for determining chlorine in organic substances, p. 292), and L. Blangey found that ignition with ammonium chloride would accomplish the same result. With 0.3 g. of perchlorate and 2 g. of ammonium chloride, 90 minutes should be sufficient for complete reduction.

* On evaporating with hydrochloric acid there is a loss without any evolution of chlorine; it is due to the volatilization of small amounts of perchloric acid.

Decomposition of Perchlorates by Ignition with Ammonium Chloride

By twice igniting an intimate mixture of 0.5 g. potassium perchlorate with 1.5–2 g. of ammonium chloride in a *platinum* crucible covered with a watch-glass, the former is completely changed to chloride. Care should be taken not to melt the residual chloride, for in that case the platinum is attacked, although the accuracy of the results is not affected. The reduction cannot be accomplished completely in a porcelain crucible unless platinium is present as catalyzer. If 0.5 g. of alkali perchlorate is mixed with 1 g. of ammonium chloride and 1 ml. of chloroplatinic acid solution (0.0918 g. Pt) is added, a complete reduction can be accomplished by igniting and repeating with 2 more additions of ammonium chloride.

Determination of Perchloric Acid in the Presence of Chloric Acid

In one portion reduce the chlorate, as described on p. 398, with ferrous sulfate, and determine the chloride formed as silver chloride. Ignite a second portion in an old platinum crucible (or in one of porcelain with the addition of 1 ml. of chloroplatinic acid) and 3 times as much ammonium chloride (as described above). In this way the total amount of chlorine is obtained and from these data the amount of each acid can be calculated.

Determination of Perchloric, Chloric, and Hydrochloric Acids in the Presence of One Another

The three acids are assumed to be present in the form of their alkali salts.

In one portion determine the chloride-chlorine by precipitation with silver nitrate. In a second sample determine the chlorate and chloride-chlorine after the former has been reduced to chloride by means of ferrous sulfate. Determine the total amount of chlorine present in a third portion after ignition with ammonium chloride.

GROUP VI

SULFURIC, HYDROFLUORIC, AND FLUOSILICIC ACIDS

SULFURIC ACID, H_2SO_4. Mol. Wt. 98.08.

Form: Barium Sulfate, $BaSO_4$

Theoretically the gravimetric determination of sulfuric acid is extremely simple, it being only necessary to precipitate with barium chloride, filter and weigh the barium sulfate. Practically, however, it is a process connected with many difficulties.

According to the manner of precipitating barium sulfate, the composition of the precipitate varies in such a way that sometimes the results are too high and sometimes too low.

Errors which may Occur in the Precipitation of Barium Sulfate

I. In the Precipitation of Barium Chloride with Pure Sulfuric Acid

If a dilute, slightly acid solution of barium chloride is treated at the boiling temperature with an excess of dilute sulfuric acid, the precipitate contains all of the barium except a very small, negligible amount. If, however, the precipitate is weighed, the result is invariably too low; and this is true even when the solution is evaporated to dryness in order to recover the last traces of barium. The precipitate always contains barium chloride in a form which cannot be removed by washing. A mixture, therefore, of barium sulfate and barium chloride is weighed, and as the molecular weight of the latter is less than that of the former, the result must be too low. To obtain accurate results, the chlorine combined with barium in the precipitate must be replaced by SO_4; and this can be accomplished by moistening the precipitate with concentrated sulfuric acid, and heating until the excess of the latter is removed by volatilization.

Not only is barium *chloride* carried down with barium sulfate, but all barium salts as well, especially the chlorate and nitrate. These are, however, readily changed to sulfate by the above treatment with concentrated sulfuric acid. It is immaterial in the estimation of barium how the precipitation is effected; whether the sulfuric acid is added quickly, or drop by drop, the results are always the same.

II. In the Precipitation of Pure Sulfuric Acid with Barium Chloride

This is the reverse process, but in this case it is not a matter of indifference whether the barium chloride is added slowly, drop by drop, or rapidly all at one time. In the first instance, the results are very near the truth without applying any correction; in the latter instance, too high results are obtained, because by the rapid addition of the reagent more barium chloride is carried down with the precipitate than when the reagent is added very slowly.

To obtain the true weight of barium sulfate, it is often necessary to make a deduction for the amount of barium chloride contained in the precipitate and to add the weight of barium sulfate remaining in solution.

The chlorine contained in the precipitate can be determined in several different ways.

1. Fuse the precipitate with 4 times as much pure sodium carbonate, extract the melt with hot water, filter, make the filtrate acid with nitric acid, and precipitate the chlorine with silver nitrate. Filter and weigh. (Cf. p. 288.)

2. Still more accurate is the process of Hulett and Duschak.* Place the ignited precipitate of barium sulfate in a U-tube of which one arm is drawn out into a thin, right-angled, gas delivery tube. Add concentrated sulfuric acid to the precipitate and heat the mixture by placing the U-tube in hot water. The barium sulfate dissolves readily in the hot concentrated sulfuric acid and the barium chloride present is decomposed. To determine the amount of hydrochloric acid set free, pass a slow stream of air, which has been washed with caustic potash solution, through the tube, with the drawn-out end of the latter dipping into a stout test-tube containing 0.01 *N* silver nitrate solution. After 2–2.5 hours all of the hydrochloric acid will have been expelled from the sulfuric acid.

Remove the decomposition apparatus, rinse out the gas delivery tube with a little water, and determine the silver remaining in solution volumetrically (cf. Volhard Method).

For the determination of the dissolved barium sulfate, evaporate the filtrate from the first precipitation to dryness, moisten the residue with a few drops of concentrated hydrochloric acid, take up with water, filter off the slight precipitate of barium sulfate and weigh. During all such work take care to prevent sulfuric acid contamination from the air in the laboratory. The evaporation should, therefore, take place on the steam bath or steam table.

Calculation of the true weight of Barium Sulfate. — If the weight of the first precipitate of crude barium sulfate is a, the weight of the barium chloride contained in this precipitate, as determined by titration of the amount of chlorine, is b, and the amount of barium sulfate in solution is c, then $a - b + c$ represents the weight of pure barium sulfate.

Experience has shown, however, that when pure sulfuric acid is precipitated by means of dilute barium chloride solution added drop by drop, the errors b and c are approximately equal and counterbalance one another so that the weight a is very close to that of the pure barium sulfate.

III. In the Precipitation of Sulfates with Barium Chloride

Here the relations are far more complicated than in the precipitation of pure sulfuric acid, partly because the barium sulfate is more

* *Z. anorg. Chem.*, **40**, 196 (1904).

soluble in salt solutions than in water containing a little acid, and partly because of the tendency of barium sulfate to occlude not only barium chloride but many other salts as well. Solutions of chromium sulfate are either violet or green. From the boiling-hot green solution only one-third of the sulfuric acid is precipitated, the remainder probably being present in the form of a complex chromium sulfate cation;* on cooling the green solution gradually becomes violet and after some time all of the sulfuric acid is precipitated. The precipitation of barium sulfate in the presence of ferric iron has been much studied. In the boiling hot solution, all of the sulfuric acid is not precipitated and considerable iron is thrown down with the barium sulfate and furthermore the precipitate then loses SO_3 on ignition. Since ferric oxide weighs less than an equivalent weight of barium sulfate sometimes the results are as much as 10 per cent too low. On the other hand, Küster and Thiel,† were able to get satisfactory results (1) by precipitating the sulfuric acid from such a solution in the cold, (2) by slowly adding the ferric chloride and sulfuric acid solution to the hot solution of barium chloride, or (3) by precipitating the iron by an excess of ammonia, heating, and adding barium chloride to the solution without filtering off the ferric hydroxide, and finally dissolving the latter in dilute hydrochloric acid.

Most chemists, however, deem it advisable to remove tervalent metals before attempting to determine the sulfuric acid. This is accomplished in the case of ferric iron by adding a liberal excess of ammonia to the dilute, slightly-acid solution which is at a temperature of about 70°. If from 5–7 ml. of concentrated ammonia (*d.* 0.90) is added in excess of the amount required for neutralization,‡ the precipitate is not likely to contain any basic ferric sulfate. If, on the other hand, the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulfate.

The bivalent metals are occluded to a much less extent, so that it is not, as a rule, necessary to remove them. On the other hand, in the presence of considerable amounts of bivalent metal with relatively small amounts of sulfuric acid, the error arising from occlusion is likely to be large, so that it is better to remove the bivalent metals in such cases. The error caused by ferric salts can be largely overcome by reducing the iron with zinc.

In the presence of nitric or chloric acid the barium sulfate precipitate will contain considerable quantities of barium chlorate and nitrate

* Recoura, *Compt. rend.*, **113**, 857; **114**, 477.

† *Z. anorg. Chem.*, **22**, 424.

‡ Pattinson, *J. Soc. Chem. Ind.*, **24**, 7.

which it is impossible to remove by washing with hot water. These acids, therefore, must be decomposed by evaporation with hydrochloric acid before attempting to precipitate the sulfuric acid.

In ordinary chemical practice it is usually a question of determining sulfuric acid in a solution containing considerable amounts of ammonium or alkali chloride, ammonium or alkali sulfate, and some free hydrochloric acid. Now ammonium and alkali sulfates are also occluded by barium sulfate, and the amount of occlusion increases as the solution is more concentrated with respect to these substances. For this reason it is evident that barium sulfate should always be precipitated in a very dilute solution. Furthermore, a small amount of free hydrochloric acid is indispensable, but larger amounts have a solvent effect upon the precipitate. One might think that adsorbed ammonium chloride would do no harm but it has been found to cause some volatilization of sulfate during ignition.

For an amount of sulfuric acid corresponding to between 1 and 2 g. of barium sulfate, the precipitation should take place in a volume of between 350 and 400 ml. and in the presence of 1 ml. of 12 *N* hydrochloric acid.

If a *neutral* solution is at hand, dilute to a volume of 350 ml. and add 1 ml. of concentrated hydrochloric acid. Carefully neutralize an *alkaline* solution with hydrochloric acid, using methyl orange as indicator, add 1 ml. of concentrated hydrochloric acid in excess, and dilute the solution to 350 ml.

Finally, in the case of an *acid* solution, either evaporate to dryness, moisten the residue with 1 ml. of concentrated hydrochloric acid and add 350 ml. of water, or, with methyl orange as indicator, neutralize the solution with ammonia, add 1 ml. of concentrated hydrochloric acid, and dilute to 350 ml.

After the solution has been prepared in accordance with the above directions it is ready for the

Precipitation of Sulfuric Acid in the Presence of Ammonium or Alkali Salts according to E. Hintz and H. Weber

Heat the solution to boiling, and use for each 0.12 g. of sulfur 100 ml. of 0.1 *N* barium chloride solution. Heat to boiling, and add the hot reagent all at once, stirring the hot solution of the sulfate. After the solution has stood for half an hour, best in a warm place, filter, wash with hot water and ignite (cf. p. 84). The use of a Gooch or Munroe crucible is to be recommended.

Remarks. — In the presence of ammonium salts the precipitation of the barium sulfate should not be effected by the slow addition of the barium chloride, as is

otherwise desirable, for, as Hintz and Weber have shown, this leads to low results, whereas the occlusion caused by the rapid addition of the barium chloride counterbalances this error.

Under no circumstances should a precipitate of barium sulfate be heated over a blast lamp, for in that case sulfuric anhydride is evolved from the barium sulfate.

To explain the occlusion of barium chloride by barium sulfate, Hulett and Duschak* have suggested that perhaps the precipitate may contain salts such as $BaCl.HSO_4$, $(BaCl)_2SO_4$, and $Ba(HSO_4)_2$ and Folin† believes that such is this case because some of his precipitates have lost SO_3 on ignition while others have lost HCl. He also suggests the possibility of salts such as $Ba(KSO_4)_2$ being precipitated.

Determination of Sulfuric Acid in Insoluble Sulfates

Calcium and strontium sulfates can be decomposed by long digestion with ammonium carbonate solution. Barium sulfate is decomposed so slowly by boiling with a soluble carbonate that it is best to mix with 4 times as much sodium carbonate, fuse in a platinum crucible, extract the melt with water, and wash the barium carbonate residue with sodium carbonate solution. Make the filtrate acid with hydrochloric acid, boil off the carbon dioxide and precipitate the sulfuric acid as usual.

Lead sulfate can be decomposed by boiling with sodium carbonate solution; after cooling, saturate the solution with carbon dioxide and filter. The lead remains behind as carbonate, while the filtrate contains all of the sulfuric acid.

For the determination of sulfuric acid in silicates, fuse the finely powdered substance with 6 times as much sodium carbonate, extract the melt with water, make the filtrate acid with hydrochloric acid and evaporate to dryness to dehydrate the silica. Moisten the residue with a little concentrated hydrochloric acid, take up in hot water, and filter off the silicic acid. Determine the sulfuric acid in this filtrate.

Determination of Sulfuric Acid in the Presence of Soluble Sulfides

Place the substance in a flask, replace the air by carbon dioxide, add dilute hydrochloric acid, and boil the solution while passing carbon dioxide through it until all of the sulfide has been expelled. Then precipitate the sulfuric acid from the solution.

This determination is used in the analysis of cements but the hydrochloric acid solution of the cement will contain much calcium as well as iron and aluminium. It is best to precipitate these metals by the

* *Z. anorg. Chem.*, **40**, 196 (1904).

† *J. Biol. Chem.*, **1**, 131 (1905).

addition of ammonia and ammonium carbonate and determine the sulfuric acid in the filtrate.

If it is desired to determine the amount of sulfide-sulfur, cover the substance with concentrated hydrochloric acid that is saturated with liquid bromine, dilute and add hydrochloric acid, boil the solution to expel the excess of the bromine. Precipitate the iron, aluminium, and calcium by ammonia and ammonium carbonate, and determine the total sulfur in the filtrate. The difference between the two results represents the amount of sulfur present as sulfide. For the volumetric determination of sulfuric acid consult Part II.

HYDROFLUORIC ACID, HF. Mol. Wt. 20.01

Forms: Calcium Fluoride, CaF_2; Silicon Fluoride, SiF_4, besides volumetric and gasometric methods

1. Determination as Calcium Fluoride

If the solution contains free hydrofluoric acid or an acid fluoride, add sodium carbonate until the reaction is alkaline and from one-fourth to one-fifth as much more in excess. By the excess of sodium carbonate the subsequent precipitate of calcium fluoride will contain calcium carbonate, and the presence of the latter renders the precipitate easy to filter. A pure precipitate of calcium fluoride is slimy and the pores of the filter become so clogged that it is almost impossible to complete the filtration. To solutions of neutral fluorides, add about 1 ml. of 2 *N* sodium carbonate solution. Heat the alkaline solution to boiling, add an excess of calcium chloride solution, filter, and thoroughly wash the precipitate of calcium fluoride and carbonate with hot water. Dry the precipitate, transfer as much of it as possible to a platinum crucible, add the ash of the filter, and ignite the contents of the crucible. The ignition makes the CaF_2 denser and hence easier to filter. After cooling, cover the mass with an excess of dilute acetic acid; this changes the lime to the soluble acetate, but does not affect the fluoride. Evaporate the mixture to dryness on the water-bath, moisten the residue with water and a few drops of 6 *N* acetic acid. Filter off the insoluble calcium fluoride, wash and dry. Transfer as much of the dried CaF_2 to the crucible as possible, burn the filter-paper, add its ash and after ignition weigh the crucible. To confirm the result treat the substance with a little concentrated sulfuric acid (added cautiously), evaporate off the excess of the latter, once more ignite and weigh the contents of the crucible as calcium sulfate. Calcium fluoride is not volatilized in an open platinum crucible heated

over a Bunsen burner. Heated over the blast-lamp, there is appreciable volatilization.

One g. CaF_2 yields 1.7436 g. $CaSO_4$.

Remark. — The results are usually a little low on account of the solubility of calcium fluoride; 100 ml. of water dissolve 0.0016 g. and 100 ml. of 1.5 *N* acetic acid dissolves 0.011 g. CaF_2 at the temperature of the water-bath.

Example: Determination of Fluorine in Calcium Fluoride. — Calcium fluoride alone is not decomposed completely by fusing with sodium carbonate; but if mixed with 2½ times as much silicic acid and then fused with 6 times as much sodium-potassium carbonate, the greater part of the silicic acid and all of the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate. The mixture must be heated gradually (best in a platinum dish), as otherwise the evolution of carbon dioxide may cause the melt to boil over. The thin liquid fusion soon changes to a thick paste or only sinters somewhat. On raising the temperature, it is almost impossible to further melt this mass, and it is not necessary. In fact too high a temperature is to be avoided on account of the danger of losing some alkali fluoride by volatilization. The reaction is complete when there is no further evolution of carbon dioxide. After cooling, treat the melt with water, filter off the insoluble residue and thoroughly wash with hot water. Remove silicic acid by adding 4 g. of ammonium carbonate,* heat for some time at about 40°, allow to stand overnight, and in the morning filter off the voluminous precipitate. Wash it with 2 per cent ammonium carbonate solution (pure water will give a turbid filtrate). The filtrate now contains only a small amount of silicic acid. Evaporate almost to dryness on the water-bath,† dilute with a little water and add a few drops of phenolphthalein indicator solution. The liquid is colored pink by the indicator; add enough nitric acid to make it colorless. Heat the solution to boiling, which causes the reappearance of the pink color. After cooling again discharge the color with nitric acid, and repeat this operation until finally the addition of 1–1½ ml. of 2 *N* nitric acid is sufficient to effect the decolorization.

The solution still contains a little silicic acid which can be removed, as recommended by Berzelius, by precipitating with 2 ml. of ammoniacal zinc oxide. To prepare this, add sodium carbonate to a neutral zinc solution, heat to boiling, filter and wash with hot water. Dissolve the precipitate in the Schaffgottsche ammonium carbonate reagent (p. 79). After the addition of the ammoniacal zinc solution, heat to boiling till the ammonia is wholly expelled, filter and wash the precipitate with hot water.

The above-prescribed use of nitric acid instead of hydrochloric acid is necessary because some phosphate is likely to be present which must be removed. To the still alkaline solution, add silver nitrate in slight excess. This serves to precipitate the phosphate (chromate), chloride and carbonate of silver. Heat slightly, filter and wash with hot water. Remove the excess silver by adding a little sodium

* Before adding the ammonium carbonate, the greater part of the alkali carbonate should be neutralized with dilute hydrochloric acid, but care should be taken not to make the solution acid.

† The liquid foams during the evaporation owing to the decomposition of the excess of ammonium carbonate; the evaporating-dish should be covered with a watch-glass until the evolution of carbon dioxide ceases.

chloride solution. Boil to coagulate, filter and wash the precipitate with hot water. Add 1 ml. of 2 *N* sodium carbonate solution and precipitate with calcium chloride as described on p. 406.

Determination as Silicon Fluoride

This method, proposed by Fresenius, depends upon the fact that many fluorides are decomposed by the action of concentrated sulfuric acid and silica; the fluorine escapes as silicon fluoride, which can be absorbed and weighed.

Procedure. — The same reagents and a very similar apparatus to that described on p. 409 are required for this determination, except that in place of the Péligot tubes (Fig. 97, p. 410) two weighed, glass-stoppered, U-tubes are used, of which the first is filled with moistened pieces of pumice, and the second has one arm filled with soda-lime and the other with calcium chloride. The analysis is carried out in exactly the same way as is described for the Penfield method (see below) but at the end of the experiment the two U-tubes are weighed. The increase in weight represents the amount of SiF_4, and from this the amount of fluorine present is calculated as follows: Assume that a g. of calcium fluoride yielded p g. of SiF_4. The treatment with the concentrated sulfuric acid caused the following reaction to take place:

$$2\,CaF_2 + 2\,H_2SO_4 + SiO_2 = 2\,CaSO_4 + 2\,H_2O + SiF_4,$$

consequently, $\frac{4\,F \cdot p \cdot 100}{SiF_4 \cdot a} = \frac{73.01\,p}{a}$ = per cent fluorine is present.

Remark. — This method is suitable for the determination of fluorine in all fluorides that are decomposed by sulfuric acid. The analysis can be carried out in the presence of phosphates, but if carbonates are present they should be decomposed by ignition before the treatment with sulfuric acid. According to K. Daniel,* exact results are obtained only when the decomposition of the fluoride takes place at the temperature at which sulfuric acid boils. The method is not suitable for the determination of fluorine in topaz and micas.

Determination of Fluorine as Fluosilicic Acid, according to S. L. Penfield†

Modified by Treadwell and Koch‡

Principle. — In this method the fluorine is expelled as silicon fluoride exactly as in the above method of Fresenius, but the gas is absorbed in 50 per cent alcoholic potassium chloride solution. By contact with water the silicon fluoride is decomposed into fluosilicic and silicic acids. The former unites with the potassium chloride, forming potassium fluosilicate, insoluble in 50 per cent alcohol:

$$3\,SiF_4 + 3\,H_2O \rightarrow 2\,H_2SiF_6 + H_2SiO_3, \qquad H_2SiF_6 + 2\,KCl = K_2SiF_6 + 2\,HCl,$$

* *Z. anorg. Chem.*, **38**, 257 (1904).

† *Chem. News*, **39**, 179; also *Am. Chem. Jour.*, **1**, **27.**

‡ *Z. anal. Chem.*, **43**, 469 (1904).

and sets free an equivalent amount of hydrochloric acid which can be titrated with 0.2 *N* sodium hydroxide solution, using cochineal as an indicator. From the above equations, it is evident that

$$1000 \text{ ml. } 0.2\ N \text{ HCl} = \tfrac{1}{10} \text{ mol. } CaF_2 = \tfrac{2}{5} \text{ F.}$$

$$\therefore 1 \text{ ml. } 0.2\ N \text{ NaOH} = 0.0234 \text{ g. } CaF_2 \text{ or } 0.0114 \text{ g. F.}$$

Requirements. — 1. *Pure Quartz Powder.* Place pieces of pure rock crystal in a platinum crucible, heat strongly over the blast-lamp, and then drop into cold water. After this treatment it is very easy to reduce the quartz to a fine powder by grinding in an agate mortar. Ignite the powder, and while still warm transfer to a flask, fitted with ground-glass stopper. Allow the open flask and its contents to cool in a desiccator, stopper and set aside.

2. *Sea Sand.* Treat clean sea sand with boiling, concentrated sulfuric acid, wash, dry, ignite and cool in a desiccator.

3. *Anhydrous Sulfuric Acid.* Heat pure, concentrated sulfuric acid in a porcelain crucible until it is reduced one-third in volume and allow to cool in an empty desiccator over phosphorus pentoxide.

Procedure. — Mix 0.1 g. of the dry fluoride in an agate mortar, which is placed upon black glazed paper, with 2 g. of the quartz powder and transfer through the cylindrical arm *A* of the perfectly dry decomposition apparatus to the pear-shaped compartment *B* shown in Fig. 97. Then add 1.5–2 g. of the sea sand, and mix with the rest of the material by shaking the apparatus. Then make connection with the dry U-tube, *D*, containing glass beads.* Place 15 ml. of alcohol saturated with potassium chloride in each of the two Péligot tubes *P* and P_1. When the apparatus is all connected as shown in the drawing, allow a dry current of air,† free from carbon dioxide, to enter at *h*, and pass through the apparatus at the rate of 2 or 3 bubbles per second. Then without stopping the air current, introduce about 20 ml. of anhydrous sulfuric acid into the decomposition apparatus through the funnel *T*. By introducing the sulfuric acid in this way, while maintaining the air current, the sulfuric acid and the greater part of the silica and fluoride mixture is made to pass directly into the compartment *B*. After adding the sulfuric acid, place the decomposition vessel in a paraffin bath which is slowly heated to a temperature of 130° to 140°. The evolution of silicon tetrafluoride at once begins to take place, as is evident from the formation of foam. Continue passing air and heating the bath for 5 hours; then turn down the flame under the bath and pass air through the apparatus for half an

* This tube serves to keep back any sulfuric acid that is carried over mechanically.

† Wash the air by passing it through caustic potash solution, and dry it by passing through granular calcium chloride and concentrated sulfuric acid.

hour longer at the rate of 3–4 bubbles per second. During the heating the apparatus should be frequently shaken in order to bring the sulfuric acid into contact with all portions of the solid mixture. It is not necessary, however, with this arrangement of the apparatus, to shake as frequently as in the forms of apparatus described by Penfield and by Fresenius, because the air in its passage through the narrow connecting tube between *A* and *B* of the decomposition apparatus serves of itself to effect a good mixing. To accomplish this end, however, it is necessary to construct the apparatus exactly as shown in Fig. 97; the connecting tube between *A* and *B* must be so narrow that it is completely filled with the bubbles of air passing, and furthermore the parts marked *c e b* must form an inclined plane upon

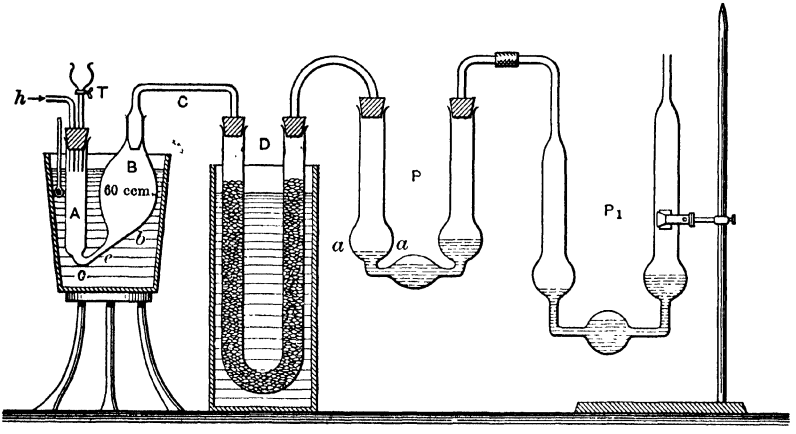


FIG. 97.

which the substance can readily pass back and forth. If there is a hollow in the apparatus at *c e b*, in which some of the substance can collect, the sulfuric acid may not come in contact with some of the fluoride so that the decomposition will be incomplete. Similarly it is necessary to guard against making the connecting tube *c e* too narrow, as otherwise the air will not pass in a uniform stream, but in spurts, so that in spite of the long tube *D* some of the sulfuric acid fumes are likely to reach the Péligot tubes and thereby give rise to high results.

If not more than 0.1 g. of the fluoride is present, the action is over at the end of 5½ hours, and this is evident, as Daniel* was the first to discover, from the fact that the foaming in the apparatus ceases; the hydrochloric acid which has been set free in the Péligot tubes can now be

* *Z. anorg. Chem.*, **38**, 257 (1904).

titrated. To this end add a few drops of fresh cochineal* solution to each tube and titrate the contents with 0.2 *N* potassium hydroxide solution with frequent shaking, until the indicator changes from yellow to red. This is, however, by no means the correct end-point, because as Penfield observed, the gelatinous silicic acid encloses very appreciable amounts of hydrochloric acid. The silicic acid, therefore, must be thoroughly worked over with a stirring rod and the addition of the alkali continued until the color change is permanent.

Remark. — This method is capable of giving excellent results but it is important that the apparatus and all the reagents added to the decomposition vessel should be perfectly dry. Phosphates do not interfere but carbonates must be removed by a preliminary ignition. In case the mineral contains "combined water" there is danger of losing hydrofluoric acid by this ignition but such loss can be prevented by adding an oxide such as lime or litharge.

The procedure can be modified to apply to the determination of fluoride in the presence of sulfides such as sphalerite.† In this case introduce 2 g. of the substance (dried at 110°), 3 g. of anhydrous copper sulfate and 10 g. of anhydrous chromic acid anhydride (CrO_3) into the decomposition vessel. After introducing the sulfuric acid, as described above, gradually raise the temperature to 130–140° during 2 hours while passing a current of dry and CO_2-free air through the apparatus and then heat 3 hours at this temperature.

In former editions of this book, it was proposed to dry the sulfuric acid over phosphorus pentoxide but such acid evolves a little sulfuric anhydride in the analysis and the results are usually about 0.4 per cent too high.

Determination of Fluorine in Mineral Waters

Evaporate 1–10 liters of the water (according to the amount of salts present) to a small volume, in a large dish, adding enough sodium carbonate to keep the solution slightly alkaline. Add an excess of calcium chloride, boil, filter off the precipitate and wash it with hot water until free from chlorides. Dry the precipitate, transfer it as completely as possible to a platinum dish, add the ash of the filter to the main precipitate and gently ignite. This residue contains all of the fluorine as calcium fluoride; besides considerable calcium (possibly strontium) and magnesium carbonates, iron, aluminium and manganese oxides, often barium sulfate, and almost invariably some calcium phosphate. Moisten it with an excess of dilute acetic acid, allow to stand for some time with frequent stirring, and then evaporate to dryness on the water-bath. Treat this residue with water, filter, and wash with hot water. Transfer as much of it as possible to a platinum

* Instead of cochineal, methyl orange may be used, although it is necessary then to add an equal volume of alcohol before titrating the hydrochloric acid.

† L. da Rocha-Schmidt and K. Krüger. *Z. anal. Chem.* 63, 29 (1923).

crucible, add the ash of the filter, and gently ignite the contents of the crucible. Mix 0.5–1 g. of ignited quartz powder with the residue in an agate mortar. Transfer the mixture to the decomposition vessel *A*, Fig. 97, and treat with concentrated sulfuric acid exactly as described on p. 409 by the method of Penfield. As only very little fluorine is present in this case, two small U-tubes can be used instead of the large Péligot tubes shown in Fig. 97.

Remark. — The formation of a precipitate in the first U-tube at the place marked *a a* in Fig. 97 indicates the presence of fluorine. It is well to confirm it by the etching-test. After carrying out the titration of the hydrochloric acid set free, transfer the contents of the U-tube to a platinum dish, add a few drops of 2 *N* sodium carbonate, and evaporate the solution to dryness. Add ammoniacal zinc oxide (cf. p. 407), and again remove the liquid by evaporation. Take up the residue in water, and filter off the zinc oxide and silicate. Treat the filtrate with calcium chloride as described on p. 406 and apply the etching test.

Gas-Volumetric Determination of Fluorine according to Hempel and Oettel

See Part III, Gas Analysis.

Separation of Fluorine

(*a*) From the Metals

For the determination of the metals present, the fluorine usually can be removed by heating with concentrated sulfuric acid. However, in the case of many silicates containing fluorine, *e.g.*, topaz, lepidolite, and other micas, this treatment will not accomplish the desired result. In such cases fuse the mineral with 4–6 times as much sodium-potassium carbonate, and remove the silica and aluminium as described on p. 407, by treatment with ammonium carbonate and ammoniacal zinc solution. Use the precipitates for the determination of aluminium and silica and the filtrate for the determination of the fluorine. The alkalies must be determined in a separate portion of the original substance (pp. 425, 426).

(*b*) Separation of Fluorine from the Acids

1. *Determination of Hydrochloric and Hydrofluoric Acids in the Presence of One Another*

In the case of soluble alkali salts, precipitate the fluorine from the solution by means of a little sodium carbonate and an excess of calcium nitrate solution, as described on p. 406. Make the filtrate acid with

nitric acid and determine the chlorine by precipitation with silver nitrate, according to p. 288.

It is simpler to treat the solution containing hydrochloric and hydrofluoric acids in a platinum evaporating dish with nitric acid and silver nitrate. Silver chloride is alone precipitated and can be filtered off, using a funnel of hard rubber, or a glass one coated over with wax. Wash the precipitate and weigh as described on p. 288. When phosphoric acid also is present, precipitate it with the chloride by the addition of silver nitrate to the slightly alkaline solution. Filter off the precipitate, wash with as little cold water as possible, and treat the precipitate with dilute nitric acid. By this means the silver phosphate goes into solution, while the silver chloride is unaffected. To determine the amount of phosphoric acid present, remove the silver from the solution by the addition of hydrochloric acid, and precipitate phosphoric acid in the filtrate by addition of magnesia mixture and ammonia (cf. p. 379).

In the filtrate from the silver phosphate and silver chloride precipitate, remove the excess of silver nitrate by the addition of sodium chloride and determine the fluorine as calcium fluoride.

In the case of an insoluble compound containing chlorine and fluorine, extract the melt obtained after fusing with sodium-potassium carbonate with water, remove the silica with ammonium carbonate and ammoniacal zinc solution as described on p. 407, and determine the chlorine and fluorine as above.

In most cases it is more convenient to determine the two acids in separate portions of the substance.

2. *Determination of Boric and Hydrofluoric Acids*

To the solution containing the alkali salts of these two acids add an excess of calcium chloride at the boiling temperature. Filter off and wash with hot water.

Gently ignite the precipitate, consisting of calcium carbonate, calcium fluoride, and some calcium borate, treat with dilute acetic acid, evaporate to dryness, and add more acetic acid and water. By this means the calcium acetate and calcium borate go into solution, while the calcium fluoride is left behind and can be determined as described on p. 406. For the boric acid determination take a second portion of the solution, make barely acid with acetic acid, and treat with a slight excess of calcium acetate solution to precipitate the fluorine. Place the solution, together with the calcium fluoride precipitate, in the Gooch retort and subject to distillation as described on p. 374.

FLUOSILICIC ACID, H_2SiF_6. Mol. Wt. 144.12

Forms: Calcium Fluoride, CaF_2; Potassium Fluosilicate; or volumetrically

1. Determination as Calcium Fluoride

Principle. — Alkali fluosilicates are decomposed on heating with sodium carbonate solution into fluoride and silicic acid:

$$Na_2SiF_6 + 2\,Na_2CO_3 + H_2O = 6\,NaF + H_2SiO_3 + 2\,CO_2.$$

If a solution to be analyzed contains free fluosilicic acid or its sodium salt, add sodium carbonate solution until the reaction is alkaline and considerable ammonium carbonate. Heat the solution to about 40°, and, after standing 12 hours, filter off the precipitated silicic acid.

The solution now contains all the fluorine as sodium fluoride, in the presence of small amounts of silicic acid, which can be precipitated by the addition of ammoniacal zinc solution (see p. 407). In the filtrate determine the fluorine as calcium fluoride, as described on p. 406.

Fuse an insoluble fluosilicate with 4 times as much sodium-potassium carbonate, extract the melt with water, and subject the solution to the above treatment.

2. Determination as Potassium Fluosilicate

This analysis is only applicable for the determination of free fluosilicic acid in aqueous solution.

Procedure. — Treat the solution with potassium chloride and an equal volume of absolute alcohol. Filter off the barely-visible potassium fluosilicate through a tared filter which has been dried at 100°. After washing with 50 per cent alcohol dry the precipitate at 100° and weigh as K_2SiF_6.

The volumetric determination of fluosilicic acid will be discussed in Part II.

Analysis of Salts of Fluosilicic Acid

For the determination of the metal present, treat the salt with concentrated sulfuric acid in a platinum dish and heat until dense fumes of sulfuric anhydride are given off; silicon fluoride and hydrofluoric acid volatilize, while the metals are left behind as sulfates (cf. Vol. I).

*Determination of Water Present in Fluosilicates (Rose-Jannasch)**

The water cannot be determined by ignition, because all fluosilicates, even topaz, evolve silicon fluoride when subjected to this treatment (cf. Vol. I). If, as proposed by Rose, the substance is fused with 6 to

* Rose-Finkener: *Lehrbuch der analyt. Ch.*, Vol. II and Jannasch, *Praktischer Leitfaden der Gewichtsanalyse.*

8 times as much lead oxide, all the water is evolved, while the fluorine remains behind:

$$R_2SiF_6 + 3\ PbO = 2\ RF + 2\ PbF_2 + PbSiO_3.$$

The analysis is best performed according to the directions of Jannasch: Blow a bulb with a capacity of about 25 ml. near one end of a tube of difficultly-fusible glass which is 26 cm. long and 1 cm. wide. Near the middle of the longer side of the tube, between asbestos plugs, place a layer 3–5 cm. long of pulverized, anhydrous lead oxide, and connect this end of the tube with two weighed calcium chloride tubes. Place the substance in the bulb, add 6–8 times as much lead oxide and mix with the substance by carefully revolving the tube. Conduct a dry current of air through the apparatus and slowly melt the contents of the bulb. All of the water and often some of the fluorine is thereby expelled, and the latter is absorbed by the layer of lead oxide. At the end of the operation cautiously heat this layer with a moving flame until no more water condenses in the cooler part of the tube. When all of the water has been driven over into the calcium chloride tubes, weigh them with the customary precautions.

GROUP VII

SILICIC ACID (ALSO TITANIC, ZIRCONIC, TANTALIC, AND NIOBIC ACIDS)

SILICIC ACID, H_2SiO_3. Mol. Wt. 78.12

Form: Silicon Dioxide, SiO_2.

Two cases must be considered:

(*a*) The silicate is decomposed by acids.
(*b*) The silicate is not decomposed by acids.

(*a*) Silicates Decomposed by Acids

Weigh out 0.5 g. of the powdered silicate into a porcelain dish, add 25 ml. of water and stir till the silicate is thoroughly wet. Add in small portions, while heating the casserole and stirring, 25 ml. of 6 *N* hydrochloric acid. Evaporate upon the water-bath with frequent stirring until the residue is obtained in the form of a dry powder. In many cases the decomposition is shown to be complete by the fact that no gritty particles can be felt with the stirring-rod on the bottom of the dish. If, however, the substance contained quartz or some silicate that is not decomposed by hydrochloric acid, this is not the case and the procedure

described on p. 418 should be followed. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica.

Moisten the dry powder with concentrated hydrochloric acid and allow the covered dish to stand for 10 minutes at the ordinary temperature, in order that basic salts and oxides formed during the evaporation and drying may be once more changed to chlorides. Then warm gently, dilute with 100 ml. of water, heat to boiling, and, after the silicic acid has been allowed to settle, decant the clear liquid through a filter supported upon a platinum cone or a hardened filter placed in the apex of the funnel. Wash the residue 3 or 4 times by decantation, with hot 2 *N* hydrochloric acid, then transfer to the filter and wash with hot water until free from chloride. Dry the precipitate by means of suction, place in a platinum crucible, and set aside for the time being. The separation of the silicic acid is not quite complete; as much as 2 mg. may remain in the filtrate. To remove this, once more evaporate the solution to dryness on the water-bath, and again heat at 120–130°, for an hour, moisten the residue with 5 ml. of concentrated hydrochloric acid, and allow to stand not more than 15 minutes.* Warm, dilute to 100 ml., boil and filter through a new and correspondingly small filter, washing with hot 2 *N* acid and with water as before. Ignite the wet filters containing the silica in a platinum crucible. Keep the temperature low till all the carbon is consumed and do not allow the filter to catch fire. Finally cover the crucible and ignite over the blast lamp or over a Méker burner.

Remark. — It is not necessary to use suction in filtering. If the precipitate is allowed to dry before placing it with the filter in the crucible there is danger of losing some of the fine powder. The heating at 120° decreases the solubility of the silica in acid but this temperature should not be exceeded. Magnesia at a higher temperature recombines with silica and iron and aluminium oxides are formed in a condition hard to dissolve.

Testing the Purity of the Silica

The silica thus obtained is never absolutely pure, except in the analysis of a water-glass. Its purity must always be tested. For this purpose cover it with 2 ml. of water,† add a drop of concentrated sulfuric acid, and about 5 ml. of pure hydrofluoric acid. Place the crucible in an air-bath and evaporate under a good hood until no more vapors are expelled. Then remove the excess of sulfuric acid by heat-

* By being kept in contact with the acid for too long a time some silicic acid will go into solution.

† If the water is not added, the mass will effervesce so strongly that there is danger of losing some of the impure silica.

ing over a free flame. Raise the temperature gradually and finally heat the crucible over a blast-lamp or Méker burner, and again weigh. Repeat the treatment with sulfuric and hydrofluoric acids, without adding any more water, until the contents of the crucible (usually Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, V_2O_5, P_2O_5, etc.) are at a constant weight. Deduct this amount from the weight of impure silica.

A great many silicates are incompletely decomposed, if at all, by treatment with hydrochloric acid in an open vessel. Inasmuch as it is necessary to test the purity of the silica by treatment with sulfuric and hydrofluoric acids, it might seem unnecessary to try to get a pure silicic acid residue before applying this treatment. Undecomposable silicates are likely to contain some alkali and alkaline earth metal as well as iron and manganese in combination with silica. When such a silicate is treated with sulfuric and hydrofluoric acids, the alkali and alkaline earths are left as sulfates, the iron is left as Fe_2O_3 and the manganese as Mn_3O_4. Moreover boron is volatilized as BF_3. Only when the silica is nearly pure and when the impurities are left as oxides in the same state of oxidation as at the start and no other volatile constituent is present, does the loss in weight upon treatment with hydrofluoric and sulfuric acids represent the silicon content. If the silicate is only partly decomposed with acid it should be treated as an insoluble silicate.

(*b*) Silicates not Decomposed by Acids

Silicates not decomposed completely by the action of 6 *N* hydrochloric acid are usually fused with sodium carbonate which converts them partly into sodium silicate and partly into an ortho- or meta-silicate which can be decomposed with acid.

Jannasch* has decomposed refractory silicates by heating the finely-ground powder in a 25 ml. platinum tube with 10 *N* hydrochloric acid. On the end of the tube, a cap is fitted which is not quite air tight. The platinum tube is placed in a larger glass tube which also contains a little hydrochloric acid. This tube is sealed and heated to 300–400° in a steel Mannesmann tube containing a little ether or petroleum ether to equalize the pressure. Owing to the high price of platinum and the fact that it is hard to get a perfect decomposition, this method of decomposition will never be popular although useful when only a little material is available for a complete analysis.

Jannasch and Heidenreich† have also recommended boric acid as a

* *Ber.*, **24**, 273 (1891); *Z. anorg. Chem.*, **6**, 72 (1894).

† *Z. anorg. Chem.*, **12**, 208 (1896). The method was originally proposed by Sir Humphrey Davy in 1805. Jannasch and Weber, *Ber.*, **32**, 1670 (1899).

flux for decomposing silicates. To free the flux from alkali salts, the commercial acid should be recrystallized 2 or 3 times and heated in a large crucible to drive off all moisture, before powdering. This flux will decompose nearly all silicates. The very-finely-powdered mineral is heated over the blast-lamp with 8 times as much or more of the flux. The contents of the crucible are cooled by means of cold water and the melt turned into an evaporating dish. By repeated evaporation with a saturated solution of hydrogen chloride gas in methyl alcohol, the boric acid can be all distilled off as methyl borate and the residue treated like that obtained after an ordinary decomposition with acid. Owing to the difficulty in getting thoroughly satisfactory fusions and trouble in removing the boric acid after the fusion, the method will never be a popular one although it permits the determination of alkalies in the same sample.

Jannasch has also recommended decomposition with lead oxide. The theory is similar to that of the dry assay for silver and gold. There the aim is to form a fusible slag with the silica and reduce the silver and gold to metal. Since the fusible slag is also decomposable with acid, it is clear that lead oxide is suitable when the determination of silica is desired. Moreover, the lead is easily removed so that alkalies can be determined in the same sample. On the other hand, if any free metal is formed, which will be the case if any precious metal is present, or if there is any reducing agent such as a few shreds of filter-paper, or if a reducing flame comes in contact with the contents of the crucible, the crucible will alloy and be spoiled.

(α) *The Sodium Carbonate Method*

Fuse 0.5 g. of the very finely-powdered substance in a platinum crucible with 3 g. of sodium carbonate. The powdered silicate should be intimately mixed with the flux and a little sodium carbonate sprinkled on top. Heat the covered crucible at first over a small flame to drive out any moisture present. Gradually raise the temperature until finally the highest heat of a good Teclu or Méker burner is obtained. As soon as the mass melts quietly and there is no further evolution of carbon dioxide, the decomposition is complete. Wind a piece of platinum wire into a spiral and insert it into the fused mass. Remove the flame and allow the crucible to cool in the air somewhat and then play a stream of water upon the outside of the crucible. As soon as the crucible does not hiss when the water strikes it, quickly introduce enough water into the crucible to cover the melt. After about a minute carefully pull on the wire; in most cases the melt can be withdrawn from the crucible. If it does not come out easily, it can usually be

loosened by carefully heating the crucible. Place the melt in a 300-ml. casserole, add 25 ml. of water, cover the casserole and carefully add 25 ml. of 6 *N* hydrochloric acid. A lively evolution of carbon dioxide at once takes place, but as the silicic acid separates, the inner part of the cake gradually becomes coated with a film of silicic acid which protects it from the further action of the acid. Consequently it is necessary to break up the cake from time to time, by means of a glass rod, until finally there is no further evolution of a gas and no more hard lumps remain. When manganese is present the melt is colored green with manganate and the solution is pink at first with permanganate but the latter gradually decomposes during the subsequent heating. After the evolution of carbon dioxide has nearly ceased, wash off the under side of the watch-glass, raise it by placing a glass triangle under it and evaporate to dehydrate the silica, continuing as described on p. 415.

Remark. — If the fusion cannot be removed from the crucible, place it, together with its cover, in the beaker and treat as above.

Substances containing considerable fluorine cannot be treated as above, for silicon fluoride will be lost by volatilization. In this case it is necessary to use the old method of Berzelius. Extract the melt from the sodium carbonate fusion with water, as in the determination of fluorine (p. 407), and remove the greater part of the silica by means of ammonium carbonate. Filter off the precipitate, ignite, and weigh.

Precipitate the silicic acid remaining in the filtrate by means of ammoniacal zinc solution. Dissolve this precipitate of zinc oxide and zinc silicate in hydrochloric acid and obtain the silica by evaporation on the water-bath as usual. As a rule, the insoluble part of the melt contains silicic acid, and this must also be removed by evaporation with hydrochloric acid. Ignite all three silica precipitates together and test the purity of the silica.

(β) *Lead Oxide Method of Jannasch**

This analysis is interesting because it permits an exact determination of the alkalies and of silicic acid in the same sample. Inasmuch as commercial lead oxide (litharge) is not free from impurities, prepare it for the analysis by the ignition of pure lead carbonate.

Prepare the lead carbonate by adding the theoretical amount of ammonium carbonate to a boiling solution of lead acetate. Wash the precipitate several times by decantation with hot water, transfer to a hardened filter, and wash thoroughly, using suction. Remove the mass from the filter-paper and dry on the water-bath.

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* Gaston Bong, *Z. anal. Chem.*, **18**, 270 (1879), first proposed that silicates be decomposed by fusion with red lead (Pb_3O_4), but Jannasch in his *Praktisches Leitfaden der Gewichtsanalyse* has greatly improved the method.

Procedure. — Use 0.5 g. of silicate with 5–6 g. of lead carbonate. First place the lead carbonate in the crucible, then the finely-powdered substance, and after mixing thoroughly with a platinum spatula heat the covered crucible 15–20 minutes over a flame which is not more than 3–4 cm. high; in this way the greater part of the carbon dioxide is expelled. Then heat the contents of the crucible more strongly until fusion is effected, taking care that the flame used is strictly non-luminous; the lower third of the crucible, and no more, may be heated to redness.

After fusing 10–15 minutes the decomposition is complete. Remove the melt as described on p. 418 and transfer to a 300-ml. casserole. Cover with hot water, carefully add 25 ml. of 6 *N* nitric acid and heat on the water-bath, breaking up the melt with a stirring-rod as much as possible. When the cake is completely disintegrated, as is shown by there remaining no more hard yellow pieces and only slightly colored flocks of silicic acid floating in the liquid, evaporate the latter on the water-bath until a dry powder is obtained; moisten this with 20 ml. of concentrated nitric acid and once more evaporate to complete dryness. Again moisten the dry residue with 20 ml. of concentrated nitric acid, and allow to stand 15 minutes; add 100 ml. of water, and heat the liquid for 20 minutes on the water-bath. Filter off the residue of silicic acid, wash first with hot water containing nitric acid, then with pure water, and weigh after the usual ignition.

Remark. — In the analysis of minerals containing fluorine, *e.g.*, topaz, Jannasch finds that the results obtained are about 0.5–1 per cent lower than when the Berzelius method is used. In such a case this method of decomposition is used only for the determination of the metals and of the alkalies, after introduction of hydrogen sulfide and removal of the lead.

ANALYSIS OF SILICATES

Orthoclase

Constituents: silicic acid (63–70 per cent); aluminium oxide (16–20 per cent); ferric oxide (0.3 per cent); potassium oxide (8–16 per cent); sodium oxide (1–6 per cent); and often small amounts of calcium oxide, magnesium oxide, and in rare cases barium and ferrous oxides.

Preparation of the Substance for Analysis

Break up large pieces of rock on a thick steel plate with a specially hardened surface and a similarly hardened pounder, such as street

pavers use. Place the small fragments in a "diamond" mortar or in one like that shown in Fig. 98. It is made of chilled and case-hardened tool steel. The dimensions of the block *A* are 12.5 × 12.5 × 6 cm. and there is a depression in the center 0.6 cm. deep. The pestle *B* is 20 cm. high and the diameter at the base is 3.5 cm. The cylinder *C* is 12.5 cm. tall and of 5 cm. outside diameter accurately fitting the depression in the block. Unlike the ordinary "diamond" mortar, the pestle has a smaller diameter than the inside diameter of the cylinder, which is 4.4 cm. The crushing is done with the pestle, without the aid of a hammer. With this mortar most of the sample can be reduced fine enough to pass through silk bolting cloth.

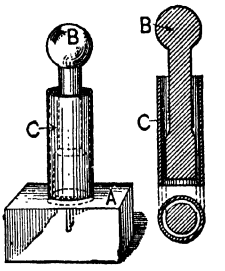


FIG. 98.

A finer powder can be obtained by hand grinding in an agate mortar but the McKenna ore grinder shown in Fig. 99 is more economical in the long run. *A* is a copper cup soldered to the head of the pestle holder and assumes, without friction, the motion of the latter. *B* is a tin plate with deep sinus and is covered by the rubber cloth *C* which fits closely about the metal shaft. These attachments *A*, *B*, and *C* prevent oil and dust from the belts and bearings entering the mortar. The spring at the top of the sliding rod to which the agate mortar is attached at the bottom, can be adjusted to give any desired pressure or can be thrown back to allow the pestle to be raised in removing the agate mortar. The pestle makes about 200 revolutions per minute and the mortar moves slowly in the same direction. The scraper keeps the material in the center and the combined rolling and sliding motion reduces the hardest ore very quickly.

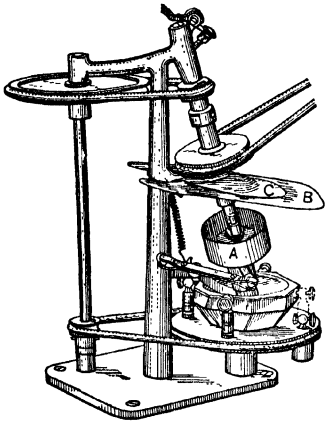


FIG. 99.

Do not attempt to grind too much at one time and frequently sift through silk bolting cloth to prevent as much as possible contaminating the sample by abrasion and loss of moisture by the heat of grinding. Prepare at least 5 times as much sample as is needed and make sure that all the powder is included; it is never admissible to take only the powder that passes through the sieve the first

time. Mix the entire sample by rolling (see p. 53) before taking a part for the analysis.

Weighing the Substance

It was formerly customary to dry the powder before weighing at 100–110° until a constant weight is obtained. If there is danger of losing combined water by this procedure, it has been recommended to dry the powder in a vacuum over concentrated sulfuric acid. The practice of drying the substance in either of the above ways is, however, to be discountenanced. It is far better to use the air-dried substance for the analysis, and to determine the moisture in a separate sample. This is more accurate, because the dry silicate powder is hygroscopic, so that a portion weighed out to-day is likely to contain a different amount of moisture than one taken to-morrow, and this is not the case when the air-dried powder is taken for the analysis. Further, as Hillebrand has conclusively shown, chemically-combined water is not only likely to be expelled by heating at 100°, but also by drying in a vacuum over sulfuric acid. This is particularly true of the zeolites. In the case of orthoclase, however, only about 0.1 per cent of moisture is present, so that in this particular case accurate results will be obtained by either method.

For the analysis weigh out 2 portions of about 0.5 g. each. The first serves for the determination of SiO_2, $Al_2O_3 + Fe_2O_3$, CaO, and MgO; the second for that of the alkalies.

Determination of Silica, Aluminium, etc.

Weigh out 0.5 g. of the air-dried substance in a spacious platinum crucible, dry for 1 hour at 105–7°, cool in a desiccator, and weigh. The difference in weight represents the amount of hygroscopic moisture.

Mix the dry substance with 3 g. of calcined sodium carbonate by means of a platinum spatula, and determine silica as described on p. 418. Treat the silica with sulfuric and hydrofluoric acids, as described on p. 416, and set the crucible with the residue of Al_2O_3, etc., aside for the present.

Determination of Aluminium and Ferric Oxides

The filtrate from the silicic acid contains, besides the chlorides of aluminium, iron, calcium, and magnesium, a little platinum, from the crucible in which the fusion was made.

To remove the platinum, heat the solution to boiling and introduce hydrogen sulfide. Filter off the mixture of platinum sulfide and sulfur, and boil the solution to expel the excess of hydrogen sulfide. Oxidize

the iron back to the ferric state by adding bromine water and boiling until the excess of the latter is expelled. After this add 10 ml. of 2 *N* ammonium chloride solution and precipitate the aluminium, iron, etc., from the boiling-hot solution, by the addition of a slight excess of ammonia, free from carbonate (cf. p. 150). Allow the precipitate to settle, filter, and wash twice by decantation with hot water. Redissolve by running hot 2 *N* hydrochloric acid through the filter into the beaker containing the greater part of the precipitate. Repeat the precipitation with ammonia as before, and after filtering and washing by decantation, transfer the precipitate to the filter and wash until free from chloride with water containing 2 per cent of ammonium nitrate. Allow the precipitate to drain as completely as possible, and ignite wet in the crucible containing the residue obtained from the treatment of the impure silica with sulfuric and hydrofluoric acids. After igniting strongly over a good Teclu or Méker burner weigh the crucible; its contents represent the sum of the aluminium and ferric oxides (also TiO_2, ZrO_2, P_2O_5, V_2O_5, Ta_2O_5 and Cb_2O_5 if present).

For the determination of the ferric oxide, fuse the mixed oxides with potassium pyrosulfate as described on p. 115. The decomposition is complete after 2–4 hours. Dissolve the melt in water containing a little sulfuric acid and determine the iron, after previous reduction with hydrogen sulfide (cf. p. 99), by titration with potassium permanganate (cf. p. 100). If the weight of the Fe_2O_3 is deducted from the weight of $Fe_2O_3 + Al_2O_3$, the weight of Al_2O_3 is obtained.*

Determination of Calcium

Evaporate the combined filtrates from the ammonia precipitate to a small volume, heat to boiling, and precipitate the calcium by means of a boiling solution of ammonium oxalate as described on p. 86. If the quantity of precipitate is small, ignite and weigh as CaO. If considerable calcium is present (cf. p. 87) redissolve the moist precipitate in hydrochloric acid, and repeat the precipitation by ammonia and a little more ammonium oxalate. Ignite strongly, and weigh as CaO. (Cf. p. 81.)

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* The amount of iron and aluminium can be determined more quickly, though less accurately, as follows: Dissolve the moist ammonia precipitate in hot, dilute sulfuric acid and dilute to a volume of exactly 250 ml. After thoroughly mixing, remove 100 ml. by means of a pipet into a beaker and place a second portion of the same volume in a 200-ml. flask. In the first portion determine the sum of $Fe_2O_3 + Al_2O_3$ by precipitating with ammonia, filtering, igniting, and weighing; in the other portion reduce the iron by hydrogen sulfide and titrate with permanganate.

Testing of the Calcium Oxide Precipitate for Barium

Although it is usually unnecessary to make either a qualitative or quantitative test for barium in a sample of orthoclase, yet it is likely to be present in traces so that it may be well to show how this can be done. As far as the author knows strontium has never been found in orthoclase. On account of the solubility of barium oxalate in a solution of ammonium oxalate, the barium will rarely be found in the calcium precipitate when a double precipitation is made, except when it is present to an extent of more than 3 or 4 mg.*

To test a calcium precipitate for barium, dissolve it in nitric acid, evaporate to dryness, and heat for some time at 140°. Dissolve the calcium nitrate by ether-alcohol (p. 89, *a*), and examine any residue remaining behind in the spectroscope for barium. If barium is found, dissolve in dilute acid and repeat the precipitation with ammonia and ammonium oxalate. If no barium is found with the lime, it is by no means safe to conclude that the former is absent; it can very well have gone into the filtrate from the double precipitation of calcium. This amount will be precipitated with the magnesium as barium phosphate unless it is removed as indicated below.

For the quantitative determination of barium a separate portion of the substance should be taken (see below).

Determination of Magnesium

To the combined filtrates from the calcium oxalate precipitation, add a drop or two of sulfuric acid and allow the solution to stand 12 hours to see if any precipitate of barium sulfate will form. In the latter case, filter off the precipitate and test for barium according to Vol. I. In the filtrate from the barium sulfate determine magnesium as described on p. 78.

Determination of Barium

If the qualitative tests have shown the presence of barium, weigh out 2 g. of the substance into a platinum dish, moisten with 10 ml. of 7 *N* sulfuric acid and 5 ml. of hydrofluoric acid. Evaporate the liquid on the water-bath, with frequent stirring, until the mineral is completely decomposed, which is recognized by there no longer being any sandy particles perceptible on stirring with a platinum spatula. Frequently a further addition of hydrofluoric acid is necessary. When the decomposition is complete, remove the greater part of the sulfuric acid by heating the contents of the dish in an air-bath. After cooling,

* W. F. Hillebrand, *J. Am. Chem. Soc.*, **16**, 83 (1894).

take up the residue in water, filter off the barium sulfate, and ignite wet in a platinum crucible. The precipitate thus obtained always contains small amounts of calcium sulfate which must be eliminated. To accomplish this, dissolve the residue in the crucible in a little hot concentrated sulfuric acid, and after cooling, dilute the solution with cold water. The barium sulfate is now completely free from calcium; filter, ignite again, and weigh

Determination of the Alkalies

(*a*) *Method of J. Lawrence Smith**

Principle. — The substance is heated with a mixture of 1 part ammonium chloride and 8 parts calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides (silicates and aluminates), and the silica is changed to calcium silicate, as represented by the following equations:

$$CaCO_3 + 2\,NH_4Cl \rightarrow CaCl_2 + 2\,NH_3 + H_2O + CO_2$$

$$2\,KAlSi_3O_8 + CaCl_2 + 6\,CaCO_3 \rightarrow 6\,CaSiO_3 + Ca(AlO_2)_2 + 2\,KCl + 6\,CO_2.$$

The alkali chlorides together with the excess calcium chloride can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved.

Preparation. — The ammonium chloride necessary for the determination is prepared by subliming the commercial salt; the calcium carbonate by dissolving the purest calcite obtainable in hydrochloric acid and precipitating with ammonia and ammonium carbonate. Carry out this last operation in a large porcelain dish. After the precipitate has settled, pour off the clear solution and wash the precipitate by decantation until free from chlorides. The product thus obtained contains traces of alkalies, but the amount present can be determined once for all by a blank test and a corresponding deduction made from the results of the analysis; it is usually sodium chloride and amounts to 0.0012–0.0016 g. for 8 g. calcium carbonate. The decomposition was performed by Smith in a finger-shaped crucible about 8 cm. long and with a diameter of about 2 cm. at the top and 1½ cm. at the bottom. Such a crucible is suitable for the decomposition of about 0.5 g. of the mineral. A larger quantity can be analyzed in a somewhat wider crucible.

Filling the Crucible. — Mix 0.5 g. of the mineral with an equal quantity of sublimed ammonium chloride by trituration in an agate mortar, add 3 g. of calcium carbonate and intimately mix again. Transfer the mixture to a platinum crucible with the help of a piece of glazed paper, rinse the mortar with one gram of calcium carbonate, and add this to the contents of the crucible.

The Ignition. — Place the covered crucible in a slightly inclined position and heat gradually over a small flame until no more ammonia is evolved (this should take about 15 minutes). During this part of the

* *Am. Jour. Science* [2], **50**, 269, and *Ann. Chem. Pharm.*, **159**, 82 (1871).

operation the heat should be kept so low that ammonium chloride does not escape. The latter is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride. It is possible to decompose the silicate by using calcium chloride alone. Gradually raise the temperature until finally the lower three-fourths (and no more) of the crucible are brought to a dull red heat, and maintain this temperature for 50–60 minutes. Then allow the crucible to cool; the sintered cake usually can be removed by gently tapping the inverted crucible. Should this not be the case, digest a few minutes with water, which serves to soften the cake so that it can be readily washed into a large porcelain, or, better, platinum dish. Heat the covered dish with 50–75 ml. of water for half an hour, replacing the water lost by evaporation, and reducing the large particles to a fine powder by rubbing with a pestle in the dish. Decant the clear solution through a filter and wash the residue 4 times by decantation, then transfer to the filter and wash with hot water until a few cubic centimeters of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with hydrochloric acid; it should dissolve completely, leaving no trace of undecomposed mineral.

Precipitation of the Calcium. — To the aqueous solution add 50 ml. of ammonium carbonate reagent, heat nearly to boiling and filter. Evaporate the filtrate to dryness in a porcelain or platinum dish, heat the contents of the dish for an hour in a drying-oven at 110°, and remove ammonium salts by careful ignition over a moving flame. After cooling, dissolve the residue in a little water and remove the last traces of calcium by the addition of ammonia and ammonium oxalate to the hot solution. After standing 12 hours, filter off the calcium oxalate and receive the filtrate in a weighed platinum dish, evaporate to dryness, and gently ignite. After cooling moisten the mass with hydrochloric acid to transform any carbonate into chloride, repeat the evaporation and ignition, and determine the weight of the dish and its contents; this shows the amount of alkali chloride present. To determine potassium, dissolve the residue in water, and follow one of the methods given on pp. 59–67. The sodium is determined by difference.

(*b*) *The Hydrofluoric Acid Method of Berzelius*

Weigh 0.5 g. of the powdered mineral into a platinum dish, moisten with 2 ml. of water and 0.5 ml. of concentrated sulfuric acid, mix with the substance by means of a platinum spatula, and after cooling add about 5 ml. of pure, concentrated hydrofluoric acid. Evaporate the liquid on the water-bath, frequently stirring with the platinum

spatula, until no more hydrofluoric acid is expelled and no more hard particles can be felt at the bottom of the dish.

Heat the dish in an air-bath until the greater part of the sulfuric acid is removed; this is necessary to make sure that the hydrofluoric acid is completely expelled. It is not advisable, however, to remove all of the sulfuric acid, on account of the danger of forming insoluble basic salts. Allow the mass to cool, cover with 200 ml. of water, and digest until all of the residue has gone into solution.* Transform the sulfates to chlorides by precipitation with as slight an excess of barium chloride as possible; and then, without stopping to filter off the barium sulfate, precipitate the aluminium, calcium, and excess of barium by the addition of ammonia and ammonium carbonate. Allow the precipitate to settle, wash 4 times by decantation, then transfer to the filter and wash free from chloride. Evaporate the filtrate to dryness, heat for an hour at 120° and remove the ammonium salts by gentle ignition. Add a few drops of 6 *N* hydrochloric acid, and remove the magnesium by the Schaffgottsche method described on p. 79. In the filtrate determine sodium and potassium as described on pp. 59–67.

Remark. — This method is in very general use, and the results obtained agree closely with those by the J. Lawrence Smith method. Many silicates, such as the feldspars, are readily decomposed by the action of sulfuric and hydrofluoric acids;† others, such as certain specimens of tourmaline, only with difficulty. According to Jannasch the members of the andalusite group are not completely decomposed by hydrofluoric acid, but this can be effected by strongly igniting with ammonium fluoride. For this purpose place the ignited mineral in a platinum dish, cover with 10 ml. of ammonia, evaporate to dryness, dilute with water, strongly acidify with concentrated hydrofluoric acid, and again evaporate to dryness. Place the dish in a nickel beaker and ignite quite strongly, until finally the excess of ammonium fluoride is driven off. Now treat the residue with 12 *N* sulfuric acid to decompose salts of fluosilicic acid, evaporate on the water-bath as far as possible, and remove then the greater part of the sulfuric acid by stronger ignition. From this point the procedure is the same as in the regular Berzelius method.

The Smith method is always applicable and has the advantage that the magnesium is practically completely removed at the start.

Analysis of Portland Cement

The American Society for Testing Materials has adopted a standard set of specifications‡ for Portland cement, including its physical and chemical testing. The chemical methods recommended were those formulated by a committee, who made

* If barium was present, it is left behind as the sulfate.

† Many silicates can be decomposed by evaporation with hydrofluoric and hydrochloric acids. F. Hinden, *Z. anal. Chem.*, **1906**, 332.

‡ *Proc. Am. Soc. Testing Materials*, **12**, 301–28 (1912).

a special study of this analysis.‡ The following directions are based upon the report of the committee but the procedure has been modified slightly in minor details and no attempt made to reproduce the same wording. This scheme of analysis is added partly because of the technical importance of Portland cement and partly because it has proved a satisfactory procedure to place in the hands of students as representative of a complete analysis.

The mode of procedure adopted by the above-mentioned committee called for two evaporations for the removal of the silica. In the discussion of the method, however, it was pointed out that by heating the residue at 120°, not correcting for impurities by the hydrofluoric acid treatment and not correcting the subsequent precipitate formed by ammonia for small traces of silica, results are obtained which are within the permissible analytical error of the correct value.† In fact, by this more rapid method, a compensation of errors takes place and the results are better in many cases than if the same operator attempted to carry out the analysis with the utmost precision possible.

The committee also recommended the use of platinum dishes and platinum crucibles as far as possible. The advantages gained are obvious, but the price of platinum has become so high that it is the duty of every practical chemist to avoid the use of platinum utensils wherever possible. The errors introduced by using porcelain instead of platinum are insignificant in most cases, although greater care must be taken to allow crucibles to cool before placing them in desiccators, and a longer time should elapse before weighing.

The following directions call for dissolving the ferric and aluminium hydroxides in nitric acid instead of hydrochloric acid. This has the advantage of making it easier to wash the second precipitate of hydroxides and the presence of ammonium nitrate is favorable during the ignition of ferric hydroxide, whereas ammonium chloride reacts to form ferric chloride, which is volatile. If the chloride content is not high it is also easier to wash the calcium oxalate precipitate; here the presence of a little chloride causes the ignited precipitate to be very hygroscopic.

The original directions call for two precipitations of the calcium and for two precipitations of magnesium. This is unessential in the commercial testing of Portland cement provided the conditions recommended are carefully fulfilled.

Procedure. — Weigh 0.5 g. of cement into a 250-ml. porcelain casserole, moisten with 40 ml. of water and add 20 ml. of 6-normal hydrochloric acid (*d.* 1.1), breaking up with a stirring-rod any lumps that form. Cover the casserole with a watch-glass and digest about 15 minutes on a hot plate until the cement is decomposed completely. Rinse off the bottom of the cover-glass with a little water and evaporate to dryness on the water-bath. During the evaporation have the cover-glass raised above the top of the casserole by means of a glass triangle. Heat the casserole and dry residue in a hot closet at 120° for an hour or more.‡

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* *J. Soc. Chem. Ind.*, **21**, 12 (1902); *Eng. News*, **50**, 60 (1903); *Eng. Record*, **48**, 49 (1903).

† This statement does not apply to rock analysis.

‡ At this temperature, the silica acid becomes dehydrated so that it is practically insoluble in dilute acids. The presence of the calcium chloride from the

Silica. — Moisten the residue with 10 ml. of 6-normal hydrochloric acid, warm slightly and add 150 ml. of water. Cover the casserole with a watch-glass and digest 10 minutes at a temperature near the boiling-point. Filter into a 300-ml. beaker, wash twice with 2-normal hydrochloric acid and then with hot water till free from chloride. Transfer the moist precipitate and filter to a weighed porcelain crucible with the paper folded so that the precipitate is entirely covered.* Smoke off the filter paper at a low heat without letting the paper take fire (cf. p. 416). Finally ignite at the full heat of the Méker burner until a constant weight is obtained of a perfectly white precipitate. Report as SiO_2.

Iron and Alumina. — Precipitate with 6-normal ammonium hydroxide as described on p. 91. Dissolve the impure aluminium and ferric hydroxides in hot 2 *N* nitric acid and reprecipitate as described on p. 423. Wash once by decantation and then on the filter with two per cent ammonium nitrate solution. Ignite the second precipitate wet in a porcelain crucible and weigh as $Fe_2O_3 + Al_2O_3$, neglecting the small quantities of TiO_2, P_2O_5, and Mn_3O_4 which it may possibly contain (see p. 156). Unite the filtrate with that obtained from the first precipitate.

Ferric Oxide. — Transfer the ignited precipitate to a small beaker. Dissolve the traces that remain adhering to the crucible by heating small portions of 6-normal hydrochloric acid in it, finally pouring each portion into the beaker. Use 20 ml. of acid in all. Do not at any time dilute the hydrochloric acid until all the iron in the beaker is dissolved. Heat the acid with the iron and aluminium oxides at about 90° until all the iron has dissolved (cf. p. 110). When a clear solution is obtained, place the beaker on a filter, reduce carefully with stannous chloride and determine the iron content by the Zimmermann-Reinhardt process (see Volumetric Analysis). Compute the per cent of Fe_2O_3 present and subtract this from the above weight of the oxides to get the per cent Al_2O_3.

Calcium Oxide. — Combine the 2 filtrates from the ammonium hydroxide precipitation. Make them slightly acid with nitric acid and concentrate to a volume of about 300 ml. Add 1 g. of oxalic acid and precipitate the calcium in the hot solution by slowly adding half-normal

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cement helps the dehydration. The quantity of silica that passes into the next filtrate is negligible and more than balanced by that obtained from the reagents and dishes. The residue should not be baked too hard. At higher temperature combination of basic magnesium salt and silicic acid takes place and alumina is made very insoluble.

* The dry silica is very pulverulent and easily lost if the gases from the paper escape too violently, as when the paper takes fire.

ammonium hydroxide during 5 minutes. When the precipitate is distinctly granular, remove from the source of heat and allow the precipitate to settle for 30 minutes or an hour. Ignite the moist precipitate and weigh as oxide (cf. p. 81), as sulfate (p. 82), or as carbonate (p. 83). The oxalate can be converted to sulfate or carbonate in a porcelain crucible but it is necessary to heat over a good burner in a *covered* platinum crucible in order to get complete conversion to the oxide and a Méker burner is desirable for this purpose.

Instead of determining the calcium gravimetrically, it is equally accurate to determine the oxalate in the precipitate by permanganate titration (see Part II). Report as CaO.

Magnesium Oxide. — Acidify the filtrate from the calcium precipitation and concentrate to about 400 ml. Precipitate the magnesium by the Schmitz method (p. 78) and weigh as pyrophosphate after careful ignition in a porcelain crucible. Report the per cent MgO.

Alkalies. — If it is desired to determine the alkalies the J. L. Smith method should be used (p. 425).

Loss on Ignition. — Heat 0.5 g. of the cement for 5 minutes in a platinum crucible over a low flame, then heat strongly for 15 minutes.

Sulfuric Anhydride. — Fuse, in an iron crucible, 0.5 g. of cement with 2 g. of sodium peroxide and an equal weight of sodium carbonate, protecting the contents of the crucible from the flame as directed on p. 317. After the fusion, extract the soluble salts by treatment with hot water. Filter, make acid with hydrochloric acid and evaporate to dryness on the steam table. Moisten the residue with 5 ml. of 6-normal hydrochloric acid, dilute with 200 ml. of water and filter. Wash thoroughly and precipitate the sulfate in 400 ml. of boiling solution by the addition of barium chloride (p. 316). Filter, ignite and weigh. Report as per cent SO_3.

Determination of Silicon in Iron and Steel

Drown Method

This method has come into very general use, is recommended by the American Foundrymen's Association for the analysis of cast iron and has been used by the Bureau of Standards at Washington, D. C., for analyzing samples of steel.

Procedure. — Treat 1 g. of borings in a porcelain casserole with 20 ml. of 6 *N* nitric acid. When all action has ceased add 20 ml. of 18 *N* sulfuric acid and evaporate until copious fumes are evolved. Cool, dilute with 150 ml. of water, and heat until all the ferric sulfate has

dissolved. At once filter the hot solution, wash with 6 *N* hydrochloric acid, and then with hot water. Place the residue in a platinum crucible without drying, ignite and weigh. Treat the contents of the crucible with 4 or 5 ml. of hydrofluoric acid and a few drops of sulfuric acid, evaporate to dryness, again ignite and weigh. The difference in the two weights is the silica.

Remark. — Instead of using 1 g. of sample and dissolving in nitric acid, many chemists prefer to dissolve 4.69 g. of sample in 20 ml. of 7 *N* sulfuric acid. The procedure is otherwise the same except that alternate washing of the precipitate with hydrochloric acid and water is recommended for a longer period. In this case 0.1 g. of SiO_2 = 1 per cent of Si.

Analysis of Lepidolite

Lepidolite is a member of the mica group and contains lithium and fluorine with the following composition:

$$Si_3O_9Al_2(Li,K,Na)_2(F,OH)_2$$

SiO_2 = 40–45 per ct.;	Al_2O_3 = 19–38 per ct.;	MnO = 0–5 per ct.;
MgO = 0–0.5 per ct.;	K_2O = 4–11 per ct.;	Li_2O = 1–6 per ct.;
Na_2O = 0–2 per ct.;	F = 1–10 per ct.;	H_2O = 1–3 per ct.

Besides the above, calcium, iron, phosphoric acid, and chlorine are frequently found, and in rare cases small amounts of cæsium and rubidium are present.

The determination of the silicic acid, aluminium, iron, manganese, and magnesium is effected as in the case of the orthoclase analysis, except that in this case the manganese must be separated from the iron and aluminium as described on p. 153, 155 or 157.

Determination of the Alkalies. — Determine the weight of NaCl + KCl + LiCl by one of the methods given under the analysis of orthoclase, and weigh the potassium as potassium chloroplatinate. Then remove the platinum by treatment with hydrogen, or heat the solution to boiling and precipitate the platinum as sulfide by the introduction of hydrogen sulfide. Evaporate the filtrate to dryness and separate the lithium from the sodium as described on p. 68 or 69.

Determination of Fluorine. — This determination is the same as in the case of analysis of fluorine in calcium fluoride (p. 407), except that it is unnecessary to add any silica, for the mineral itself already contains a sufficient quantity.

Determination of Water. — This is effected by the method of Rose-Jannasch (p. 414).

Determination of Ferrous Iron in Silicates and Rocks

Weigh out 0.5–1.0 g. of the powdered mineral into a platinum dish, cover with 5–10 ml. of 7 *N* sulfuric acid and place upon the little triangle (*a*) Fig. 100, made of glass or, better, platinum. Place this in the lead vessel *C* which rests in a paraffin bath (*B*). After placing the cover upon *C*, pass a rapid current of carbon dioxide through *A*, whereby the air within the apparatus will be replaced in about 3 minutes. Quickly remove the cover, and add 5–10 ml. of concentrated hydrofluoric acid. At once replace the cover, and continue the stream of carbon dioxide, while stirring the contents of the dish repeatedly during the whole operation by means of a platinum spatula or piece of coarse wire introduced through the other hole in the cover (in the drawing this opening is placed too far to the right). At the same time heat the paraffin bath to 100° and keep at this temperature for about an hour. As soon as no more gritty particles are to be felt, raise the temperature of the bath to about 120° to remove the large excess of hydrofluoric acid. This requires about another hour. Allow the dish to cool in the carbon dioxide atmosphere and finally wash its contents into 400 ml. of cold distilled water. Add 10 ml. of concentrated sulfuric acid, and titrate the solution with standard potassium permanganate solution until a pink color is obtained which is permanent for several seconds. This end-point is fugitive in proportion to the amount of hydrofluoric acid remaining in the solution.

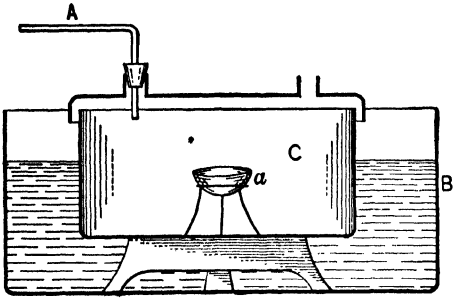


FIG. 100.

Remark. — The above method has been used in the author's laboratory with success for several years. It is a modification of Cooke's* method in which the decomposition with hydrofluoric acid took place under a glass funnel upon the water-bath. In this case a large amount of hydrofluoric acid remains in solution and it is difficult to obtain a sharp end-point.

W. F. Hillebrand,† of the U. S. Bureau of Standards, prefers the

Modified Pratt Method

Place 0.5–1.0 g. of the fine powder in an 80–100 ml. platinum crucible, cover with water and add 10 ml. of 9 *N* sulfuric acid, cautiously if any

* *Am. J. Science* [2], **44**, 347 (1867).

† U. S. Geol. Survey, *Bull.* 700.

carbonate is present. Add air-free hot water till the crucible is nearly half full. Place the crucible, with its cover on, on a triangle near a very low flame protected from draughts. Displace the air in the crucible by introducing a stream of carbon dioxide through a small tube placed under the cover of the crucible. In a short time the liquid in the crucible boils but before this happens stop the current of gas and drop the crucible cover in place. From a small platinum crucible held in one hand, while the other draws the crucible cover to one side, add 5–7 ml. of hydrofluoric acid. Quickly replace the lid and increase the heat but take care not to let the liquid boil over. As soon as steam issues, lower the flame and keep so that there is steady boiling without danger of loss for about 10 minutes. Then transfer the crucible, without removing the cover, to 200 ml. of cold, saturated boric acid solution. Remove the crucible with a stirring rod, rinse it out and titrate at once with permanganate, added rapidly until the first pink blush appears throughout the whole liquid.

If an unattacked residue remains in the beaker, filter it off and repeat the above treatment.

Another method for the determination of the amount of ferrous iron present in insoluble silicates is that of Mitscherlich. The silicate is decomposed in a closed tube with sulfuric acid ($8\ H_2SO_4 : 1\ H_2O$) under pressure, and the resulting solution titrated with potassium permanganate. This method usually gives good results in the case of a silicate analysis, but it is worthless for the analysis of rocks containing pyrite or other sulfides, which on treatment with sulfuric acid are decomposed.* The sulfur serves to reduce iron that was originally present in the ferric form, so that a high result is obtained.

Separation of Soluble from Insoluble Silicic Acid: Lunge and Millberg†

Frequently a mixture of silicates is to be analyzed which is partly decomposed on treatment with acids, with the separation of gelatinous silicic acid, and partly unaffected. The silicic acid deposited from solution by the addition of acids is soluble in 5 per cent sodium carbonate solution, while quartz and feldspar are not appreciably attacked by the latter (cf. Vol. I).

If it is desired to separate the deposited silicic acid from the unattached silicate (usually feldspar and quartz), treat the substance with acid (hydrochloric or nitric) and evaporate on the water-bath until a

* L. L. de Koninck, *Z. anorg. Chem.*, **26**, 125 (1901), Hillebrand and Stokes, *J. Am. Chem. Soc.*, **22**, 625 (1900), Stokes, *Am. J. Sci.*, Dec., 1901.

† *Z. angew. Chem.*, **1897**, 398, 425.

dry powder is obtained. Moisten this with acid, dilute, boil and filter. After washing, digest the residue with 5 per cent sodium carbonate solution on the water-bath, in a porcelain dish for 15 minutes. Filter, wash the residue first with soda solution and finally with water.

The alkaline filtrate contains the soluble silicic acid; this can be determined by acidifying and evaporating to dryness. The residue from the sodium carbonate treatment, consisting of quartz and feldspar, is weighed. To determine the quartz, treat with sulfuric and hydrofluoric acids, remove the excess of the latter by heating to fumes of sulfuric acid, and dissolve the cold residue in water. In this solution precipitate the alumina, as described on p. 91, and weigh the Al_2O_3. If this weight is multiplied by 5.41, the corresponding amount of feldspar is obtained, and if this is deducted from the weight of the quartz + feldspar, the weight of the quartz will be found.

Determination of Soluble Silicic Acid in Clay

Clay contains besides alumina, sand (quartz + breccia) and small amounts of calcium and magnesium carbonates.

Moisten 2 g. of the coarsely powdered substance, which has been dried at 120°, with water and add 150 ml. of 12 *N* sulfuric acid.* Cover the porcelain dish with a watch-glass and heat over a free flame until dense fumes of sulfuric acid vapors are evolved. Allow the contents of the dish to cool, add 150 ml. of water and 3 ml. of concentrated hydrochloric acid, boil for 15 minutes, filter, wash completely, and treat the mixture of soluble silicic acid, quartz and insoluble silicate as above.

Remark. — It was formerly the custom to separate the soluble silica from the insoluble silica by boiling with potassium hydroxide solution. According to the experiments of Lunge and Millberg, however, this is not permissible because quartz is appreciably soluble in caustic potash solution. If, on the other hand, the substance is obtained in a very finely-divided condition, even sodium carbonate solution cannot be used for the same reason.

Analysis of Chromite

Although chromite (chrome iron ore) is not a silicate, it is insoluble in all acids, and can be brought into solution by fusion with alkali carbonates, or borates, so that its analysis will be discussed at this place.

Chromite contains 18–39 per cent FeO, 0–18 per cent MgO, 42–64 per cent Cr_2O_3, 0–13 per cent Al_2O_3, and 0–11 per cent SiO_2. Calcium, manganese, and nickel are also occasionally present.

* Alexander Subech, *Chem. Ind.*, **1902**, 17.

Of the finely-powdered and bolted mineral, fuse 0.5 g. in an inclined, open platinum crucible with 4 g. of pure sodium carbonate* for 2 hours over a good Teclu or Méker burner. After cooling, leach the melt with water, acidify with hydrochloric acid,† evaporate in a porcelain dish until a dry powder is obtained, moisten with hydrochloric acid, take up in water, and filter off the silica. Ignite, weigh, and test the purity with hydrofluoric acid (p. 416). Introduce hydrogen sulfide into the hot filtrate from the silicic acid and filter off the precipitate of platinum sulfide and sulfur. Catch the filtrate in an Erlenmeyer flask, add 10 ml. of ammonium chloride, enough ammonia (free from carbonate) to make the solution alkaline, and a little freshly-prepared ammonium sulfide. Cork up the flask and allow the contents to stand over night. In the morning filter off the precipitate, wash twice with water containing a little ammonium sulfide, dissolve it in hydrochloric acid, and repeat the precipitation with ammonium sulfide. Determine calcium and magnesium in the filtrate as described on p. 86.

Dissolve the ammonium sulfide precipitate in cold 2 *N* hydrochloric acid, filter off any residue of nickel or cobalt sulfide and dry. Ignite this residue first in air, then in a current of hydrogen, and finally weigh as metal. It is not worth while to attempt the separation of the nickel from the cobalt on account of the small amount present. Expel hydrogen sulfide from the filtrate from the sulfides of nickel and cobalt by boiling, oxidize the iron present by adding bromine and separate the iron, chromium, and aluminium from the manganese by means of the barium carbonate method (p. 152) and from one another as described on p. 108 *et seq.* In the filtrate from the barium carbonate precipitate, separate the manganese from the barium as described on p. 130, *b*, and determine as sulfide or as sulfate.

Remark. — If it is desired to determine the chromium alone, this is best accomplished by means of a volumetric process (see Part II).

Determination of Thorium in Monazite, according to E. Benz‡

Monazite is a phosphate of the rare earths [(Ce,La,Di,Th)PO_4]. It occurs in so-called " monazite sand " mixed with quartz, rutile, zircon, tantalates, etc., and is at present the raw material used for the prep-

* Bunsen fused the chromite with one-third as much SiO_2 and 6–8 parts Na_2CO_3 and then subtracted the amount of silica added from the total amount found. This makes the decomposition take place more readily, but the author prefers not to add the silica on account of the possibility of thereby introducing an error.

† If a dark residue of undecomposed mineral should remain, filter it off and again fuse with sodium carbonate.

‡ *Z. angew. Chem.*, **15**, 297 (1902).

aration of thoria (used in the Welsbach mantle). The value of a sample of monazite sand depends upon the amount of thorium present, and its determination is best effected as follows:

Of the bolted monazite sand, intimately mix 0.5 g. with 0.5 g. sodium fluoride and 10 g. of potassium pyrosulfate in a spacious platinum crucible; cover and slowly heat until the mixture is at a gentle fusion. This is best accomplished by placing the platinum crucible within a larger porcelain one which is provided with an asbestos ring. After no more gas is given off, heat the crucible carefully over the free flame, and, after cooling, digest with water and a little hydrochloric acid until the melt is completely disintegrated. After allowing the residue to settle, filter, digest the residue with a little concentrated hydrochloric acid, dilute with water, and again filter.* In the combined filtrates nearly neutralize the hydrochloric acid with ammonia (the formation of a permanent precipitate is to be avoided, for it will be difficult to redissolve it), heat the solution to boiling, and add 3–5 g. of solid ammonium oxalate while stirring vigorously. The oxalates of the rare earths are immediately deposited in the form of a coarse powder. To make sure that the precipitation is complete, add a little ammonium oxalate solution. After standing 12 hours, filter off the precipitated oxalates, wash once with 0.5 per cent nitric acid, transfer to a porcelain dish, and dissolve the last portions of the precipitate by washing the filter with hot, concentrated nitric acid and water. Evaporate the liquid nearly to dryness. Add 10 ml. of concentrated nitric acid and 20 ml. of fuming nitric acid, cover the dish with a watch-glass and heat on the water-bath. After a short time the nitric acid begins to decompose the oxalic acid, shown by the lively evolution of gas. After no more gas is given off, wash down the watch-glass and sides of the dish and evaporate the solution to dryness. To remove the free nitric acid, add a little water and evaporate the solution once more; after this remove the filter fibers by filtration. It is now necessary to separate the thorium from the remaining earths. This is effected by precipitating the former with hydrogen peroxide as thorium peroxide. On ignition the latter is changed into ThO_2, in which form it is weighed.

The precipitation with hydrogen peroxide takes place as follows: Dilute the neutral solution of the nitrates with 10 per cent ammonium nitrate solution to a volume of 100 ml., heat to 60–80° and precipitate thorium peroxide by the addition of 20 ml. of pure 3 per cent hydrogen peroxide solution. Filter off the precipitate, which is colored

* This residue is free from thorium, and consists chiefly of silicic and tantalic acids.

yellow by traces of cerium peroxide (at the most 0.3 mg. of the latter is present), immediately wash with hot water containing ammonium nitrate, ignite wet in a platinum crucible, and weigh as ThO_2.

If it is desired to obtain an absolutely pure thorium oxide, dissolve the moist precipitate in nitric acid and repeat the above precipitation with hydrogen peroxide.

Remark. — The above process for the determination of thorium in monazite is quicker and more accurate than either that of Glaser* or that of Hintz and Weber,† so that it is to be recommended for both technical and scientific purposes.

The determination of thorium oxide in thorite is carried out in the same way with the difference that instead of fusing the mineral with sodium fluoride and potassium pyrosulfate, it is decomposed by treatment with hydrochloric acid, and the silica removed as usual. The filtrate from the silica is analyzed as above.‡

For the

Analysis of Incandescent Mantles

consult the work of T. B. Stillman, *Chem. Zeit.*, 1906, 60.

Water in Silicates

The total hydrogen content of any substance can be determined under suitable conditions as water. Hillebrand§ has classified the condition of hydrogen in minerals as follows: —

A. Essential hydrogen representing a part of the characteristic molecular or crystalline structure.

I. Present in definite stoichiometric proportions
  (*a*) As acidic or basic hydrogen (*e.g.*, $KH_2Al_3(SiO_4)_3$)||
  (*b*) As water of crystallization.

II. Not present in stoichiometric relations with reference to the substance as a whole but present in one of the above forms in some constituent, the entire substance being a solid solution or isomorphous mixture of two or more individuals.

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* *Chem. Ztg.*, **1896**, 612.

† *Z. anal Chem.*, **36**, 27 (1897).

‡ As members of the hydrogen sulfide group are usually present, it is advisable to first remove them and to effect the precipitation of the rare earths with ammonium oxalate from the slightly acid filtrate from the hydrogen sulfide precipitate.

§ U. S. Geol. Survey, *Bull.* 700.

|| Inasmuch as hydrated alumina does not ionize appreciably as either an acid or a base, and the above formula can be rewritten to make the hydrogen appear basic $KAlO(AlOH)_2(SiO_3)_3$, and the mineral a meta instead of an ortho silicate, it is idle to spend much time arguing whether the hydrogen in such a mineral is really acidic as the first formula indicates or possibly basic as the second formula shows.

B. Nonessential hydrogen, not necessary for the characterization of the mineral.

I. In liquid solution, as in deliquescent powders or in amorphous material including supercooled liquids.

II. Held by surface forces.

(*a*) Adsorbed in films of molecular thickness.

1. On walls of cavities within grains of aggregates.
2. On the exteriors of grains.

(*b*) Held by capillarity, in liquid form.

1. In colloids with mesh structure.
2. In definite openings within aggregates.
3. In spaces between grains.

III. Included hydrogen.

(*a*) As liquid droplets in cavities.

(*b*) As included grains of other minerals.

There is no rule to lay down to enable the chemist to differentiate between these different classes.

If the mineral on ignition loses nothing but water, the amount of the latter can be determined by the loss in weight. In most cases, however, other constituents (*e.g.*, CO_2, SO_2, Cl, F, etc.) are lost and the substance may undergo an oxidation (FeO is changed to Fe_2O_3; PbS to $PbSO_4$, etc.). In such cases the procedure recommended by Jannasch can be used to advantage. The substance is heated with lead oxide, the water vapor conducted over a heated mixture of lead oxide and lead peroxide and absorbed in a weighed calcium chloride tube (see p. 415).

If the substance on ignition loses simply water and carbon dioxide the former may be accurately determined by the method of Brush and Penfield.*

Various forms of tubes used by Penfield are shown in Fig. 101. To dry a tube, heat and aspirate dry air through tubing that reaches to the bottom of the larger tube. Introduce the weighed substance, by means of a thistle tube, into the bottom of the tube. Connect the open end with the capillary, *e*, place in a horizontal position, cover the outer bulb or bulbs with wet blotting paper and heat the bottom of the tube with the flame of a good burner. The water is expelled and condenses in the colder portion of the tube. As soon as no more water can be expelled, heat the end of the tube until it softens, draw out the tube and seal it. The front end of the tube now contains the water and possibly a little carbon dioxide, which must be removed. For this purpose

* *Am. J. Sci.* [3], **48**, 31 (1894), and *Z. anorg. Chem.*, **7**, 22 (1894).

incline the tube at an angle of 40°, so that the heavier carbon dioxide will run out of it. The weight of the tube slowly diminishes, but at the end of about 3 hours it becomes constant, losing about 0.0003 g. per hour, due to the evaporation of water. If, therefore, the tube is allowed to stand 3 hours before weighing, 0.0009 g. must be added to the weight of the water. If the substance contained a large amount of carbonate, the escaping carbon dioxide will carry aqueous vapor with it, so that a further correction must be made. One gram of CO_2 at an average barometric pressure (760 mm.) and at room temperature (20°) will cause a loss of 0.0096 g. water vapor. If the amount of carbon dioxide present is known, it is, therefore, only necessary to multiply its weight by 0.0096 to obtain the amount of water that would otherwise escape the determination.

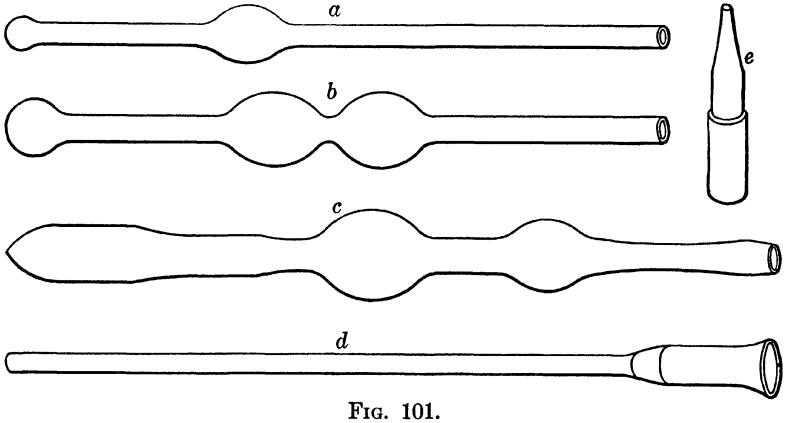


FIG. 101.

The tubulated crucible devised by Gooch is useful for the determination of hydrogen (or water) in minerals which require a flux and a high temperature. Mix 0.5 g. of the powder with 2.5 g. of fully-dehydrated sodium carbonate (heated nearly to melting and cooled in a desiccator) in the crucible *C*, Fig. 102. Place the crucible on a triangle, put the top in place and connect on one side with a calcium chloride tower and soda-lime tubes to free the air from moisture and carbon dioxide and connect on the other side with a sulfuric acid bulb-tube. If it is desired to determine carbon at the same time, use 10 g. of fused lead chromate instead of the sodium carbonate as flux. Seal the top of the crucible by pouring powdered sodium tungstate (free from arsenic which would ruin the crucible), or sodium carbonate, into the flanged lip *L*, immerse the crucible in cold water and melt the flux in the lip by the flame from a blast-lamp. As soon as the flux is fused

withdraw the flame and stopper the tubes through which air is passed. When the flux cools, a tight joint is made as shown by the maintenance of the height of sulfuric acid in the bulb tube as it is sucked back during the contraction of the crucible on cooling.

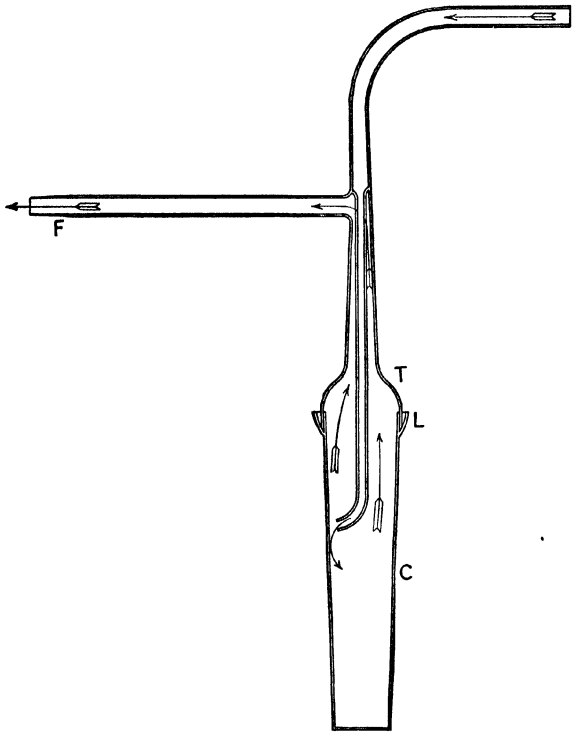


FIG. 102.

Dry at 105° for an hour by means of an air or toluene bath while passing dry air through the crucible. Then connect the crucible with a weighed calcium chloride tube and the latter with a weighed ascarite bulb (p. 153) if the determination of carbon is to be made also. Shield the sodium tungstate joint from the flame by a horizontal piece of asbestos board and place a similar vertical shield between the crucible and the weighed absorption tubes. Connect the outer absorption tube with the sulfuric acid bulb to show the rate at which the gas is passing through the apparatus. Slacken the air stream and carefully heat the crucible with a free flame beginning at the top of the rock mixture. When the fusion is complete, as shown by a lessening of the rate at which gas escapes, extinguish the flame and allow a current of air to continue until the apparatus is cold. Only a few minutes are required for the heating. Cool and weigh the absorption bulb with the usual precautions.

Obviously the determination can be made in a glass tube in a short combustion furnace.

PART II

VOLUMETRIC ANALYSIS

A gravimetric analysis is accomplished by adding to the solution of the substance to be analyzed a reagent of only approximately-known strength, separating one of the products of the reaction from the solution and weighing it. A *volumetric* analysis is made by causing the reaction to take place by means of a measured volume of a solution of accurately-known strength (*titer*) and computing the amount of substance present by the volume of the solution which reacts with it (cf. p. 1). For this sort of analysis accurately-calibrated measuring instruments are necessary.

Measuring Instruments

1. *Burets* are tubes of uniform bore throughout the entire length; they are graduated in milliliters* and are closed at the bottom, as shown in Fig. 103, by means of a glass stop-cock, or with a piece of rubber tubing containing a glass bead *h*. The latter form was devised by Bunsen and is used as follows: Seize the tubing between the thumb and forefinger at the place where the glass bead is, and by means of a gentle pressure at the top of the bead, form a canal at one side of the bead through which the liquid will run out. Instead of the glass bead an ordinary pinch-cock is sometimes used.

Besides the above forms of burets, a great many others are in use, but it is unnecessary to describe them here.

* It has been found that the volume occupied by 1 kilogram of water at 4° C. (one liter) is 1000.027 cc. so that the thousandth part of a liter is really 1.000027 cc. This error, 27 parts in 1 million, is not greatly in excess of the tolerance error of brass weights and since the chemist does not work with an accuracy much greater than 1 part in 1 thousand, it is evident that we are safe in regarding 1 cc. = 0.001 liter. Makers of burets, pipets and all other volumetric measuring instruments now mark them in " ml." rather than " cc." in response to requests from the Bureau of Standards but although several years have passed since this request was made, the editors of our leading chemical journals have refused to drop the " cc." and substitute " ml."

2. *Pipets.* — A distinction must be made between a *transfer* pipet and a *measuring* one. A transfer pipet has only one mark upon it, and serves for measuring off a definite amount of liquid. Transfer pipets are constructed in different forms; usually they consist of a glass tube with a cylindrical widening at the middle. The lower end is drawn out, leaving an opening about 0.5–1 mm. wide. Pipets of this nature are constructed which will hold respectively 1, 2, 5, 10, 20, 25, 50, 100 and 200 ml.

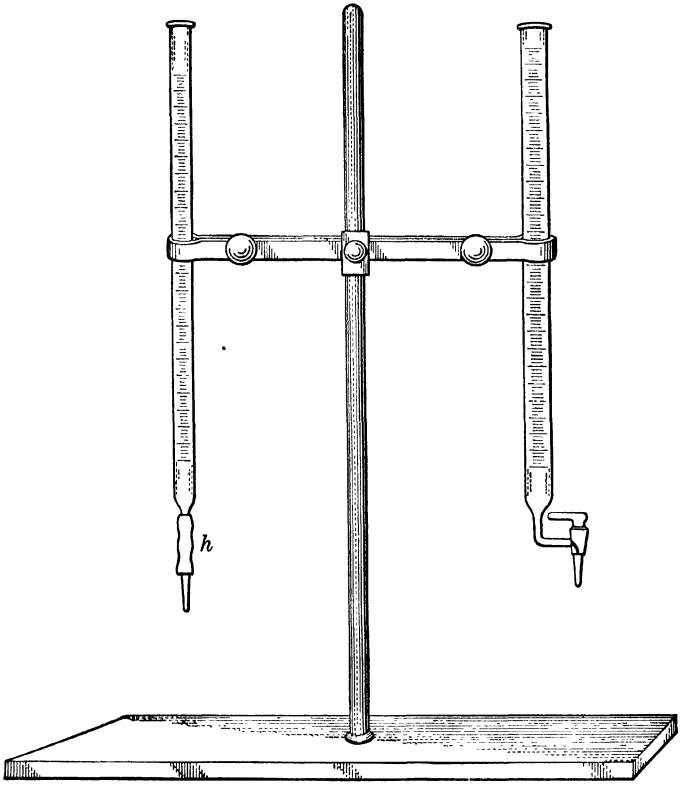


FIG. 103.

Measuring pipets are buret-shaped tubes graduated in cubic centimeters and drawn out at the lower end. They serve to measure out any desired amount of liquid and are obtained with a total capacity of 1, 2, 5, 10, 20, 25, and 50 ml.

3. *Measuring-flasks* are flat-bottomed flasks with narrow necks provided with a mark, so that when they are filled to this point they will contain respectively 50, 100, 200, 250, 300, 500, 1000, and 2000 ml.

They serve for the preparation of standard solutions and for the dilution of liquids to a definite volume.

4. *Measuring-cylinders* are graduated into cubic centimeters and are used only for rough measurements.

It is clear that accurate results can be obtained by a volumetric analysis only when the instruments used are accurately calibrated. It should never be taken for granted that a purchased instrument is correct, but it should always be carefully tested.

Normal Volume and Normal Temperature

A liter, which is the volume of a kilogram of water at its maximum density, is taken as the normal volume. If it is desired to mark on the neck of a liter-flask the point to which this volume reaches, the position of the mark depends upon the temperature of the vessel. It is necessary, therefore, to choose for the vessel itself a definite temperature, the so-called *normal temperature.* At present the temperature of + 20° C. is taken as the normal temperature by the United States Bureau of Standards. According to this, then, the flask should be marked at 20° with the volume occupied by a kilogram of water at + 4°, and as the kilogram is the unit of mass, the weighing should also take place in a vacuum.

TABLE I. — DENSITY OF WATER AT DIFFERENT TEMPERATURES*

t	Density	*t*	Density	*t*	Density
0°	0.999867	14°	0.999271	28°	0.996258
1	9926	15	9126	29	0.995969
2	9968	16	8969	30	5672
3	9992	17	8801	31	5366
4	1.000000	18	8621	32	5052
5	0.999992	19	8430	33	0.994728
6	9968	20	8229	34	4397
7	9929	21	8017	35	4058
8	9876	22	0.997795	36	0.993711
9	9808	23	7563	37	3356
10	9727	24	7321	38	0.992993
11	9632	25	7069	39	2622
12	9524	26	0.996808	40	0.992244
13	9404	27	6538		

This experimental impossibility can be overcome inasmuch as the weight of a liter of water is known accurately at temperatures other than + 4°, and also the expansion of the glass with rise of tempera-

* Thiesen, Scheel and Diesselhorst, 1904. The other tables are taken from Circular No. 19 of the U. S. Bureau of Standards

ture, and the buoyancy which the weights and the water experience as a result of weighing in the atmosphere. The weights which must be placed upon the balance pan in order to determine the space occupied by a true liter of water, therefore, depend upon the temperature of the water and of the vessel, as well as the density of the air at the time of the experiment. The density of the air varies somewhat from day to day and depends upon the barometric pressure, the temperature, and the amount of moisture. It suffices in most cases, however, to assume the average values of these factors corresponding to the locality.

TABLE II. — BUOYANCY CONSTANTS IN MG. PER ML.

Observed Pressure in Millimeters	Temperature in Degrees Centigrade			
	15	20	25	30
640	0.904	0.886	0.869	0.852
650	0.918	0.900	0.883	0.866
660	0.932	0.914	0.897	0.879
670	0.946	0.928	0.911	0.893
680	0.960	0.942	0.924	0.906
690	0.975	0.956	0.938	0.920
700	0.989	0.970	0.952	0.933
705	0.996	0.977	0.958	0.940
710	1.003	0.984	0.965	0.947
715	1.010	0.991	0.972	0.953
720	1.017	0.998	0.979	0.960
725	1.024	1.004	0.985	0.967
730	1.031	1.011	0.992	0.973
735	1.038	1.018	0.999	0.980
740	1.045	1.025	1.006	0.987
745	1.052	1.032	1.013	0.994
750	1.059	1.039	1.020	1.000
755	1.067	1.046	1.027	1.007
760	1.074	1.053	1.034	1.014
765	1.081	1.060	1.040	1.020
770	1.088	1.067	1.047	1.027
775	1.095	1.074	1.054	1.034
780	1.102	1.081	1.061	1.041

It was shown on p. 13 how to reduce an apparent weight to the true mass or weight in a vacuum and, by the same formula, it is easy to compute what the apparent weight in air will be of any given mass. For convenience, however, it is simpler to use the above Table II, which gives the difference in milligrams between the mass and the apparent weight of one milliliter of water weighed with brass weights in air at various temperatures and unreduced barometer readings.

A humidity of 50 per cent is assumed. To find the weight of one milliliter of air under the conditions assumed in this table, multiply the buoyancy constant by 1.135.

From the above two tables, the following table has been computed and shows the apparent weight for temperatures between 15° and 30° under 50 per cent humidity and an unreduced barometer reading of 76 cm. The table assumes the water and the air to be at the same temperature.

TABLE III. — APPARENT WEIGHT IN GRAMS OF WATER IN AIR

Temp. in Degrees C.	2000 ml.	1000 ml.	500 ml.	400 ml.	300 ml.	250 ml.	150 ml.
15	1996.11	998.05	499.03	399.22	299.42	249.51	149.71
16	1995.80	997.90	498.95	399.16	299.37	249.48	149.68
17	1995.48	997.74	498.87	399.10	299.32	249.43	149.66
18	1995.13	997.56	498.78	399.03	299.27	249.39	149.63
19	1994.76	997.38	498.69	398.95	299.21	249.34	149.61
20	1994.36	997.18	498.59	398.87	299.15	249.30	149.58
21	1993.95	996.97	498.49	398.79	299.09	249.24	149.55
22	1993.51	996.76	498.38	398.70	299.03	249.19	149.51
23	1993.06	996.53	498.26	398.61	298.96	249.13	149.48
24	1992.58	996.29	498.15	398.52	298.89	249.07	149.44
25	1992.09	996.04	498.02	398.42	298.81	249.01	149.41
26	1991.57	995.79	497.89	398.31	298.74	248.95	149.37
27	1991.04	995.52	497.76	398.21	298.66	248.88	149.33
28	1990.49	995.24	497.62	398.10	298.57	248.81	149.29
29	1989.92	994.96	497.48	397.98	298.49	248.74	149.24
30	1989.33	994.66	497.33	397.87	298.40	248.67	149.20

If the glass vessel is at 20° no other correction is necessary. The glass, however, expands with rise of temperature. The coefficient of cubical expansion varies from 0.000023 to 0.000028. The following table assumes the value 0.000025 for the coefficient of expansion of glass and shows the correction to be added to give the capacity at 20°. Conversely by changing the signs in the table the corresponding capacities at other temperatures are given when the vessel has a definite volume at 20°.

To illustrate the use of these tables, suppose it is desired to find the actual capacity of a liter measuring flask. Assume that the

Apparent weight of the flask filled with water at 24° is . . . 995.82 g.
According to Table III one liter of water at 24° weighs 996.29 g., therefore the actual volume of the water is 995.82 ÷ 996.29 = 0.9995 liters but from Table IV, we find that the volume at 20° will be 0.1 ml. less. Therefore the true volume of the flask is . . . . . 999.4 ml.

TABLE IV. — TEMPERATURE CORRECTION FOR GLASS VOLUMETRIC APPARATUS

Temp. in Degrees C.	2000 ml.	1000 ml.	500 ml.	400 ml.	300 ml.	250 ml.
15	+0.25	+0.12	+0.06	+0.05	+0.04	+0.031
16	+ .20	+ .10	+ .05	+ .04	+ .03	+ .025
17	+ .15	+ .08	+ .04	+ .03	+ .02	+ .019
18	+ .10	+ .05	+ .02	+ .02	+ .02	+ .012
19	+ .05	+ .02	+ .01	+ .01	+ .01	+ .006
21	−0.05	−0.02	−0.01	−0.01	−0.01	−0.006
22	− .10	− .05	− .02	− .02	− .02	− .012
23	− .15	− .08	− .04	− .03	− .02	− .019
24	− .20	− .10	− .05	− .04	− .03	− .025
25	− .25	− .12	− .06	− .05	− .04	− .031
26	−0.30	−0.15	−0.08	−0.06	−0.04	−0.038
27	− .35	− .18	− .09	− .07	− .05	− .044
28	− .40	− .20	− .10	− .08	− .06	− .050
29	− .45	− .22	− .11	− .09	− .07	− .056
30	− .50	− .25	− .12	− .10	− .08	− .062

To simplify the computation still more, the following tables are useful for calculating the capacities of glass vessels from the weight in air of the water delivered. They give the amounts to be added to the apparent weight in grams to obtain the actual capacity in milliliters. Only three of these tables will be given, one for 250 ml. and

TABLE V. — INDICATED CAPACITY 250 ML.

[Amounts to be added to apparent weight of water in grams to obtain actual capacity in milliliters at 20° C.]

Temp. in Deg. C.	Tenths of Degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.518	0.521	0.524	0.528	0.530	0.534	0.537	0.540	0.543	0.546
16	.550	.554	.556	.560	.563	.567	.570	.574	.578	.581
17	.584	.588	.592	.596	.599	.603	.606	.610	.614	.618
18	.622	.626	.630	.633	.638	.642	.646	.649	.654	.658
19	.662	.666	.670	.674	.679	.683	.687	.692	.696	.700
20	.705	.709	.714	.718	.722	.727	.732	.736	.741	.746
21	.750	.754	.760	.764	.769	.774	.778	.784	.788	.793
22	.798	.804	.808	.813	.818	.824	.828	.834	.839	.844
23	.849	.854	.860	.865	.870	.875	.881	.886	.892	.897
24	.902	.908	.913	.919	.924	.930	.936	.941	.947	.952
25	.958	.964	.969	.975	.981	.986	.993	.998	1.004	1.010
26	1.016	1.022	1.028	1.034	1.040	1.046	1.052	1.058	1.064	1.070
27	1.076	1.082	1.089	1.095	1.101	1.108	1.114	1.120	1.126	1.132
28	1.139	1.146	1.152	1.158	1.165	1.172	1.178	1.184	1.191	1.198
29	1.204	1.211	1.218							

one for 50 ml. From these the corrections for other capacities can be easily computed. Thus in the above case the weight at 24° was 995.82 g. and the correction for a 250 ml. flask is given in Table V as 0.902 g. for this temperature and would be 3.61 for one liter. Adding 3.61 to 995.82 gives 999.43 which agrees with the result obtained above. In these tables the barometer reading is assumed to be 760 cm. and the relative humidity 50 per cent.

TABLE VI. — INDICATED CAPACITY 100 ML.

15	0.207	0.208	0.210	0.211	0.212	0.213	0.215	0.216	0.217	0.219
16	.220	.221	.223	.224	.225	.227	.228	.230	.231	.232
17	.234	.235	.237	.238	.240	.241	.243	.244	.246	.247
18	.249	.250	.252	.253	.255	.257	.258	.260	.261	.263
19	.265	.266	.268	.270	.272	.273	.275	.277	.278	.280
20	.282	.284	.285	.287	.289	.291	.293	.294	.296	.298
21	.300	.302	.304	.306	.308	.310	.311	.314	.315	.317
22	.319	.321	.323	.325	.327	.329	.331	.333	.336	.338
23	.340	.342	.344	.346	.348	.350	.352	.354	.357	.359
24	.361	.363	.365	.368	.370	.372	.374	.376	.379	.381
25	.383	.386	.388	.390	.392	.395	.397	.399	.402	.404
26	.406	.409	.411	.414	.416	.418	.421	.423	.426	.428
27	.431	.433	.436	.438	.440	.443	.446	.448	.451	.453
28	.456	.458	.461	.463	.466	.469	.471	.474	.476	.479
29	.482	.484	.487							

TABLE VII. — INDICATED CAPACITY 50 ML.

15	0.104	0.104	0.105	0.106	0.106	0.107	0.107	0.108	0.109	0.109
16	.110	.111	.111	.112	.113	.113	.114	.115	.116	.116
17	.117	.118	.118	.119	.120	.121	.121	.122	.123	.124
18	.124	.125	.126	.127	.128	.128	.129	.130	.131	.132
19	.132	.133	.134	.135	.136	.137	.137	.138	.139	.140
20	.141	.142	.143	.144	.144	.145	.146	.147	.148	.149
21	.150	.151	.152	.153	.154	.155	.156	.157	.158	.159
22	.160	.161	.162	.163	.164	.165	.166	.167	.168	.169
23	.170	.171	.172	.173	.174	.175	.176	.177	.178	.179
24	.180	.182	.183	.184	.185	.186	.187	.188	.189	.190
25	.192	.193	.194	.195	.196	.197	.199	.200	.201	.202
26	.203	.204	.206	.207	.208	.209	.210	.212	.213	.214
27	.215	.216	.218	.219	.220	.222	.223	.224	.225	.226
28	.228	.229	.230	.232	.233	.234	.236	.237	.238	.240
29	.241	.242	.244							

If it be desired to take into consideration the deviation of the temperature and barometric pressure from that assumed in the above tables it is sufficient to add (or subtract) to the figure given in the table 1.4 mg. for each millimeter that the barometer reads above (or below)

760 mm., and to subtract (or add) 4 mg. for each degree that the temperature is above (or below) 20° C.

In the early days of volumetric analysis, it was not customary to calibrate burets in true milliliters but, for convenience it was assumed that the liter was the volume occupied by one kilogram of water weighed in the air at the laboratory temperature. Mohr assumed the average laboratory temperature to be 17.5°. If all of the measuring instruments are calibrated on this assumption the work of the laboratory is just as accurate as when true liters are used but since the best apparatus is now calibrated in true milliliters by the makers, the Mohr liter, which is equal to 1002.3 true milliliters, has lost its usefulness. It is still a wise precaution to test the graduations as marked on the instrument but it is unwise to attempt to change them to the old scale. Throughout this book, therefore, a liter will always mean a true liter and a milliliter, ml., is used synonymously with cubic centimeter, cc., because the difference between the true cubic centimeter and the true milliliter (cf. p. 441) is only 0.000027 cc.; a liter contains one drop more than 1000 cc. of water. In Germany the normal temperature has been taken at 15°. A flask containing 1000 ml. at 15° will contain 1000.08 ml. at 20°.

Calibration of Measuring-flasks

A good measuring flask should fulfill the following requirements prescribed by the U. S. Bureau of Standards.

At the capacity mark or marks on a flask the inside diameter must be within the following limits:

Diameter (in millimeters)	Capacity of flask (in millimeters) up to and including —											
	25	50	100	200	250	500	1000	2000	3000	4000	5000	6000
Maximum	8	10	12	13	15	18	20	25	30	35	40	45
Minimum	6	6	8	9	10	12	14	18	20	22	25	30

The neck of a flask must not be contracted above the graduation mark. The capacity mark on any flask must not be nearer the end of the cylindrical portion of the neck than specified below:

Capacity	Distance from upper end	Distance from lower end
	cm.	cm.
100 ml. or less	3	1
More than 100 ml	6	2

Flasks may be graduated both *to contain* and *to deliver* provided the intention of the different marks is clearly indicated and provided the distance between two adjacent marks is not less than 1 mm. In flasks graduated to more than one capacity, the error in the volume between two consecutive marks shall not exceed one-half of the permissible error in the volume indicated by the first mark.

To calibrate a flask, carefully clean and dry it. Place it upon a balance sensitive to one ten-thousandth part of the desired volume and use weights of the same degree of accuracy. Counterpoise the flask by a tare. Beside the tare weights place weights corresponding to the volume of the flask as indicated in Table V on p. 446, or by the values in Tables III and IV on pp. 445–446. Restore equilibrium by pouring distilled water at the laboratory temperature into the flask. Take care that no drops of water are left suspended from the sides of the neck above the water-level; if any are present, remove them by touching with a piece of filter-paper wrapped around the end of a glass rod. Establish an exact equilibrium by adding or removing a little water with a small pipet. Place the flask upon a level surface and fasten a piece of gummed paper with a straight edge around the neck of the flask so that its upper edge is just tangent to the deepest point of the water meniscus. Empty the flask, dry, cover its neck with a uniform layer of beeswax, and allow to cool; this usually requires about 15 minutes. Then hold the flask, as is shown in Fig. 104, against the piece of wood *s*, place the blade of a pocket-knife firmly against the upper edge of the thick paper ring, and revolve the flask through 360° around its horizontal axis; in this way a circle is cut in the wax layer. By means of a feather (Fig. 8, p. 33) place a drop of hydrofluoric acid along this circle while holding the flask in the horizontal position. By turning the flask around its axis, allow the drop of hydrofluoric acid to act upon the glass where the wax coating has been cut. After 2 minutes wash the excess of hydrofluoric acid off, dry the neck of the flask by means of filter-paper, heat until the wax melts, and wipe it off. Remove the last traces of wax by rubbing with a cloth wet with alcohol.

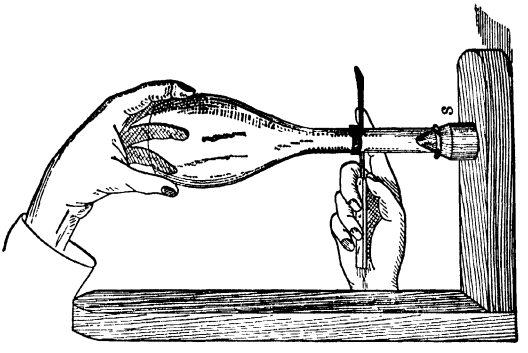


FIG. 104.

As it is possible that the etched circle will not exactly coincide with the upper edge of the paper, the flask should always be tested.

Testing Calibrated Flasks

To read the lowest point of the meniscus it is advisable to place a shade of some dark material immediately below the meniscus. A strip of blue glazed paper with a horizontal edge is excellent for this purpose. Hold the strip tightly about the neck of the flask with the blue side on the inside. Then when the eye is parallel with the bottom of the meniscus, the blue of the paper will be barely visible and will darken the meniscus. Another convenient device is a collar-shaped section of thick black rubber tubing, cut open at one side and of such a size as to clasp the tube firmly.

Clean the flask well with hot, soapy water, rinse out and fill with a warm solution of chromic acid in concentrated sulfuric acid. To prepare this, add 10 g. of powdered alkali bichromate to each 500 ml. of concentrated sulfuric acid and heat to about 70°. Allow this mixture to remain in the flask 15 minutes. Pour out the acid and rinse thoroughly with water. Dry and weigh with a tare.

Fill the flask entirely full of water that has stood in the laboratory long enough to acquire its temperature. Take the temperature of the water, pour out the excess water, and after waiting 3 minutes for the sides to drain, bring the water exactly to the mark, place on the balance and add weights until equilibrium is obtained. From Tables III–VII on pp. 445–447, the exact capacity of the flask can be told at once.

Capacity (in milliliters) less than and including—	Permissible error		Capacity (in milliliters) less than and including—	Permissible error	
	Calibrated for Contents	Calibrated for Delivery		Calibrated for Contents	Calibrated for Delivery
	ml.	ml.		ml.	ml.
25	0.03	0.05	1000	0.30	0.50
50	.05	.10	2000	.50	1.00
100	.08	.15	3000	.75	1.50
200	.10	.20	4000	1.00	2.0
300	.12	.25	5000	1.2	2.4
500	.15	.30	6000	1.5	3.0

Some flasks are calibrated to *deliver* a definite volume. To test the calibration of such a flask the procedure is the same except that after weighing the filled flask, it is emptied by gradually inclining it until,

when the continuous stream has ceased, the flask is nearly vertical. Keep the flask inverted to permit drainage and at the end of 30 seconds touch the mouth of the flask, where a drop of water adheres, to the surface of the poured-out liquid. Then weigh the flask again by counterbalancing the original tare with weights.

A calibration should be regarded as correct if the error as determined by experiment falls within the above limits established by the Bureau of Standards at Washington.

Calibration of Pipets

Clean the pipet as described for the calibration of a flask. If it is a *transfer* pipet, dip the point of the pipet into a weighed amount of water and suck up liquid to just above the graduation mark. Place the forefinger on the top of the pipet and allow the liquid to fall until the bottom of the meniscus just reaches the graduation. Touch the point of the pipet to the surface of the liquid, withdraw and weigh the water in the beaker again. From Tables V–VII on pp. 445–447 determine the volume of the pipet.

To test the calibration on a *measuring* pipet, fill the cleaned pipet with water at the laboratory temperature and after adjusting the level, wipe off with filter paper any liquid adhering to the outside. Hold the pipet in a vertical position, all the time. Allow the water to flow unrestrictedly into a tared beaker, and, as soon as the flow ceases, touch the tip of the pipet to the surface of the liquid to remove the adhering drop. Do not wait for a second drop to form and never blow into the pipet. Determine the volume as before.

A pipet or buret is considered correct if the error, as determined by experiment, falls within the following limits:

Transfer Pipets. —

Capacity (in milliliters) less than and including—	Permissible error	Capacity (in milliliters) less than and including—	Permissible error
	ml.		ml.
2	0.006	50	0.05
5	.01	100	.08
10	.02	200	.10
30	.03		

Burets and Measuring Pipets. —

Capacity (in milliliters) of total graduated portion less than and including —	Permissible error of total or partial capacity		Capacity (in milliliters) of total graduated portion less than and including—	Permissible error of total or partial capacity	
	Burets	Measuring pipets		Burets	Measuring pipets
	ml.	ml.		ml.	ml.
2	.....	0.01	30	0.03	0.05
5	0.01	.02	50	.05	.08
10	.02	.03	100	.10	.15

Calibration of Burets

In volumetric titrations it is advisable to begin each titration with the solution at the zero point of the buret. It is proper, therefore, to calibrate a buret in the same way. Clean the buret with soapy water and chrome-sulfuric acid mixture as described on p. 450. Fill the clean and well-rinsed buret to about 1 cm. above the zero point, and drain to that mark, taking care to see that there is no air in the tip of the buret. Wipe off the tip with a filter paper and allow a definite volume, *e.g.*, 5 ml., to run into a tared flask with a narrow neck, finally allowing the tip of the buret to touch the surface of the liquid in the beaker. To avoid loss by evaporation it is well to provide a stopper for the flask with a thermometer in it. After determining the weight of the water, again fill the buret to the zero point and withdraw 10 ml. in exactly the same way. Repeat for each 5 ml. until finally the 50 ml. mark is reached, each time determining the weight of the water withdrawn and the temperature. In withdrawing liquid from a buret until a given point is reached, without waiting for the buret to drain, evidently the amount actually withdrawn depends upon the rate at which it flows from the buret. It is necessary, therefore, to have the tip restricted in size so that the time of free outflow does not exceed 3 minutes nor take less than the following for the respective lengths: —

Length graduated	Time of outflow not less than—	Length graduated	Time of outflow not less than—
cm.	sec	cm.	sec.
15	30	45	80
20	35	50	90
25	40	55	105
30	50	60	120
35	60	65	140
40	70	70	160

On 50-ml. and 100-ml. burets the highest graduation mark should not be less than 3 cm. nor more than 10 cm. from the upper end of the buret. On burets having a capacity of 25 ml. or less this distance should not be less than 2 cm. nor more than 6 cm. Buret and pipet tips should be made with a gradual taper of from 2 cm. to 3 cm., the taper at the extreme end being slight. A sudden contraction at the orifice is not permitted, and the tip must be well finished. To facilitate the removal of drops and to avoid splashing when the instrument is vertical, the tip should be bent slightly.

Burets with rubber tubing at the bottom gradually change with regard to the amount delivered on account of the rubber losing its elasticity. For this reason the tubing should be made quite short and when it becomes old it should be renewed.

The corrections obtained as above are best tabulated by means of a graph in which the buret readings are taken as abscissas and the corrections as ordinates. By connecting the points, a curve is obtained by means of which the correct reading of all parts of the buret can be obtained at a glance.

Until recently burets were not graduated with the lines extending around the tube, as now recommended by the Bureau of Standards, and it was necessary to use some sort of a screen to avoid parallax error. The device of using a strip of blue-glazed paper, with a straight edge, placed around the buret just below the bottom of the meniscus, is as satisfactory as any for reading the meniscus. Some chemists still prefer the old burets because there are not so many confusing lines and because the numbers are usually placed opposite the long lines instead of just above them, as in the newer burets.

Schellbach recommended a buret with a dark vertical line upon a background of milky glass but these burets are not altogether reliable in the hands of some operators so that the Bureau of Standards refuses to test them. The Bureau will, however, test and certify other burets, pipets and flasks at a cost of not over 35 cents per mark and such certified instruments can be purchased from dealers.

The calibration and testing of burets and pipets often seems unnecessary because they are so often found accurate. Occasionally, however, a buret is found with a serious error. Moreover, a buret is rarely accurate at all points, although its total content may be correct. The calibration of a buret is excellent practice for starting a beginner in quantitative analysis.

In case flasks or burets are to be tested in large numbers, or when a class is set to work calibrating burets with a limited supply of balances, it is better to use a volumetric method. Thus for testing flasks

at the Bureau of Standards a series of volumetric standards have been made up, each standard having a capacity slightly less than that of the flask it is intended to test. When the water from the appropriate standard is delivered into a flask, the flask is filled nearly to the graduation mark. The filling is then completed by means of a finely grad-

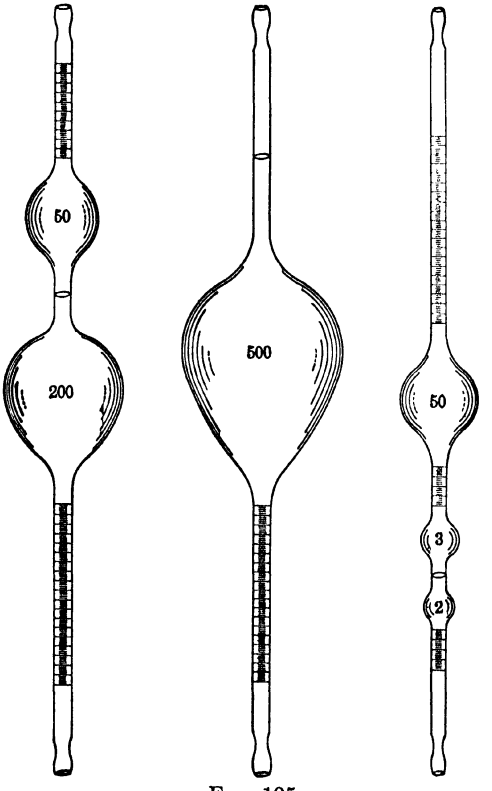


FIG. 105.

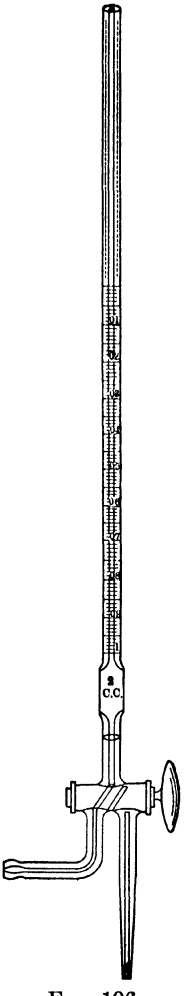


FIG. 106.

uated buret. The capacity of the flask is found from the known volume delivered by the standard and the additional volume delivered by the buret. The flask standard and the buret are themselves calibrated by weighing the water delivered.

For the same purpose, Morse and Blalock devised a set of standard

bulbs as shown in Figs. 105–108, inclusive. In calibrating these bulbs it is necessary to determine, with the aid of Tables III–VII on pp. 445–447, the capacity from the single mark to the first stem division and the capacity of the stem for the smallest subdivision.

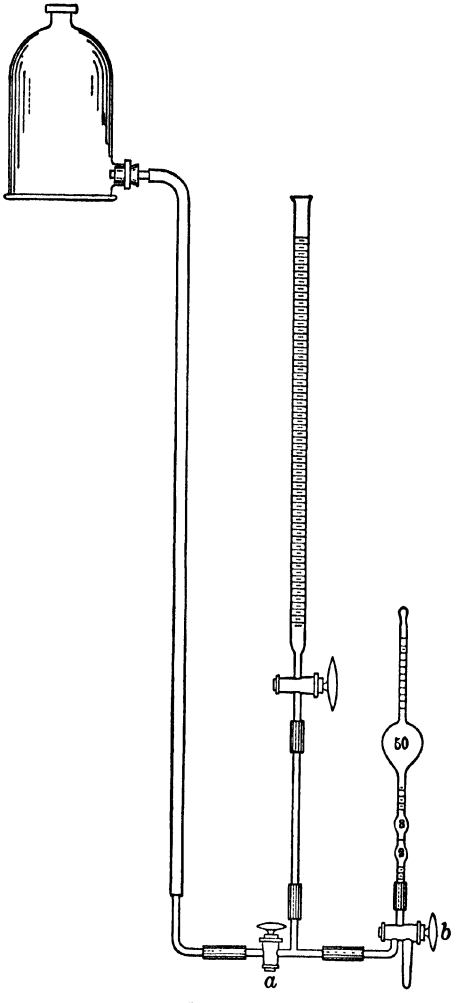


FIG. 107.

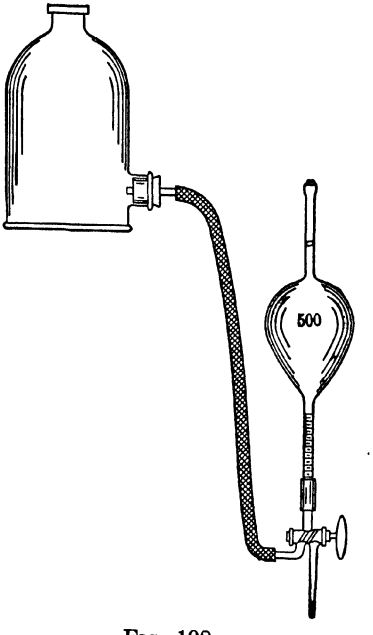


FIG. 108.

In using this Morse-Blalock apparatus it is not necessary to pay any attention to the temperature after the calibration is once made because if the temperature of the water is constant during the work, the volume of the flask or buret will correspond to that of the calibrating vessel.

To calibrate a standard bulb, first clean it with soapy water and chrome-sulfuric mixture as described on p. 450. Place the bulb so that the graduated stem is at the bottom as shown in Fig. 107. Use a glass stop-cock for controlling the outflow and the tip of the outflow must be restricted so that the outflow corresponds to the table on p. 452. Fill the bulb to the upper mark. With the stop-cock wide open allow water to flow into a weighed flask until the first division (zero) is reached. Stopper the flask and weigh. With the aid of the foregoing tables compute the volume of water and capacity of the bulb. Adjust the liquid again to the zero mark, place a smaller weighed flask under the delivery tube, and allow the stem to drain from the zero mark down to the bottom mark. Weigh and compute the volume of each scale division with the aid of the data given in the tables. From these data compute the proper mark on the stem to which the water should fall in order to make the apparatus deliver the desired volume of water and check this by trial.

To calibrate a flask, place the flask under the delivery tube and allow water to run into it from the Morse-Blalock bulb until the proper mark on the stem is reached and mark the position of the water in the neck as described on p. 449.

To calibrate a buret, set up the apparatus as shown in Fig. 107. The reservoir must be higher than the top of the buret and this, in turn, must be placed so that the lowest graduation is higher than the bulbs. With the 3-way cock *b* closed, open the cock *a* and fill the buret with water. Close *a* and open *b* so that the 2 ml. and 3 ml. bulbs can fill, then drain the buret to the zero mark and the bulbs to that mark on the stem of the 2 ml. bulb which represents exactly 2 ml. This leaves the bulbs properly moistened. Leave the buret cock open. Turn the cock *b* and measure 5 ml. of water from the buret into the small bulbs. Observe the position of the meniscus upon the stem of the 3-ml. bulb and calculate the true capacity of the first portion of the buret from the values of the stem divisions as determined in the calibration of the bulbs.

For a more accurate calibration of the buret, 2 ml. portions may be withdrawn or, by means of the standard tube shown in Fig. 106, the value of each ml. or any fraction may be determined.

For very accurate work, *weight* burets are desirable. These are stoppered and weighed after each titration. It is possible to weigh a solution more accurately than to read its volume but as a rule the end-point is not accurate enough to warrant this extra bother of weighing.

Normal Solutions

By a *normal solution* is understood one which contains one *gram-equivalent* of the active reagent dissolved in one liter of solution.* By *gram-equivalent* is meant the amount of substance equivalent to one gram-atom (1.008 g.) of hydrogen. One milliliter of a normal solution contains one *milli-equivalent* of active reagent. For convenience in computation the concentration of solutions used for volumetric purposes are expressed in terms of their normality; *i.e.*, a solution is 2 normal, 0.5 normal, 0.1 normal, etc. The letter *N* is used as an abbreviation for *normal.*

The gram equivalent, or weight required to make a liter of normal solution, depends upon the nature of the reaction involved. It often happens that the same solution has a certain normal concentration when used for one purpose and a different normal concentration when used for another purpose. The reagents used in volumetric analysis are acids, bases, oxidizing agents, reducing agents and precipitants.

The equivalent weight of an acid is determined by the number of replaceable hydrogen atoms in the acid molecule. Thus, to make a normal solution of the monobasic hydrochloric, hydrobromic, hydriodic, nitric or acetic acids, it is necessary to have a molecular weight in grams of the acid dissolved in a liter of solution. A molecular weight in grams is often called one *mole* (cf. Vol. I) and 0.001 mole is called a *milli-mole.* To make one liter of normal solution of the dibasic sulfuric acid only one-half mole of the acid is necessary.

Sometimes, however, it is not convenient to react with all the replaceable hydrogen atoms of an acid. In fact some acids are so weak that they cannot be used in volumetric analysis. Carbonic acid, for example, has no appreciable effect upon methyl orange and only one of the two hydrogen atoms in H_2CO_3 is acid toward phenolphthalein.

Phosphoric acid, H_3PO_4, really has three replaceable hydrogens but only the first is acid toward methyl orange and two hydrogen atoms are acid toward phenolphthalein. In titrating with methyl orange, phosphoric acid acts as a monobasic acid and the normal solution contains one mole per liter. With phenolphthalein as an indicator, phosphoric acid acts as a dibasic acid and one-half mole per liter will make a normal solution of phosphoric acid.

* It is important to note that a normal solution is not properly defined as one containing a gram equivalent in 1 liter of *solvent.* In volumetric analysis the unit is always referred to the volume of the solution.

A normal solution of a base will contain one mole of replaceable hydroxyl. Thus of potassium hydroxide, KOH, sodium hydroxide, NaOH, and ammonium hydroxide, NH_4OH, one mole per liter makes a normal solution. Of barium hydroxide, $Ba(OH_2)$, calcium hydroxide, $Ca(OH)_2$, and strontium hydroxide, $Sr(OH)_2$, only one-half mole is required. Magnesium hydroxide is not appreciably soluble in water, but it is convenient to use the conception of normal solution to determine how much will be dissolved by an acid solution of known strength. One liter of normal hydrochloric acid will dissolve one-half mole of $Mg(OH)_2$.

Salts of weak acids and strong bases have an alkaline reaction. With methyl orange as indicator, sodium carbonate reacts with two moles of hydrochloric acid; hence the equivalent weight is one-half mole of sodium carbonate. With phenolphthalein, however, the end point is reached when one mole of sodium carbonate has reacted with one mole of hydrochloric acid; in this case the normal solution will contain one mole of sodium carbonate.

The equivalent weight of an oxidizing agent is determined by the change in polarity which the reduced element experiences. The polarity of an element is the sum of the positive and negative valence bonds which it has in a compound; it represents the state of oxidation. Usually the polarity is the same as the valence except that a positive or negative sign is prefixed, but sometimes, as is true of the nitrogen atom of an ammonium salt, there is a difference. Nitrogen in the ammonium radical has a valence of five, but four of the bonds are negative toward hydrogen atoms and the fifth bond is positive toward the acid ion of the ammonium salt. The polarity of nitrogen in an ammonium salt is -3 and it corresponds to the same state of oxidation as ammonia, NH_3.

When potassium permanganate is used as an oxidizing agent, the manganese drops to a lower polarity. In permanganate the polarity of the manganese atom is $+7$ and in most reactions used in volumetric analysis, the manganese is reduced to manganous salt in which the manganese has a polarity of $+2$:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O,$$

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O.$$

A normal solution of potassium permanganate, therefore, will contain one-fifth of a mole of $KMnO_4$ because the atom of manganese loses 5 positive charges in changing from a polarity of $+7$ to $+2$.

Sometimes, however, the manganese of potassium permanganate is reduced only to the quadrivalent state. Thus a nearly neutral solu-

tion of a manganous salt can be made to react with permanganate as follows:

$$2\ MnO_4^- + 3\ Mn^{++} + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+.$$

In this case the manganese atom in permanganate only loses 3 charges and a normal solution of permanganate will contain only one-third of a mole of the reagent. Usually permanganate is standardized by a reaction in which it is reduced to manganous salt. Throughout this book, therefore, a normal solution of permanganate will refer to one containing one-fifth mole of $KMnO_4$ per liter.

Potassium dichromate is often used as an oxidizing agent. In it each chromium atom has a polarity of +6 and by reduction two trivalent chromic ions are formed. There is a loss in polarity of 3 charges for each chromium atom and a normal solution of potassium dichromate, $K_2Cr_2O_7$, will contain one-sixth of a mole.*

$$Cr_2O_7^= + 6\ Fe^{++} + 14\ H^+ \rightarrow 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O;$$
$$Cr_2O_7^= + 6\ I^- + 14\ H^+ \rightarrow 2\ Cr^{+++} + 3\ I_2 + 7\ H_2O;$$
$$Cr_2O_7^= + 3\ Sn^{++} + 14\ H^+ \rightarrow 2\ Cr^{+++} + 3\ Sn^{++++} + 7\ H_2O;$$
$$Cr_2O_7^= + 3\ H_2S + 8\ H^+ \rightarrow 2\ Cr^{+++} + 3\ S + 7\ H_2O.$$

In like manner, the equivalent weight of a reducing agent is determined by the gain in polarity which the oxidized element experiences. Ferrous salts are oxidized to ferric salts and the iron is changed from +2 to +3 in polarity. Of ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$, or ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, a normal solution will contain one mole of either salt per liter.

As precipitants, the normal solutions are referred to the simplest type of salt in which each constituent has a valence of one. Thus of sodium chloride NaCl, and of silver nitrate, $AgNO_3$, a normal solution will contain one mole per liter. Of sodium sulfate, Na_2SO_4, barium chloride, $BaCl_2$, and magnesium sulfate, $MgSO_4$, a normal solution will contain one-half mole per liter.

If potassium dichromate is used as a precipitant in the following reaction

$$Cr_2O_7^= + 2\ Ba^{++} + 2\ C_2H_3O_2^- + H_2O \rightarrow 2\ \mathbf{BaCrO_4} + 2\ HC_2H_3O_2,$$

the normal solution will contain one-fourth mole per liter.

* The valence of an ion is the algebraic sum of the polarities of its constituents. Except in peroxides, oxygen has a polarity of −2 in nearly all compounds. The polarity of the chromium can be determined from the charge of the ion and that of the oxygen. The same is true of permanganate or of any other complex ion.

Oxalic acid and the acid oxalates are used sometimes as acids and sometimes as reducing agents. Oxalic acid, $H_2C_2O_4$, has two replaceable hydrogens when titrated against alkali with phenolphthalein as indicator, and a normal solution as an acid contains one-half mole per liter;

$$H_2C_2O_4 + 2\ NaOH \rightarrow Na_2C_2O_4 + 2\ H_2O,$$

or

$$2\ H^+ + 2\ OH^- \rightarrow 2\ H_2O.$$

Oxalic acid also reacts with permanganate in accordance with the following equation:

$$5\ C_2O_4^{=} + 2\ MnO_4^- + 16\ H^+ \rightarrow 2\ Mn^{++} + 8\ H_2O + 10\ CO_2.$$

From the fact that the normal solution of permanganate contains one-fifth mole per liter, it is clear that the equivalent weight of oxalic acid as a reducing agent is one-half mole, just as when acting as an acid. In this case, however, the reducing power has nothing whatever to do with the hydrogen ion content of oxalic acid, for the above reaction takes place in the presence of a mineral acid. The valence of carbon in oxalic acid is four and the structural symbol, leaving out the water of crystallization, is written thus:

$$\begin{array}{l} O = C - O - H \\ \quad\ | \\ O = C - O - H \end{array}$$

This structural symbol shows that three valence bonds of each carbon atom are positive toward 2 atoms of oxygen but, on the assumption that one end of each valence bond is positive and the other negative, one bond of a carbon atom is positive toward another atom of carbon. The polarity of one carbon atom is, therefore, +4 while that of the other carbon atom is +2. When oxalic acid is heated, H_2O, CO and CO_2 are formed, which agrees with this assumption. The average polarity of the carbon in oxalic acid is +3 and this same result is obtained by applying to the $C_2O_4^{=}$ ion the rule given in the foot-note on p. 459.

By the reaction with permanganate, each carbon atom is changed to carbon dioxide. The reducing power of oxalic acid, therefore, is due to the $C_2O_4^{=}$ ion, and this ion is equivalent to two atoms of hydrogen as a reducing agent.

Potassium acid oxalate, KHC_2O_4, can be used as an acid

$$KHC_2O_4 + KOH \rightarrow K_2C_2O_4 + H_2O,$$

in which case the equivalent weight is one mole of KHC_2O_4, but as a reducing agent the reducing power is due to the oxalate group and a normal solution will contain only one-half mole of KHC_2O_4. A solu-

tion of KHC_2O_4 which is normal as an acid will be 2 N as a reducing agent.

Potassium tetroxalate behaves similarly. As an acid it has three replaceable hydrogens and the equivalent weight is one-third of a mole:

$$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2\,H_2O + 3\,NaOH \rightarrow KNaC_2O_4 + Na_2C_2O_4 + 5\,H_2O.$$

As a reducing agent, potassium tetroxalate has two $C_2O_4^=$ groups and the equivalent weight is one-fourth mole. If a solution of potassium tetroxalate contains one mole per liter, it is 3 N as an acid and 4 N as a reducing agent and the same relation holds of all concentrations.

Preparation of Normal Solutions

The required amount of substance should be dissolved in water and diluted to a volume of 1 liter at 20°. Often, however, the water is not at the normal temperature, so that it is customary to dissolve the substance in water at the laboratory temperature and then dilute the solution up to the mark in a liter flask. After thoroughly mixing the solution, its temperature is taken by a sensitive thermometer. If the temperature is above 20°, the volume of the solution would be less than 1 liter if it were cooled to exactly 20°, so that the solution as made up is a little too strong. The following table shows how to correct for the temperature effect:

TEMPERATURE CORRECTION FOR VOLUMETRIC SOLUTIONS

Temp. of measurement, °C.	Capacity of apparatus in milliliters at 20° C.						
	2000	1000	500	400	300	250	150
	Correction in milliliters to give volume of water at 20° C.						
15	+1.54	+0.77	+0.38	+0.31	+0.23	+0.19	+0.12
16	+1.28	+0.64	+0.32	+0.26	+0.19	+0.16	+0.10
17	+0.99	+0.50	+0.25	+0.20	+0.15	+0.12	+0.07
18	+0.68	+0.34	+0.17	+0.14	+0.10	+0.08	+0.05
19	+0.35	+0.18	+0.09	+0.07	+0.05	+0.04	+0.03
21	−0.37	−0.18	−0.09	−0.07	−0.06	−0.05	−0.03
22	−0.77	−0.38	−0.19	−0.15	−0.12	−0.10	−0.06
23	−1.18	−0.59	−0.30	−0.24	−0.18	−0.15	−0.09
24	−1.61	−0.81	−0.40	−0.32	−0.24	−0.20	−0.12
25	−2.07	−1.03	−0.52	−0.41	−0.31	−0.26	−0.15
26	−2.54	−1.27	−0.64	−0.51	−0.38	−0.32	−0.19
27	−3.03	−1.52	−0.76	−0.61	−0.46	−0.38	−0.23
28	−3.55	−1.77	−0.89	−0.71	−0.53	−0.44	−0.27
29	−4.08	−2.04	−1.02	−0.82	−0.61	−0.51	−0.31
30	−4.62	−2.31	−1.16	−0.92	−0.69	−0.58	−0.35

[This table gives the correction to various observed volumes of water, measured at the designated temperatures, to give the volume at the standard temperature, 20° C. Conversely, by subtracting the corrections from the volume desired at 20° C., the volume that must be measured out at the designated temperatures in order to give the desired volume at 20° C., will be obtained. It is assumed that the volumes are measured in glass apparatus having a coefficient of cubical expansion of 0.000025 per degree centigrade. The table is applicable to dilute aqueous solutions having the same coefficient of expansion as water.]

The above table is for pure water and holds approximately for dilute solutions. For the following standard solutions more accurate results will be obtained if the numerical values of the above corrections are increased by the percentages given below:

Solution	Normality		
	N	N/2	N/10
HNO_3	50	25	6
H_2SO_4	45	25	5
NaOH	40	25	5
KOH	40	20	4
HCL	25	15	3
$H_2C_2O_4$	30	15	3
Na_2CO_3	40	25	5

SUBDIVISIONS OF VOLUMETRIC ANALYSIS

I. Acidimetry and Alkalimetry.
II. Oxidation and Reduction Processes.
III. Precipitation Processes.

I. ACIDIMETRY AND ALKALIMETRY

This covers the analysis of acids and bases. In order to determine the amount of acid present, an alkaline solution of known strength is required; and conversely, in the analysis of a base, an acid solution is required. In both cases the " end-point " of the reaction is determined with the help of a suitable indicator. The accuracy of the result depends largely upon the choice of the indicator, so that at this place a few words will be said with regard to the indicators most frequently used for detecting the presence of acids or alkalies.

INDICATORS

The indicators used in acidimetry and alkalimetry are dyestuffs which are of one color in acid solutions and another color in dilute

alkali. They are, as a rule, weak acids; though some of them are weak bases. It has been found that in organic compounds the color can usually be traced to a particular arrangement of atoms called a *chromophor*. The change in color, therefore, is caused by a slight rearrangement of the atoms in the molecule. Thus, if the salt of an indicator acid is yellow and on treatment with acid it turns red, this is due to the fact that when the indicator acid is liberated by the action of the stronger acid, the molecule undergoes a slight change in the way the atoms are linked together, and in fact thereby loses temporarily the ability to dissociate electrolytically as an acid. It is not sufficient, however, to assume that this change of color is caused solely by the fact that the ions have a color other than that of the undissociated molecule; on the contrary it has been shown in certain cases that the ions have the same color that the undissociated molecule has before the rearrangement of the atoms in the molecule has taken place. On the other hand, as regards the proper use of indicators it is necessary simply to bear in mind how salts of weak acids behave in the presence of stronger acids and how the acids themselves behave in the presence of alkali.

The progress of the neutralization of an acid by a base in dilute solution can be followed electrometrically. In Vol. I it was shown in the discussion of Electromotive Series and Oxidation Potentials that an electromotive force results when a metal is placed in contact with a solution of its ions and that this potential difference can be expressed mathematically by means of the Nernst formula, $E_{18°} = \frac{0.058}{n} \log \frac{P}{p}$ in which $E_{18°}$ represents the electromotive force at 18°, or the approximate laboratory temperature, n is the valence of the ion, P is the electrolytic solution tension, which has a constant value for any given metal, and p is the osmotic pressure. This Nernst formula shows the influence of the osmotic pressure, which is proportional to the concentration, upon the electromotive force developed; the more dilute the solution, the smaller becomes the value p and the greater the value of $E_{18°}$. An electrolytic cell is developed whenever two different metals differing in solutions of their respective ions are used as electrodes as in the Daniell cell, or when the electrodes are the same metal dipping in solutions of different concentration. Thus if metallic silver, as anode, is dipped into 0.01 N silver nitrate solution which is separated by a porous cell from 0.1 N silver nitrate and another silver electrode as cathode, a current will flow on connecting the electrodes externally and the electromotive force will be approximately 0.058 volt at 18°. This is evident from the Nernst formula because the factors are all the same in developing the values of $E_{18°}$ at each electrode except the value

p which has a tenfold increase in the concentrated solution corresponding to a difference of 1 in the logarithm.

If a hydrogen electrode (an S-shaped platinum electrode covered with platinum black and kept saturated with hydrogen gas) is placed in a solution together with an electrode of known electromotive force such as a calomel electrode, and the electrodes are connected externally, a current will flow if there is any difference in potential between the hydrogen electrode and the standard electrode. The voltage can be measured by interposing a current from a dry cell and measuring the voltage of this second current when it just suffices to neutralize the original current.

Fig. 109 is a diagram of such an arrangement as used by Hillebrand.* A beaker contains the hydrogen electrode h and the calomel electrode C; the latter is connected through the switch K with the galvanometer G and thence to the positive pole of the dry cell B. By means of the sliding contact S, a variable fraction of the current can be made to pass from the dry cell through the galvanometer to the calomel electrode, opposing the current which results from the potential difference between the two electrodes in the solution. When the two currents are equal, no current flows in the wire as shown by the needle of the galvanometer and the voltage can be read at V.

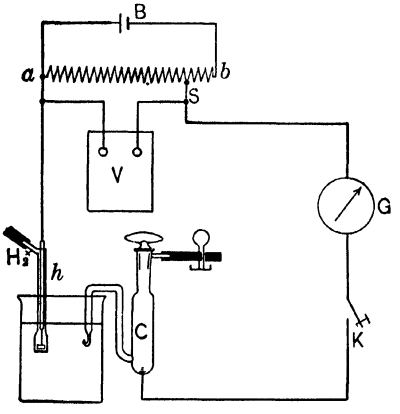


FIG. 109.

In any aqueous solution at 25° the equation [concn. H^+] × [concn. OH^-] = 10^{-14} holds, when the concentrations are expressed in moles per liter. If, therefore, the concentration of the hydrogen ion is established by measurement, the concentration of the hydroxyl ion is also known and the alkalinity as well as acidity of any solution can be expressed by simply stating the hydrogen ion concentration of the solution.

If the electromotive force is compared with that of a normal hydrogen electrode, the Nernst formula takes the form $E_{18} = 0.058 \log \frac{1}{c}$ in which c is the concentration of hydrogen ion in the solution tested.

To compute the actual hydrogen ion concentration, the logarithm of its reciprocal is first obtained. Sörensen has proposed to call the

* *J. Am. Chem. Soc.*, **35**, 847 (1913).

ACIDITY OF SOLUTIONS AT THE CHANGE OF COLORS FOR CERTAIN INDICATORS*

p_H value	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Dimethylaminazobenzene	Cherry Red	+	Flesh Colored	Golden Yellow	+	+	+	+	+	+	+	+	+	
Methyl Orange	Rose Red	+	+	Orange Red	Yellow	+	+	+	+	+				
Na Alizarin sulfonate	Green-yellow	+	+	+	+	Red	+	+	+	+				
Methyl Red		+	Red	+	Pink	Yellow	+	+	+	+				
Cochineal		+	+	Yellow	Yellow Pink	Lilac	+	+	+	+				
Litmus			+	+	Red	Red Violet	Violet	Blue		+				
Rosolic Acid			Yellow	+	+	+	Rose	Red		+	+			
Guiaic Tincture			+	Color-less	+	+	+	Greenish Yellow		+	+			
Phenolphthalein					Color-less	+	+	+	Red	+	+	+		
Thymolphthalein						Color-less	+	+	+	Blue	+	+	+	
Trapaolin O							Yellow	+	+	+	+	Orange Yellow	+	+
Trinitrobenzene									Color-less	+	+	+	Orange	+
Benzopurpurin										Yellow	+	+	+	Red

* W. A. Noyes, *Textbook of Chemistry*.

value of $\log \frac{1}{c}$ the hydrogen exponent, p_H, of the solution. This does away with the minus exponents in expressing the hydrogen ion concentrations. In water the concentration of the hydrogen ion is 10^{-7} moles per liter and this may be expressed as $p_H = 7$ because the value of $\log \frac{1}{10^{-7}} = 7$.

If a solution of an acid is titrated with a solution of an equally strong base, then at the neutral or saturation point the hydrogen exponent will be about 7 as in pure water. If, on the other hand, a weak acid like acetic acid is titrated with a strong base like sodium hydroxide the end point to show complete formation should take place with the p_H value distinctly above 7. An aqueous solution of sodium acetate reacts alkaline.

When a weak base like ammonium hydroxide is titrated with a strong acid like hydrochloric acid, the correct end point should be with p_H = less than 7.

On titrating electrometrically a solution of an acid with a base there is a marked change in the hydrogen ion concentration at the end point when the base is present in excess but this marked change will take place at various hydrogen ion concentrations with different acids and bases. In fact it is possible to titrate two acids electrometrically in the presence of one another provided there is a marked difference in the degrees of ionization so that the weaker acid is not neutralized appreciably until all of the stronger acid has reacted with the base.

By means of electrometric tests it is possible to determine the hydrogen ion concentration at which any indicator changes color. Indicators are known which change at quite different concentrations of hydrogen ion as the following table shows, and for any special case an indicator should be chosen which will change color as nearly as possible at the same hydrogen ion concentration as corresponds to the saturation point of the acid and base used in the analysis. In all cases, either the acid or the base should be quite completely ionized in dilute solutions as no indicator will show a good end point if neither the acid nor the base is largely ionized.

As a result of comparisons between colorimetric and electrometric methods for the determination of hydrogen ion concentrations in solutions of interest to biologists, Clark and Lubs* suggested the use of the following indicators:

* *J. Bacteriol.*, **2**, 1, 109, 191 (1917); cf. *The Determination of Hydrogen Ions*, by W. M. Clark.

Chemical Name	Common Name	Color Change	p_H Range
Thymolsulfonphthalein	Thymol Blue	Red-yellow	1.2–2.8
Tetrabromophenolsulfonphthalein	Bromophenol Blue	Yellow-blue	3.0–4.6
o-Carboxybenzeneazodimethylaniline	Methyl Red	Red-yellow	4.4–6.0
Dibromo-o-cresolsulfonphthalein	Bromocresol Purple	Yellow-purple	5.2–6.8
Dibromothymolsulfonphthalein	Bromothymol Blue	Yellow-blue	6.0–7.6
Phenolsulfonphthalein	Phenol Red	Yellow-red	6.8–8.4
o-Cresolsulfonphthalein	Cresol Red	Yellow-red	7.2–8.8
Thymolsulfonphthalein	Thymol Blue	Yellow-blue	8.0–9.6
o-Cresolphthalein	Cresolphthalein	Colorless-red	8.2–9.8

To prepare suitable indicator solutions, triturate 0.1 g. of each of the above powders, excepting methyl red and o-cresolphthalein, with an equivalent quantity of 0.05 *N* solution of sodium hydroxide. Dilute with water to 500 ml. in the case of cresol red and phenol red and to 250 ml. in the case of thymol blue, bromothymol blue, bromophenol blue and bromocresol purple. With methyl red, dissolve 0.1 g. in 300 ml. of alcohol and dilute with water to 500 ml. With o-cresolphthalein, dissolve 0.1 g. in 500 ml. of 95 per cent alcohol.

The indicators most used in quantitative analysis are *methyl orange, methyl red, lacmoid, litmus,* and *phenolphthalein.*

1. Methyl Orange

Under methyl orange,* Lunge,† who first proposed the use of this indicator, understood either the free sulfonic acid of dimethyl-amino-azo-benzene or its sodium or ammonium salt.

In the free state, the sulfonic acid is obtained in the form of reddish-violet scales, soluble in considerable water. If some of the solid is dissolved in as little water as possible, a distinct reddish-orange colored solution is obtained; but on the further addition of water this color gradually changes to yellow. If a trace of an acid is added to the yellow solution, it becomes red again and on further dilution with water the color changes to orange and finally to yellow once more, if too much acid was not added. The color changes which take place between $p_H = 2.9–4.0$ can be easily explained.

In the sensitive neutral solution there is a condition of equilibrium

* This dyestuff is known commercially as helianthin, orange III, tropäolin D, Poirrier's orange III, dimethylaniline orange, mandarine orange, and gold orange.

† *Berichte,* **1878,** II, 1944; *Chem. Industrie,* **1881,** 348; *Handbuch für Sodaindustrie,* I, 52 (1879); II, 151 (1893).

between two isomeric forms of methyl orange as expressed by the equation:

$$HSO_3 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4N(CH_3)_2 \rightleftarrows SO_3 \cdot C_6H_4 \cdot NH \cdot N{:}C_6H_4{:}N(CH_3)_2.$$

The formula on the left represents the yellow substance and the color is due to the azo group N : N, whereas the formula on the right represents the red substance which has for its chromophor the quinoid group $:C_6H_4:$. The formula on the left has a sulfonic group which imparts acid properties to the molecule and at the other end is an $N(CH_3)_2$ group which has weakly basic properties. The formula on the right, therefore, represents an inner salt inasmuch as the acid and base forming groups are united.

The sodium salt of methyl orange is yellow and has the formula

$$NaSO_3 \cdot C_6H_4N{:}NC_6H_4N(CH_3)_2$$

and when decomposed by acids the free sulfonate at once reverts to the red form:*

$$SO_3 \cdot C_6H_4 \cdot NH \cdot N{:}C_6H_4{:}N(CH_3)_2.$$

Methyl orange is an excellent indicator for weak bases, but cannot be used for the titration of weak acids.

If it is desired to titrate a solution containing sodium hydroxide with a tenth-normal acid, add a little methyl orange to the alkaline solution and titrate with acid until the solution is colored a distinct red. The latter color will not appear permanently until an excess of the acid has been added. This causes a slight error in the analysis which is greater in proportion to the amount of indicator employed, and the more dilute the solution.

It is apparent that the weaker the acid character of the indicator the more sensitive it will be, and the opposite is true of indicators which are bases.

From what has been said the following rule holds:

In any titration a small amount of indicator should be used, and inasmuch as the change of color is proportional to the concentration and not to the absolute amount of acid present, the analyzed solution should have as nearly as possible the same concentration as was the case in the standardization of the solution added.

If a normal acid is used for the titration, the change of color is very sharp when the volume of the solution titrated amounts to about

* Cf. Stieglitz, *J. Am. Chem Soc.*, **25**, 1117.

100 ml. Even with a fifth-normal solution the change of color is very distinct, but less so with tenth-normal solutions; but these can be titrated provided the standardization was made at the same dilution as that used in the analysis.

How is it with the end-point in the titration of an acid with an alkaline hydroxide solution?

If a few drops of methyl orange are added to 100 ml. of water, the latter will be colored distinctly yellow. If the solution contains the same amount of hydrochloric acid as is contained in 10 ml. of a tenth-normal solution of this acid, the solution will be colored a deep red. In order that the solution shall assume its original yellow color, it is only necessary to add exactly 10 ml. of 0.1 *N* alkali hydroxide solution, but no excess of alkali, because the water is itself sufficient to decompose the dyestuff sufficiently to produce the yellow color.

It is evident, then, that it is not a matter of indifference in the analysis whether the titration is completed by the addition of acid or by the addition of alkali. In the former case, for the titration of T ml. of 0.1 *N* alkali solution, T + *t* ml. of 0.1 *N* acid would be necessary.

Methyl orange is more sensitive toward alkali than it is toward acid, but many prefer to finish the titration by the addition of acid, for most eyes can detect the change from yellow to red with greater accuracy. In principle it is more accurate to accomplish the titration the other way, as was recommended by F. Glaser.

Preparation of Methyl-orange Solution. — Dissolve 0.02 g. of solid methyl orange* in 100 ml. of hot water, allow to cool, and filter off any deposited meta-sulfonic acid.

Use. — Methyl orange is suitable for the titration of strong acids (HCl, HNO_3, H_2SO_4) as well as phosphoric and sulfurous acids. Hydrochloric and nitric acids can be titrated with this indicator with a sharper end-point than is the case with sulfuric acid. If free phosphoric acid is titrated with sodium hydroxide using this indicator, the solution changes from red to yellow when one-third of the phosphoric acid has been neutralized:

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$

The primary phosphates are neutral toward methyl orange, while the secondary and tertiary phosphates react alkaline toward it. With

* Of the sodium salt dissolve 0.022 g. in 100 ml. of water, add 0.67 ml. 0.1 *N* HCl and after standing some time filter off any deposited crystals.

half-normal solutions, the end-point of the reaction is fairly sharp, with tenth-normal solutions it is less so; in the latter case an excess of about 0.3 ml. of the tenth-normal alkali is necessary to cause the change from red to yellow.

Sulfurous Acid. — In titrating sulfurous acid with sodium hydroxide, the yellow color is obtained when half the acid has been neutralized,

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O,$$

so that $NaHSO_3$ is neutral toward this indicator.

The weak acids HCN, H_2CO_3, H_2S, H_3AsO_3, H_3BO_3 and $HCrO_4$ - when present in moderate quantities do not act upon the indicator. CO_2 and H_2S produce an orange-red coloration only when present in large amounts. For this reason dilute solutions of the alkali salts of these acids can be titrated with accuracy by means of this indicator.

Organic acids cannot be titrated with methyl orange.

The strong and weak bases NaOH, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, and $Mg(OH)_2$ can be titrated with great accuracy by means of this indicator, and the same is true of the amine bases (methyl and ethyl amines, etc.); on the other hand, such weak bases as pyridine aniline, and toluidine cannot be titrated.

Nitrous acid ordinarily cannot be titrated with this indicator because the acid destroys it. If, however, an excess of alkali is first added to the solution of nitrous acid, then the methyl orange, the titration can be accomplished with accuracy.

2. Methyl Red*

$$(CH_3)_2N - C_6H_4 - \overset{1}{N} = \overset{2}{N} - C_6H_4 - \overset{1}{COOH}.$$

Para-dimethyl-aminoazo-benzene-o-carboxylic acid

This valuable indicator is suitable for titrating weak organic bases and ammonia. The aqueous solution of methyl red is orange, but if a few drops are added to 50–100 ml. of water, the latter is colored a pale yellow. The addition of a drop of 0.1 *N* HCl at once turns the liquid a violet red without passing through any intermediate shade and by the addition of a drop of ammonia the solution becomes nearly colorless again. Methyl red is not very sensitive toward carbonic acid, but more so than is methyl orange, so that it is less suitable for the titration of carbonates. The chief advantage of this indicator lies in the sharp color change from a very pale yellow to a violet red, even in titrating ammonia. The color change is at $p_H = 4.2$–6.3.

* E. Rupp and R. Loose, *Ber.*, **41**, 3905 (1908).

Preparation of the Indicator. Dissolve 0.02 g. of the free acid in 100 ml. of hot water, allow the solution to cool, and then filter. Add 2–3 drops of this solution to every 100 ml. of the solution to be titrated.

3. Lacmoid, or Resorcin Blue,

$C_{12}H_9O_8N$

Lacmoid is prepared by heating resorcinol with sodium nitrite at not too high a temperature. The constitution of the dye has not been completely established. Pure lacmoid is soluble in water (the impure product is difficultly soluble), but more soluble in alcohol, glacial acetic acid, acetone, and phenol, and less so in ether. To determine whether a sample of commercial lacmoid is suitable for use as an indicator, boil a little of it with water; if the water is colored an intense and beautiful blue, it can be used. In this case the alcoholic solution will be of a pure blue color, and not with a tinge of violet, as is the case with the impure substance.

Preparation of Pure Lacmoid. — Filter the solution of the good commercial product in hot 96 per cent alcohol and allow it to evaporate in vacuo over concentrated sulfuric acid.

Preparation of the Indicator. — Use a solution containing 0.2 g. of the purified lacmoid in 100 ml. of alcohol.

Behavior of Lacmoid toward Acids and Bases. — If the solution after it has been colored reddish by acid is treated with a solution of an alkali hydroxide, the red color is gradually changed to a violet-red, and on further addition of alkali, it suddenly changes to a pure blue at $p_H = 5–6$. If the violet solution is diluted with considerable water, it becomes blue.

Uses. — Lacmoid is suitable for the titration of strong acids and bases as well as for ammonia, but is not suited for the titration of nitrous acid or weak acids.

4. Litmus

The chief coloring principle of litmus, the azolitmin, is a dark-brown powder only slightly soluble in water and insoluble in alcohol and ether. With alkalies it forms a readily soluble blue salt. Besides the azolitmin, there are other dyestuffs present in litmus which are soluble in alcohol with a red color.

Commercial litmus is obtained in small cubes mixed with considerable calcium carbonate; the dyestuffs are then in the form of their calcium salts, soluble in water. If the commercial material is dissolved in water, a solution of blue and reddish-violet coloring matter is obtained, which

becomes red on the addition of acid. On making alkaline again, a pure blue color is not obtained at first, but a reddish-violet, which becomes blue on the addition of considerable alkali. Such a solution, therefore, is far from being a sensitive indicator and cannot be used for accurate work. A number of different methods have been proposed for obtaining a sensitive litmus solution, and that of F. Mohr* will be described.

Purification of Litmus. — Place the cubes of litmus in a porcelain dish (without powdering), cover with 85 per cent alcohol, and digest on the water-bath for some time with frequent stirring. Decant off the solution and repeat the operation 3 times. By this means the undesired coloring matter is removed. Extract the residue with hot water, and as it is very difficult to filter the solution, pour it into a tall cylinder, and after standing several days, siphon off the clear liquid. Evaporate the solution to about one-third of its volume and make acid with acetic acid to decompose the potassium carbonate present. Evaporate to sirupy consistency upon the water-bath and cover the mass with considerable 90 per cent alcohol. By this means the blue coloring matter is precipitated, while the remainder of the violet substance remains in solution with the potassium acetate. Filter off the residue and dissolve it in sufficient hot water so that 3 drops of the solution will be necessary to impart a distinct color to 50 ml. of water.

Use. — Litmus can be used for the titration of inorganic and strong organic acids, alkali and alkaline-earth hydroxides, and ammonia, as well as for the titration of carbonates in hot solution. Keep the indicator solution in bottles with a stopper loosely plugged with cotton. Mold forms in a tightly stoppered bottle and the indicator is spoiled.

5. Phenolphthalein

Phenolphthalein is a very weak acid forming red salts which contain the strongly chromophoric quinoid group $:C_6H_4:$. The free acid, however, is unstable and when set free from one of its colored salts reverts instantly into a colorless lactoid form, containing no chromophor group:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH):C_6H_4:O \rightleftarrows \underset{\llcorner\!\!\lrcorner}{O} \cdot OC \cdot C_6H_4 \cdot C(C_6H_4OH)_2.$$

In the case of the free acid, therefore, the condition of equilibrium favors the lactoid form and only minimal traces of the quinoid acid

* *Lehrbuch der chemisch-analytischen Titrirmethoden.*

are present. This trace of quinoid acid is ionized and is in equilibrium with its ions:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O \rightleftarrows$$
$$\rightleftarrows H^+ + OOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O^-.$$

The addition of an alkali causes the hydrogen ions to disappear, so that more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn are reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthalein is a very sensitive indicator towards acids, but on account of being such a weak acid it does not form stable salts with weak bases.

Preparation of the Indicator. — Dissolve 1 g. of pure phenolphthalein in 100 ml. of 86 per cent alcohol.

Uses. — Phenolphthalein is particularly suited for the titration of organic and inorganic acids and strong bases, but not for the titration of ammonia.

If the red-colored solution containing phenolphthalein and a little alkali is treated with an excess of concentrated alkali hydroxide solution, the red color disappears at $p_H = 8.3$–10 but returns on diluting the solution with water. Phenolphthalein, therefore, cannot be used as an indicator for the titration of concentrated alkali without previous dilution with water.

Phenolphthalein is one of the most sensitive indicators toward acids, far more sensitive than methyl orange, for in this case not only can the presence of weak acids be detected, but very small amounts can be titrated with accuracy.

Ordinary distilled water usually contains carbon dioxide, as can be shown by slowly adding 0.1 *N* barium hydroxide solution, drop by drop, to 100 ml. of water containing a drop of the indicator solution. Where the alkali first meets the water, a red color is produced which disappears on stirring, so that often as much as 0.5 to 1.8 ml. of the alkali must be added before a permanent red color is obtained. The disappearance of the red shows the presence of acid (in this case carbonic acid), and its amount corresponds to the alkali neutralized.

Phosphoric Acid. — If a solution of phosphoric acid containing phenolphthalein is titrated with normal sodium hydroxide solution, a permanent coloration is produced when two-thirds of the phosphoric acid is neutralized:

$$H_3PO_4 + 2\ OH^- \rightarrow HPO_4^{=} + 2\ H_2O.$$

Apparently Na_2HPO_4 reacts neutral toward phenolphthalein, but this is not quite correct, for a pure solution of disodium phosphate is

colored by phenolphthalein a pale pink, and on diluting with water the intensity of the color increases owing to progressive hydrolysis:

$$HPO_4^{=} + H_2O \rightleftarrows OH^- + H_2PO_4^-.$$

During the titration of phosphoric acid with sodium hydroxide, a pale-pink color is obtained somewhat too soon, and this color gradually increases in intensity until finally a maximum is reached; the latter point is taken as the end-point. It is possible that this hydrolysis could be prevented by the addition of a large excess of sodium chloride and cooling to about 0° Centigrade.

Carbonic Acid. — If the solution of a neutral alkali carbonate is treated with phenolphthalein a red color is obtained, showing the presence of hydroxyl ions in the solution, due to hydrolysis:

$$CO_3^{=} + H_2O \rightleftarrows OH^- + HCO_3^-.$$

If hydrochloric acid is added to such a solution which is not too dilute and is at a temperature of 0°, decolorization is effected when half of the soda has been neutralized. At ordinary temperatures a sharp end-point cannot be obtained; the color gradually fades. Pure sodium bicarbonate dissolved in ice-cold water is not colored by the addition of phenolphthalein; if it is warmed to the temperature of the room it turns red, but on cooling the color disappears (Küster).

Silicic acid seems to be without influence upon phenolphthalein, for alkali silicates (the water-glasses) can be titrated with accuracy.

Chromic Acid and Acid Chromates are changed by the addition of alkali to neutral chromates and the latter have no action upon phenolphthalein.

Alkali aluminates can be titrated accurately with this indicator for aluminium hydroxide does not affect it.

Almost all the problems involved in acidimetry and alkalimetry can be solved by the use of one or the other of these two indicators: methyl orange and phenolphthalein. For further information with regard to numerous other indicators which have been proposed, the student is referred to Glaser's *Indicatoren der Acidimetrie und Alkalimetrie*, Clark's *The Determination of Hydrogen Ions* and Prideaux's *Theory and Use of Indicators.*

Standardization of Acids and Bases

For the standardization of the solutions used in acidimetry and alkalimetry, many different methods have been proposed, all of which more or less satisfactorily answer the purpose. It was Gay-Lussac who first proposed the use of chemically-pure, calcined sodium car-

bonate, and in simplicity and accuracy this method has never been excelled.

Standardization with Sodium Carbonate. — Prepare the sodium carbonate from pure sodium bicarbonate. To purify the latter, make a saturated solution of the salt by dissolving 35 g. of the commercial salt in 350 ml. of water. Filter and evaporate at a temperature not higher than 40° until crystals begin to separate. Allow to cool and remain protected from dust until about 25 g. of salt have deposited. Pour off the solution, wash the crystals once with cold water and press between filter paper. Dry at 120° for an hour or more. Place about 8 g. of the pure, dry bicarbonate in a platinum or nickel crucible. Embed the crucible in a sand bath so that the sand extends on the outside of the crucible as high as the bicarbonate on the inside and heat 30 minutes after the temperature inside the crucible has been raised to 270° but take care that the temperature of the sand outside the crucible does not rise higher than 300°. Stir the mixture occasionally. Cool the crucible and its contents in a desiccator, weigh and heat again to see if the weight is constant. The heating can take place over a small free flame if care is taken not to allow the temperature to rise above 300° in the crucible. In this case insert the crucible in a hole in a piece of asbestos board with half the crucible above the board. Use a very small flame, raise the temperature gradually to prevent mechanical loss and allow only the bottom of the crucible to show any sign of redness. Stir with a thermometer and remove the flame if the temperature rises to 300°. Above this temperature sodium carbonate begins to decompose and if the carbonate is sintered or fused it will give too low results. Keep the pure carbonate in a desiccator or in a glass-stoppered weighing tube. Take 1 g. of the pure bicarbonate for the standardization of 0.5 *N* acid, dissolve it in 100 ml. of water and titrate with methyl orange in the cold. Or, using phenolphthalein as indicator, add an excess of acid, boil gently till all carbon dioxide is removed, cool and titrate the excess acid with sodium hydroxide solution. Then, if the relative strengths of the acid and base are determined by titration with the same indicator, the concentration of both solutions can be computed.

Standardization with Sodium Oxalate. — Sörensen prefers to weigh out pure sodium oxalate, such as can be obtained from the Bureau of Standards, and to convert the weighed sample to sodium carbonate. In this case it makes no difference if a little carbon dioxide is lost. Weigh out the standard oxalate, after suitable drying to remove hygroscopic moisture, and heat it very carefully in an air-bath (p. 38). A slight carbonization does no harm but this should be avoided by keep-

ing the temperature low and raising the temperature gradually. It is well to heat first for an hour at 270° in an electric oven. Finally, after there is no more danger of mechanical loss being caused by the escaping carbon monoxide, raise the temperature to about 500°. Cool and titrate the sodium carbonate. $Na_2C_2O_4 = Na_2CO_3 + CO$.

If the product is very black, moisten it with water, evaporate carefully and again heat.

*Standardization with Benzoic Acid.** — The Bureau of Standards also furnishes pure benzoic acid which is used as a calorimetric standard or for the direct standardization of a base or the indirect standardization of an acid. Because of the bulkiness of the sublimed acid, it is convenient to melt it in a covered dish, heat to 140° in an oven, and pour into a test tube. Break the solid into convenient pieces and preserve in a test tube. Weigh 1 g. of the acid into a 300-ml. flask, add 20 ml. of alcohol and stopper the flask. Let stand until the acid has all dissolved. Add 3 drops of phenolphthalein indicator and titrate directly with 0.1 *N* alkali hydroxide or dilute to 100 ml. and titrate with 0.5 *N* alkali hydroxide. Run a blank with the alcohol and the same volume of water as present at the end of the titration and make a corresponding deduction in all titrations for the volume of base required to react with the indicator.

Gravimetric Standardizations. — Hydrochloric acid and sulfuric acid solutions can be standardized very accurately by weighing the silver chloride or barium sulfate formed from 25–50 ml. of the corresponding acid. (Cf. pp. 288, 401.)

Normal Hydrochloric Acid

1000 ml. contain 36.47 g. of HCl.

Dilute pure, concentrated hydrochloric acid of the laboratory with 11 volumes of water. In this way a solution is obtained that is slightly more than normal in strength. To obtain an exactly normal solution, titrate it against a weighed amount of chemically-pure sodium carbonate, and from the result obtained compute the volume of water to be added.

In the standardization of any volumetric solution it is advisable to take a weight of substance such that the titration can be accomplished with one filling of the 50 ml. buret and heavy enough so that the normal titration error will not amount to more than 0.001 of the total volume of standard solution used. This is accomplished by taking enough substance to react with 35–40 ml. of the solution to be stand-

* G. W. Morey, *J. Am. Chem. Soc.*, **34**, 1027 (1912).

ardized. It is always well to run a blank with the water used, to see how much of the solution is required to give an end point similar to that used in the analysis. The blank titration should have the same volume of water, the same amount of indicator and the same temperature as the main solution and in working with methyl orange it is best to match the shades.

To standardize the acid, proceed as directed on p. 475. Of pure sodium carbonate, use about 2 g. for a normal solution, add 100 ml. of water and 2 drops of methyl orange indicator solution. Start the titration at approximately the zero reading of the buret. Record the reading in the note book, estimating to the nearest hundredth of a milliliter. Titrate slowly with constant stirring until the color changes from yellow to orange. With a little practice it is easy to tell when the end point is nearly reached by the fact that a pink color is produced which fades slowly on stirring. Finally, at the right end-point, the color changes from yellow to orange throughout solution. It is advisable to match the color with that obtained by adding the indicator solution to pure water and adding just enough acid to give an orange tint to the solution.

If the end-point is over-stepped, add enough standard sodium hydroxide (p. 479) to restore the yellow color and finish with acid again. Titrate the sodium hydroxide against the acid as described on p. 479.

Computation. — If no sodium hydroxide is used the computation is very simple. By definition, 1 ml. of normal acid reacts with 1 milliequivalent of sodium carbonate (molecular weight 106.05), or 0.05303 g. of Na_2CO_3. To find the ratio to the normal, or *normality* of the acid, it is only necessary to find out how much sodium carbonate was actually neutralized by 1 ml. of the acid and divide this value by the milliequivalent, or *norm*, of sodium carbonate.

Thus if t ml. of acid were required to neutralize s g. of sodium carbonate, the solution is $\frac{s}{t \times 0.05303}$ normal.

If the end-point was over-stepped it is necessary to know the relative strengths of the acid and base used in the titration. Assume that by titration it was found that a ml. of HCl = b ml. of NaOH.

Then 1 ml. NaOH = $\frac{a}{b}$ ml. of HCl. If in the titration of s g. of sodium carbonate p ml. of HCl and q ml. of NaOH were used then $t = p - \frac{a}{b}q$ and the above equation holds. If N_A is the normality of the acid, $N_A \times \frac{a}{b} = N_B$, the normality of the sodium hydroxide.

When many analyses have to be made as a part of the routine work of a commercial laboratory it is convenient to make the solutions of acid and base of exactly the same strength and to keep the solutions always exactly normal, or 0.1 N, or 0.5 N as the case may be. Since it is not practical to concentrate a large volume of solution to a definite volume by evaporation it is advisable to make up the solution so that it is a little stronger than desired. If N is the desired normality and N' the normality of the solution as first made up, then the solution is $\frac{N}{N'}$ as strong as desired and should be diluted accordingly.

Thus if the solution is 1.023 N it is only necessary to add 23 ml. of water to each liter of solution to make it 1 N; if it is 0.5012 N, add 1.2 ml. of water to each 500 ml. of solution to make it exactly 0.5 N. Measure out the solution in a measuring flask calibrated for delivery and add the required volume of water from a buret.

Place a label on each reagent and write on it the normal concentration with 4 significant figures and the date that the standardization was made. This is desirable because solutions often change on standing as a result of evaporation, the action of the reagent on the glass container or by decomposition as a result of impurities present.

For most purposes a normal solution is too strong, and 0.1 or 0.5 N solutions are more commonly used. Prepare these in exactly the same way but by using correspondingly smaller quantities of reagents. In titrating with 0.1 N solutions it is quite necessary to make allowance for the acid or base required to react with the indicator and important to keep all conditions the same, such as temperature, volume and quantity of indicator used in duplicate titrations. Alkaline solutions should not be used in burets with a glass stop-cock.

All volumetric titrations should be carried out in duplicate. Burets should be rinsed with at least three 10 ml. portions of the liquid before filling them. They must be kept clean so that no drops form on the sides as they drain. In using measuring flasks, they should also be well cleaned (see p. 450) and when used as above, should be rinsed with at least three 25 ml. portions of the liquid before filling them.

Normal Nitric and Sulfuric Acid Solutions

These are prepared in the same way as was described in the preparation of normal hydrochloric acid.

0.1 *N* Oxalic Acid

$$1000 \text{ ml. contain } \frac{H_2C_2O_4 \cdot 2\,H_2O}{20} = \frac{126.06}{20} = 6.303 \text{ g.}$$

An oxalic acid solution of this strength can be prepared by dissolving exactly 6.303 g. of pure, crystallized oxalic acid in water and diluting to a volume of 1 liter in a calibrated flask with water at the laboratory temperature, (cf. p. 461). Titration with this acid should be made with phenolphthalein as indicator.

Normal Sodium Hydroxide Solution

1000 ml. contain 1 NaOH = 40.01 g.

Dissolve about 45 g. of commercial caustic soda in a little more than a liter of water. Allow the solution to stand for about one hour beside the hydrochloric acid against which it is to be titrated, in order that both solutions may be at the same temperature. Measure off about 40 ml. of the solution from a buret, and titrate with normal hydrochloric acid after the addition of 2 drops of methyl orange solution. The necessary computation was indicated on p. 477.

Titration of Alkali containing Carbonate with Phenolphthalein in Hot Solutions

To the alkaline solution introduce 2 drops of phenolphthalein indicator and add from the buret hydrochloric acid of approximately the same strength until the red color disappears. Heat the solution to boiling; the red color soon reappears. Cool by placing the beaker in cold water,* again decolorize with hydrochloric acid and repeat the process until finally the red color does not reappear on boiling. This method of titration is tedious, but the results obtained are accurate.

On titrating 0.1 *N* acids with methyl orange as indicator, there is no sharp change from yellow to pink, as is the case with normal and half-normal solutions, but first a brownish-orange color is obtained which becomes pink on the addition of more acid. The correct end-point is the change from yellow to yellowish brown. Only when considerable carbonate is present will this change occur before enough acid has been added, for in this case the carbon dioxide exerts an action upon the methyl orange. The disturbing action of carbon dioxide is best prevented by first titrating in the cold, then heating to remove the carbon dioxide, again titrating the *cold* solution with acid. If only a

* With phenolphthalein the titration can be finished in the hot solution, but the end-point is not so sharp.

small amount of carbonate is present, it exerts no appreciable effect upon methyl orange.

The titration of oxalic acid with alkali which contains carbonate is best effected with phenolphthalein in hot solution. The process is carried out as follows: Measure out about 40 ml. of the sodium hydroxide into a beaker, add 2 drops of phenolphthalein, and run in oxalic acid from a buret until the solution is decolorized. Heat the solution upon the water bath until the red color reappears, decolorize with oxalic acid and continue the process until finally the color does not reappear on heating the solution. This point is reached, however, only after the solution has been evaporated to dryness and the residue taken up with a few milliliters of distilled water. A slight red color will appear after this first evaporation, but it will be discharged by the fraction of a drop of oxalic acid and will not reappear upon a second evaporation.

Remark. — By heating the solution of oxalic acid over a free flame there is likely to be some decomposition. Sörensen thought that the trouble was caused by the following hydrolysis, $2\ Na_2C_2O_4 + H_2O = Na_2CO_3 + 2\ HCO_2Na + CO_2$ but Treadwell is of the opinion that the following reaction takes place when the sides of the containing vessel are overheated, $Na_2C_2O_4 = Na_2CO_3 + CO$.

Preparation of Sodium Hydroxide Solution Free from Carbonate

This is best effected as proposed by Küster.* Place about 40 ml. of pure alcohol in a small round-bottomed flask, heat to boiling on the water-bath, and add little by little 2.5 g. of bright metallic sodium, freed from petroleum by rubbing between pieces of blotting-paper. The reaction between the boiling alcohol and the sodium is at first very violent and large amounts of hydrogen and alcohol vapors are evolved. During this time keep the flask covered with a watch-glass. Gradually the reaction begins to diminish and finally stops. In the flask there will be a deposit of sodium alcoholate and some undissolved sodium on account of the insufficient amount of alcohol. Add small quantities of water free from carbon dioxide† a test-tube full at a time. Boil off most of the alcohol and, in order to remove it completely, pass a current of air free from carbon dioxide through the solution until the odor of alcohol can no longer be detected. Cool quickly, adding cold water free from carbon dioxide, immediately place in a liter flask, and dilute to the mark with pure water at 17–18°. This solution will give the same value when titrated with phenolphthalein in a cold

* *Z. anorg. Chem.*, **13**, 134.

† Pass air, freed from carbon dioxide by a soda lime tube, through the boiling water.

solution as when the latter is hot.* With methyl orange correct results are also obtained if the orange color is taken as the end-point.

Such a solution quickly absorbs carbon dioxide from the air. In order to prevent this, place it in a bottle as shown in Fig. 109 which is connected with a soda-lime tube, *N*, and with the buret by means of the tubes *p* and *r*. The buret is filled through the valve at *a*. In this way a solution can be kept free from carbon dioxide for a long time. To determine whether the solution is free from carbonate, make 2 parallel titrations with phenolphthalein as an indicator, one in the cold and the other in the hot solution. If the results agree the solution is free from carbonate. Otherwise it is necessary to prepare a fresh solution or to make a corresponding correction in each analysis after determining the amount of carbonate present as described on p. 485.

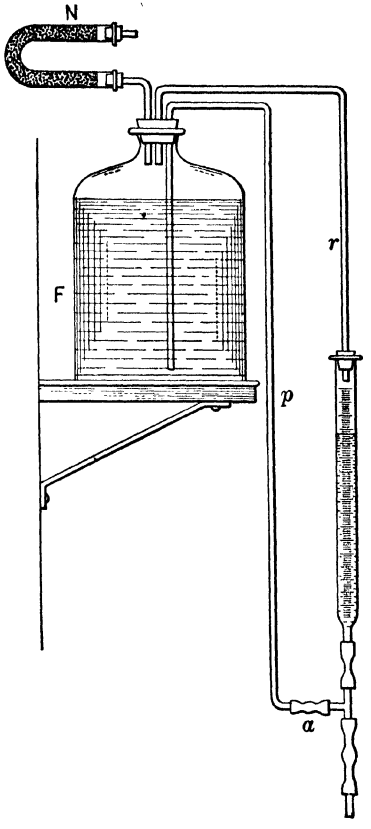


FIG. 109.

In many cases it is better to use a 0.1 normal barium hydroxide solution; as long as it remains clear it is free from carbonate.

Preparation of 0.1 *N* Barium Hydroxide Solution

1000 ml. contain

$$\frac{Ba(OH)_2 + 8\,H_2O}{20} = \frac{315.51}{20} = 15.78\text{ g.}$$

The crystallized barium hydroxide of commerce always contains barium carbonate, so that the solution cannot be prepared by simply weighing out the necessary amount and diluting to 1 liter. Dissolve about 20 g. of the commercial hydroxide in the necessary amount of distilled water within a large flask. Close the flask and shake until the crystals have completely disappeared and a light, insoluble powder of

* Provided the hydrochloric acid solution was prepared with water free from carbonate, otherwise too little acid will be necessary when the titration takes place in the cold.

barium carbonate remains. Allow the solution to stand for 2 days, until the barium carbonate has completely settled, siphon it off into a bottle through which a current of air free from carbon dioxide has been passed for 2 hours previous. Connect this bottle with a soda-lime tube and with a buret as shown in Fig. 109. For the titration, place 50 ml. of 0.1 *N* hydrochloric acid in an Erlenmeyer flask, add a little phenolphthalein and titrate with the barium hydroxide solution. The normality found should be written upon the label. It is not advisable to make the solution exactly 0.1 *N*, for it usually becomes turbid on diluting.

A. ALKALIMETRY

1. Determination of Alkali Hydroxides

Rule. — If the substance to be analyzed is a solid, dissolve an accurately weighed quantity in enough water to make the solution of about the same concentration as that of the acid to be used in the titration. If a solution of an alkali hydroxide in water is to be analyzed, determine the specific gravity of the solution, then dilute accordingly.

(*a*) *Determination of Sodium Hydroxide in Commercial Caustic Soda*

For the titration 0.5 *N* hydrochloric acid solution can be used. As sodium hydroxide absorbs carbon dioxide from the air it is difficult to get a good sample. Place the material in a weighing beaker and weigh out a sample of 4–6 g. into a liter measuring-flask. Dissolve in water that has been freed from carbon dioxide (p. 480) and dilute the cold solution up to the mark. Mix, measure out 100 ml. aliquot portions for the titration with methyl orange as indicator.

Computation. — If 5.001 g. were taken for analysis and in the titration of the aliquot 24.18 ml. of 0.5 *N* acid were used, the percentage purity of the sample can be computed as follows: —

1 ml. of 0.5 *N* HCl = 0.02000 g. NaOH (NaOH = 40.01).

Therefore,

$$\frac{24.18 \times 0.02000 \times 100}{0.5001} = 96.72 \text{ per cent NaOH.}$$

In this particular case, note that the volume of NaOH solution used is exactly one-fourth the per cent of pure NaOH present. This is because the weight of sample in the aliquot (0.5001 g.) was 25 times the value of 1 ml. of 0.5 *N* acid in terms of NaOH. The practice of using an original weight such that the final computation can be done mentally is very common in commercial work.

(*b*) *Determination of Sodium Hydroxide Present in Caustic Soda Solution*

Assume caustic alkali solution of *d.* 1.285 is to be analyzed. The table in the back of this book shows that the solution should contain 25.8 per cent of NaOH by weight. One ml. of solution should contain $1.285 \times 0.258 = 0.3315$ g. NaOH.

If it is desired to know the per cent by weight of sodium hydroxide (or its equivalent, as base) present, weigh out about 3 g. of solution into a small beaker, add 50 ml. of water and titrate with 0.5 normal alkali using methyl orange as indicator.

If it is desired to know the weight of NaOH per ml., measure out 25 ml. of the caustic soda solution, dilute with water at the laboratory temperature to 1000 ml., mix and use 100 ml. for the titration.

Remark. — The titration of alkali hydroxides with methyl orange as an indicator will only give correct results when the alkali hydroxide is free from carbonate, which with commercial material is never the case. The above results are too high, for they represent the total amount of alkali, *i.e.*, the amount of NaOH + Na_2CO_3, though the latter is expressed in terms of NaOH. For an accurate determination of alkali hydroxide in the presence of alkali carbonate, see pp. 485, 486.

(*c*) *Determination of Ammonia in Aqueous Ammonia*

The procedure is the same as under (*b*).

(*d*) *Determination of Ammonia in Ammonium Salts*

Place a weighed quantity of the ammonium salt in the flask *K* (Fig. 32, p. 72),* dissolve in about 200 ml. of water, and treat with 10 ml. of a boiled solution of 10 per cent caustic soda. Distil, and receive the distillate in a known volume of 0.5 *N* acid in the receiver *V*, as described on p. 73. Titrate the excess of acid with 0.5 *N* caustic alkali, using methyl orange as an indicator and calculate the ammonia from the difference between the amount of acid now found and that originally in the receiver.

Computation. — 17.03 g. of commercial ammonium sulfate were dissolved in 500 ml. of water and one-tenth of the solution (1.703 g.) placed in the flask. The distillate was caught in 60 ml. of 0.5 *N* HCl and the excess of acid reacted with *t* ml. of 0.5 *N* NaOH. Since the equivalent weight of NH_3 is 17.03 there is present

$$\frac{(60 - t)\, 0.008515 \times 100}{1.703} = \frac{60 - t}{2} = \text{per cent } NH_3.$$

* Or better, the apparatus shown in Fig. 94, p. 393, can be used.

(e) *Titration of Pyridine Bases**

1000 ml. N. acid = C_5H_5N = 79.08 g. pyridine.

The pyridine bases are so weak that they cannot be titrated with ordinary indicators. If, however, an aqueous pyridine solution is treated with an aqueous solution of ferric chloride, the iron is precipitated as ferric hydroxide:

$$FeCl_3 + 3\,C_5H_5N + 3\,HOH = 3\,(C_5H_5N, HCl) + Fe(OH)_3.$$

If normal sulfuric acid is very carefully added with constant stirring until the precipitate redissolves, each milliliter of the acid required will correspond to $\frac{C_5H_5N}{1000}$ = 0.07908 g. pyridine.

Procedure. — Dissolve 5 ml. of pyridine in 100 ml. of water, treat 25 ml. of the resulting solution with 1 ml. of 5 per cent aqueous ferric chloride solution, and titrate the precipitate of reddish-brown ferric hydroxide with normal sulfuric acid until completely dissolved.

2. Determination of Alkali Carbonates

Alkali carbonates can be titrated in the cold by using methyl orange as an indicator, the end-point being taken as the change from yellow to reddish orange. When fifth-, half-, and normal acids are used this is the correct end-point, but with tenth-normal acids this change is obtained a little too soon, for large amounts of carbonic acid exert a slight action upon the indicator. In this case the difficulty is best overcome by titrating the solution until the orange color is obtained, then heating to boiling to expel the carbon dioxide, cooling, and again titrating until the now yellow solution becomes orange again.† With phenolphthalein, accurate results may be obtained by titrating the hot solution (cf. p. 479). According to Warder,‡ sodium bicarbonate solution reacts neutral toward phenolphthalein in the cold, so that when a sample of sodium carbonate is titrated in the cold, with phenolphthalein as an indicator, an end-point is obtained when the carbonate is changed to bicarbonate:

$$Na_2CO_3 + HCl = NaCl + NaHCO_3.\S$$

* K. E. Schulze, *Ber.*, **20**, 3391 (1887).

† Küster recommends in titrating carbonates with methyl orange, to make a blank experiment to see how much effect an equal amount of water saturated with carbon dioxide has upon the same amount of indicator solution. (*Z. anorg. Chem.*, **13**, 140.)

‡ *Z. Chem.*, **21**, 102.

§ *Z. anorg. Chem.*, **13**, 140.

If the acid is allowed to run upon the carbonate solution, a part of the carbon dioxide from the sodium bicarbonate is likely to be lost, so that too much acid must be added before the end-point is reached. On the other hand, correct results may be obtained if the titration is carried out slowly at 0° in the presence of NaCl (cf. p. 474) and with the solution gently and continuously stirred to prevent local concentration of the acid. This is important, for in this way a convenient method is obtained for determining the amount of hydroxide in the presence of carbonate.

3. Determination of Alkali Carbonate and Hydroxide in the Presence of one Another

(*a*) *Method of C. Winkler*

Of the many methods which have been proposed for this determination that of Winkler is the best.

In one portion determine the total amount of alkali present by titration with acid, using methyl orange as an indicator, and determine the hydroxide in a second portion as follows: To the solution add an excess of barium chloride solution; the following reactions take place:

$$Na_2CO_3 + BaCl_2 = 2\,NaCl + BaCO_3 \text{ (insoluble).}$$
$$2\,NaOH + BaCl_2 = 2\,NaCl + Ba(OH)_2 \text{ (soluble).}$$

Add phenolphthalein and titrate slowly with hydrochloric acid with constant stirring; decolorization is effected as soon as the hydroxide is neutralized before any barium carbonate is dissolved. The amount of acid used corresponds to the amount of hydroxide originally present.

Example:

1. 20 ml. (Na_2CO_3 + NaOH) require T ml. 0.1 N acid for Na_2CO_3 + NaOH,
2. 20 ml. (Na_2CO_3 + NaOH) require t ml. 0.1 N acid for NaOH alone,

so that

20 ml. (Na_2CO_3 + NaOH) require $T - t$ ml. 0.1 N acid for Na_2CO_3; 20 ml. of the solution, therefore, contain $t \times 0.004001$ g. NaOH, and $(T - t) \times 0.005300$ g. Na_2CO_3.

Remark. — It has been proposed to add an excess of barium chloride solution to the mixture of alkali carbonate and hydroxide in a measuring-flask, then dilute to the mark, thoroughly mix, filter through a dry filter and take an aliquot part of the filtrate for the titration. This method, however, will only give accurate results when the water used for the dilution is absolutely free from carbon dioxide, and this will be the case only when it is previously boiled with a current of air free from carbon dioxide passing through it. Further, no attention is paid to the volume occupied by the precipitated barium carbonate, and in the case of a large amount

of the latter, a considerable error is introduced. The method of Winkler does not have these disadvantages. Care must be taken, however, with regard to the addition of the hydrochloric acid in the titration; unless it is added very slowly some of the barium carbonate will be acted upon before the end-point is reached.

(b) Method of R. B. Warder

To the *cold** solution containing phenolphthalein, add 0.1 *N* hydrochloric acid while gently stirring. Decolorization takes place when all of the hydroxide and half of the carbonate are neutralized:

$$NaOH + HCl = NaCl + H_2O,$$
$$Na_2CO_3 + HCl = NaCl + NaHCO_3.$$

To the colorless solution add methyl orange, and again titrate the solution with acid until the other half of the carbonate is neutralized, and the solution turns brownish-red.

If the amount of acid used for the titration with phenolphthalein is represented by T, and that necessary for the titration with methyl orange by t, then

$2t$ ml. of the acid is equivalent to the amount of carbonate present, and $T - t$ represents the amount of hydroxide.

4. Determination of Alkali Bicarbonates

Titrate the cold solution in the cold until an orange color is obtained with methyl orange, or until a colorless solution is obtained by titrating hot with phenolphthalein. (See p. 479.)

5. Determination of Alkali Carbonates in the Presence of Alkali Bicarbonates

(a) Method of C. Winkler

Determine the total alkali in one portion by titration with hydrochloric acid, using methyl orange as an indicator, and in a second portion determine the amount of bicarbonate as follows:

To a definite volume of the solution add an excess of sodium hydroxide; the bicarbonate is changed to neutral carbonate:

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

The solution now contains sodium carbonate with the excess of sodium hydroxide. Determine the latter as described under 3 by adding barium chloride, then phenolphthalein, and titrating until colorless.

* The results are accurate only when the solution is at 0° and NaCl is present. Cf. Küster. *Z. anorg. Chem.*, **13**, 134 (1897).

The acid now used corresponds to the excess of sodium hydroxide added, and if this amount is deducted from the total sodium hydroxide, the corresponding weight of bicarbonate can be computed.

Example:

25 ml. of Na_2CO_3 and $NaHCO_3$ solution required T ml. of 0.1 N acid with methyl orange.

25 ml. of Na_2CO_3 and $NaHCO_3$ solution after treatment with T_1 ml. of 0.1 N NaOH and excess $BaCl_2$, required t ml. of 0.1 N acid with phenolphthalein.

25 ml. of Na_2CO_3 and $NaHCO_3$ required $T_1 - t$ ml. of 0.1 N acid for the $NaHCO_3$ and $T - (T_1 - t)$ ml. of 0.1 N acid for the Na_2CO_3.

25 ml. of the original solution contain

(*a*) $(T_1 - t) \times 0.008401$ g. $NaHCO_3 = (T_1 - t)\, 0.0044$ g. CO_2 as bicarbonate.

(*b*) $(T - T_1 + t) \times 0.005300$ g. $Na_2CO_3 = (T - T_1 + t) \times 0.0022$ g. CO_2 as carbonate.

Remark. — In order to make sure that enough sodium hydroxide solution is present, add the same volume of 0.1 N alkali as there was used of 0.1 N acid in the determination of the total alkali; in this case, then, $T = T_1$, and t, the excess of alkali, corresponds at the same time to the amount of Na_2CO_3 present. The caustic alkali solutions, even when originally free from carbonate, gradually absorb it from the air, so that in every case the amount of carbonate in the alkali should be determined before making the above analysis and a corresponding correction applied to the calculation.

(*b*) *Method of Warder**

Using phenolphthalein as indicator, titrate the solution with hydrochloric acid until colorless, and in this way determine half of the carbonate. Add methyl orange and titrate the solution until a brownish-red color is obtained; in this way the total amount of the bicarbonate together with half of the carbonate is determined. If t represents the amount of acid used in the first titration, and T the total amount used, then:

$2t$ ml. of acid correspond to the amount of carbonate and $(T - 2t)$. ml. correspond to the bicarbonate.

6. Determination of Alkaline-earth Hydroxides

Titrate with phenolphthalein as indicator to a colorless end-point.

7. Determination of Alkaline-earth Carbonates

Dissolve the carbonate in an excess of the standard acid, boil to remove the carbon dioxide, cool and titrate the excess of acid with alkali, using methyl orange as indicator.

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* Cf. *Am. Chem. J.*, **3**, No. 1, and *Chem. News*, **43**, 228.

8. Determination of Alkaline-earth Oxide together with Alkaline-earth Carbonate

This analysis is based upon the fact that calcium carbonate, as well as calcium oxide, neutralizes a solution which is acid to methyl orange and changes the color of the indicator. One mole of $CaCO_3$ reacts with 2 moles HCl before the solution is acid to methyl orange. Toward phenolphthalein calcium oxide is basic, but calcium carbonate is not, and the end-point is reached when all the calcium oxide is neutralized and the calcium carbonate begins to dissolve.

Suppose, for example, it is desired to determine the amount of oxide and carbonate in a sample of "quicklime." Break up the lime into pieces about the size of a pea, weigh out 14 g. and slake with boiled water. Wash the paste into a 500-ml. flask and dilute to the mark with water free from carbon dioxide. After thoroughly mixing, transfer 50 ml. of the turbid liquid to a second 500-ml. flask and again dilute to the mark.

Determination of the Total Calcium. — To 50 ml. (0.14 g. of substance) of the last solution add 60 ml. of 0.1 *N* hydrochloric acid and heat until there is no further evolution of carbon dioxide. Cool, and titrate the excess of acid with 0.1 *N* sodium hydroxide solution, using methyl orange as an indicator. For this purpose t ml. of the latter are required; consequently $60 - t$ ml. of 0.1 *N* acid were necessary to neutralize the calcium hydroxide and calcium carbonate in the 50 ml. of the solution taken for analysis.

Determination of the Calcium Oxide. — Titrate a second portion of the freshly-shaken solution with 0.1 *N* hydrochloric acid added drop by drop to the cold solution, using phenolphthalein as an indicator. Assume that t_1 ml. of the acid were necessary to neutralize the calcium oxide.

Consequently, for the neutralization of the $CaCO_3 + CaO = 60 - t$ ml. of 0.1 *N* acid were required, and for the CaO, t_1 ml. of 0.1 *N* acid were necessary. For the neutralization of the $CaCO_3$, therefore, $60 - (t + t_1)$ ml. of 0.1 *N* acid were necessary.

50 ml. solution (0.14 g. lime) contain:

(*a*) $t_1 \times 0.002805$ g. CaO, (*b*) $[60 - (t + t_1)] \times 0.5005$ g. $CaCO_3$,

and the sample contains

$$\frac{t_1 \times 0.2805}{0.14} = 2\,t_1 \text{ per cent CaO}$$

and

$$\frac{[60 - (t + t_1)] \times 0.5005}{0.14} = \text{per cent } CaCO_3.$$

The above method of titration fails to take into consideration the fact that commercial lime contains more or less magnesia. As a result of coöperative analyses made by the U. S. Geological Survey the Bureau of Chemistry and the Bureau of Standards using seven methods of analysis, Miss Alice I. Whitson has published the following modified Scaife method for the

9. Determination of Available Lime in Quicklime and Hydrated Lime

Weigh 1.4 g. of the carefully-prepared and finely ground lime (passing 100 mesh) into a 400-ml. beaker, add 200 ml. of hot water, cover, heat carefully, and then boil for 3 minutes.

Cool, wash down the cover glass, add two drops of phenolphthalein and titrate with *N* hydrochloric acid, adding the acid dropwise as rapidly as possible and stirring vigorously to avoid local excess of acid. When the pink color disappears in streaks, retard the rate of addition of acid somewhat, but continue until the pink color fades throughout the solution for 1–2 seconds. Note the reading and ignore the return of color.

Repeat the experiment, substituting for the 400-ml. beaker a one liter graduated flask carrying a one-hole stopper fitted with a short glass tube drawn out to a point. Cool, and add dropwise, and with vigorous stirring, 4.5 ml. less acid than before. Call the number of ml. used " A." Grind up any small lumps with a glass rod flattened at one end, dilute to the mark with freshly-boiled distilled water, close the flask with a solid stopper, mix thoroughly for 4–5 minutes and let settle for half an hour.

Pipet off a 200-ml. portion, add phenolphthalein, and titrate slowly with 0.5 *N* hydrochloric acid until the solution remains colorless on standing one minute. Call this additional number of ml. " B." Then the percentage of available CaO = 2 A + 5 B.

10. Determination of Alkaline-earth Bicarbonates

This determination finds a practical application in the determination of the temporary hardness of water.

The hardness of a water is caused by the presence of alkaline-earth salts, either those with strong acids ($CaSO_4$, $MgCl_2$) or bicarbonates. A hard water is recognized by the fact that it gives with a clear soap solution a turbidity or even a precipitate, and considerable soap must be added before a lather is obtained on shaking. In most cases calcium salts, and chiefly calcium bicarbonate, predominate in such a solution, and hardness is usually expressed in parts of calcium carbonate (or calcium oxide) in 100,000 parts of water.

If the solution contains 1 part of calcium carbonate in 100,000 parts of water it is said to possess one degree of hardness (French); if such a water contains n parts of $CaCO_3$ in the same quantity of water it possesses n degrees of hardness. In Germany the hardness is expressed in parts of CaO per 100,000 parts of water, while in England the hardness is expressed in grains of calcium carbonate per Imperial gallon. In the United States hardness is usually expressed in grains of calcium carbonate per U. S. gallon, which is five-sixths as large as the Imperial gallon. One degree of hardness on the French scale = 0.56 degree on the German scale = 0.70 degree on the English scale = 0.585 degree on the U. S. scale. When magnesium salts are present, these are expressed in terms of the equivalent amounts of $CaCO_3$ or CaO. The error caused by this assumption is not great, for the amount of magnesium present is usually small compared with the amount of calcium. If a water containing calcium bicarbonate and calcium sulfate is heated to boiling, the former is decomposed with the precipitation of calcium carbonate,

$$Ca(HCO_3)_2 = H_2O + CO_2 + CaCO_3,$$

while the calcium sulfate remains in solution. In other words, the hardness produced by the presence of alkaline-earth bicarbonates disappears on boiling, and is designated, therefore, as " temporary hardness " to distinguish it from " permanent hardness," which is usually caused by alkaline-earth salts of the stronger acids, usually calcium sulfate. The sum of the temporary and permanent hardness of a water represents the total hardness.

According to O. Hehner, the temporary as well as permanent hardness may be determined accurately by an alkalimetric process.

(*a*) *Determination of Temporary Hardness*

Place 100 ml. of the water to be examined in a white porcelain evaporating-dish, add a few drops of methyl orange and titrate the solution with 0.1 N hydrochloric acid until the first change from yellow to orange takes place. From the amount of hydrochloric acid used the amount of calcium carbonate present can be calculated.

Example:

100 ml. water required 2.5 ml. of 0.1 N hydrochloric acid.

As 1000 ml. of 0.1 N hydrochloric acid neutralize $\frac{CaCO_3}{20} = 5.005$ g. $CaCO_3$, 1 ml. of 0.1 N hydrochloric acid will neutralize 0.005005 g. $CaCO_3$ and 2.5 ml. of 0.1 N hydrochloric acid corresponds to $0.005005 \times 2.5 = 0.0125$ g. $CaCO_3$.

Then if 100 ml. of water contain 0.0125 g. $CaCO_3$, 100,000 ml. of water will contain 12.5 g. $CaCO_3$.

(b) *Determination of the Permanent Hardness*

Treat another portion of 100 ml. of the water with an excess of 0.1 *N* sodium carbonate solution, evaporate on the water-bath to dryness, and take up in a little freshly-boiled, distilled water. Filter off the residue and wash 4 times with hot water. Allow the filtrate to cool and afterwards titrate with 0.1 *N* hydrochloric acid, using methyl orange as indicator. If the amount of hydrochloric acid used for the titration is deducted from the total amount of sodium carbonate added to the water, the difference represents the amount of sodium carbonate required for the precipitation of the alkaline-earth salts of the strong acids.

Example. — 100 ml. of water + 10 ml. of 0.1 *N* Na_2CO_3 were evaporated to dryness, the residue extracted with water, and the filtrate titrated with 0.1 *N* hydrochloric acid; this required 8.7 ml. of HCl. Consequently, for the precipitation of the calcium sulfate 10 − 8.7 = 1.3 ml. of 0.1 *N* Na_2CO_3 were necessary, which corresponds to $1.3 \times 0.005 = 0.0065$ g. $CaCO_3$ per 100 ml. water and 6.5 g. $CaCO_3$ per 100,000 ml. of water.

The permanent hardness amounts to 3.8 U. S. degrees.

Remark. — The above methods of Hehner for the determination of hardness will give reliable results only when the water contains no alkali carbonates in solution, as is usually the case with drinking-waters. For the determination of the amount of alkaline earth present in many *mineral waters* it is obvious that these methods cannot be used.

11. Determination of Alkaline-earth Salts of Strong Acids

The determination is practically the same as was indicated above. The alkaline-earth salt is precipitated by means of an excess of titrated sodium carbonate solution, and after filtration the excess of the latter is determined by titrating back with acid.

Procedure. — A solution containing calcium chloride and hydrochloric acid is to be analyzed. Place it in a measuring-flask, treat with a few drops of methyl orange and with sodium hydroxide solution until the neutral point is reached; after this add an accurately measured amount of sodium carbonate solution. Heat the solution until the precipitated calcium carbonate becomes crystalline, allow to cool, dilute to the mark, mix, filter through a dry filter, and titrate the excess of sodium carbonate titrated in an aliquot part of the filtrate. From the amount of sodium carbonate required for the precipitation of the calcium the amount of the metal can be calculated.

Remark. — Other metals which are precipitated by sodium carbonate can be determined in this way.

B. ACIDIMETRY

Acids are determined either by titration with standard alkali solution or a known amount of the latter is added and the excess titrated with standard acid. The latter method requires more buret readings and is, therefore, less satisfactory than the former.

1. Determination of the Acid Contents of Dilute Mineral Acids (HCl, HNO_3, H_2SO_4)

Determine the density of the acid by means of an areometer and from the tables in the back of this book estimate the approximate amount of acid present. Dilute a weighed amount of the acid so that the solution will have approximately the same concentration as that of the alkali to be used for the titration. Analyze by one of the following methods:

1. Place an accurately-measured portion of the diluted acid (20–25 ml.) in a beaker, add methyl orange, and titrate the solution with sodium hydroxide solution until a yellow color is obtained.

2. Place the dilute solution to be analyzed in a buret and titrate with it a definite volume of normal alkali hydroxide solution.

3. Titrate a definite volume of the diluted acid with 0.1 N $Ba(OH)_2$ solution or with sodium hydroxide free from carbonate, using phenolphthalein as an indicator.*

Example. — For the analysis 0.5 N NaOH was used.

The hydrochloric acid analyzed had at 15° a density of 1.122, corresponding to about 24 per cent HCl by weight.

100 ml. 0.5 N sodium hydroxide are equivalent to 1.823 g. of HCl, and consequently $\frac{1.823}{0.24} = 7.595$ g. of the above acid would be required to make 100 ml. of 0.5 N acid, if it contained exactly 24 per cent HCl. Weigh out about this quantity (say 8 g.), and as the density of the solution is 1.122, this will require $\frac{8}{1.122} = 7$ ml. Place 7 ml. of the acid in a tared, glass-stoppered weighing-tube, weigh the tube and its contents, rinse the latter into a 100-ml. measuring-flask and dilute with distilled water up to the mark. After thoroughly mixing, measure off 25 ml. of the acid and analyze by one of the above methods. If in an analysis the original weight of the acid amounted to 7.962 g. and 25 ml. of the diluted acid required 25.80 ml. of 0.5 N alkali, then 100 ml. would require $25.80 \times 4 = 103.2$ ml. of 0.5 N alkali, corresponding to $103.2 \times 0.01823 = 1.881$ g. HCl. The acid, therefore, contains $\frac{1.881 \times 100}{7.962} = 23.6$ per cent HCl.

Remark. — Instead of weighing out the acid for the analysis, it can be measured and from the per cent by volume found the per cent by weight calculated. As,

* When phenolphthalein is used as an indicator in cold solutions the acids must be diluted with water free from carbonate.

however, the density as determined by an areometer is not very accurate, it is better to weigh the acid. If the density of the acid is taken with a pycnometer, using all necessary precautions (cf. Kohlrausch, *Leitfaden der praktischen Physik*), it is a matter of indifference whether the acid used for the analysis is weighed or measured.

2. Analysis of Commercial Hydrous Stannic Chloride

Stannic chloride, as used for a mordant in dyeing, is obtained as the solid salt $SnCl_4 + 5\,H_2O$, or in a concentrated aqueous solution of about 50° Bé. (*d.* 1.52). The latter is obtained by dissolving metallic tin in hydrochloric acid and oxidizing the stannous chloride formed either with potassium chlorate or potassium nitrate. The preparation should contain no free acid, especially nitric acid, no stannous chloride, and no iron. The substance is, therefore, tested qualitatively for these substances as follows:

For *stannous* chloride, by dissolving in water (or diluting the concentrated solution) and adding mercuric chloride; a white precipitate of mercurous chloride shows the presence of bivalent tin.

For *nitric acid,* by means of ferrous sulfate and concentrated sulfuric acid.

For *sulfuric acid* (caused by the use of impure hydrochloric acid in the preparation of the salt) with barium chloride.

For *iron,* with potassium thiocyanate.

The solid salt $SnCl_4 + 5\,H_2O$, made by treating anhydrous stannic chloride with the calculated amount of water, is usually very pure.

The gravimetric determination of both the tin and the chlorine has been described on p. 289, but here will be given a method for determining the amount of the latter volumetrically.

If stannic chloride is diluted with water, the salt undergoes hydrolysis and the solution reacts acid:

$$SnCl_4 + 4\,HOH \rightleftarrows Sn(OH)_4 + 4\,HCl.$$

Consequently if methyl orange is added to the diluted solution, the acid content can be titrated with sodium hydroxide solution, and from the amount used the chlorine combined with the tin can be calculated, provided no other acid is present. If the stannic chloride was prepared by oxidation with potassium chlorate or nitrate,* the solution will also contain chlorine combined with potassium. The total chlorine can be determined by adding a few drops of neutral potassium chromate

* The potassium nitrate is acted upon by the excess of hydrochloric acid present forming the chloride, and the excess of the acid is afterwards removed by evaporation as much as possible.

solution to the solution which has been titrated with sodium hydroxide and titrating with silver nitrate solution. If in this way more chlorine is found than corresponds to the amount of hydrochloric acid neutralized by the alkali, the difference is expressed in terms of potassium chloride. If, on the other hand, less chlorine is found, the presence of some other acid in the tin solution is assured.

To illustrate the accuracy of such an analysis, the following results will be given: A sample of solid stannic chloride ($SnCl_4 + 5\,H_2O$) was analyzed gravimetrically, as described on p. 289. It was found to contain 42.02 per cent of chlorine and 34.73 per cent of tin.

Two portions were then analyzed volumetrically by titration first with sodium hydroxide and then with silver nitrate:

A. 0.8533 g. of tin salt required 20.06 ml. of 0.5 *N* sodium hydroxide and 20.34 ml. of 0.5 *N* silver nitrate. The total chloride content was therefore

$$\frac{0.03546 \times 0.5 \times 20.35 \times 100}{0.8533} = 42.25 \text{ per cent.}$$

The chloride present as $SnCl_4$ was

$$\frac{0.03546 \times 0.5 \times 20.06 \times 100}{0.8533} = 41.76 \text{ per cent.}$$

B. 0.8383 g. of tin salt required 19.79 ml. of 0.5 *N* sodium hydroxide and 19.92 ml. of 0.5 *N* silver nitrate. This corresponds to 42.12 per cent of total chlorine and 41.84 per cent of chlorine as stannic salt.

The above analysis shows that the tin salt was practically free from potassium chloride by the comparative agreement of the results obtained by titration with sodium hydroxide with those of the silver nitrate titration. In the absence of excess hydrochloric acid, the tin can be determined from the amount of chlorine found:

$$\frac{19.79 \times 0.5 \times 0.02968 \times 100}{0.8383} = 35.13 \text{ per cent tin,}$$

instead of 34.73 per cent as found gravimetrically.

3. Determination of the Acid Content of Fuming Acids

Highly concentrated acids must be always weighed and not measured, in order to avoid loss by evaporation. The weighing is best accomplished by means of the Lunge-Rey pipet, shown in Fig. 110.

Remove the lower tube, introduce 0.5 ml. of water, and weigh together with the dry upper pipet, but leaving the 2 parts unconnected. Close the lower stop-cock, open the upper one, and produce a slight

vacuum in the bulb by sucking through the upper tube and then closing the stop-cock. Dip the dry point of the pipet into the fuming acid (in the case of solid pyrosulfuric acid, first melt it by warming slightly) and open the lower stop-cock. As soon as the widened part of the pipet below the lower bulb is $\frac{1}{2}$ to $\frac{3}{4}$ full, close the stop-cock, taking care that none of the liquid reaches up to it.

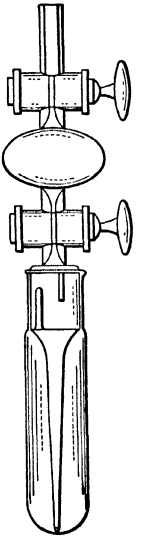


FIG. 110.

Carefully wipe off the acid on the outside of the pipet with filter-paper; connect the two parts of the pipet and again weigh The quantity of acid taken for the analysis should amount to from 0.5–1 g. Dip the point of the pipet into about 100 ml. of distilled water contained in a beaker, and, by opening first the upper stop-cock and then the lower, allow the acid to run into the water. Rinse out the pipet and add the rinsings into the beaker.

If the acid to be analyzed is hydrochloric or sulfuric acid, add methyl orange and titrate the solution with a 0.5 *N* sodium hydroxide. If it is nitric acid, first add an excess of sodium hydroxide, then a little methyl orange, and then titrate with 0.5 *N* hydrochloric acid. In this way the action of the ever-present nitrous acid upon the indicator is avoided. When one of the above pipets is not available, the weighing out of the sample for analysis can be effected as follows: Make a thin-walled bulb with about 1 ml. capacity between two ends of capillary tubing. After weighing, connect the upper piece of capillary tubing with a small, ordinary pipet at the ends of which are attached pieces of rubber tubing, closed with pinch-cocks. Fill the bulb as follows:

Close the lower pinch-cock, open the upper one and produce a vacuum by sucking through the upper tube and then closing the pinch-cock. Dip the lower point of the weighed tube into the acid and open the lower pinch-cock. When the small bulb is one-third full, close the pinch-cock, melt the upper end of the capillary tubing, and, after wiping off the acid from the outside, likewise seal the lower end and weigh the bulb. Place 100 ml. of water in a flask with a closely fitting ground-glass stopper, drop in the weighed bulb and break it by shaking. In this way the very strongest, fuming sulfuric acid can be dissolved in water without loss. On the o her hand, the pipet shown in Fig. 110 is not so good for the weighing out of an acid containing 70 per cent or more of SO_3. If the acid is not too concentrated, this bulb may be emptied as was described for the pipet.

For the analysis of the solid anhydride, Stroof places a little in a

dry weighing tube, and adds concentrated sulfuric acid of known strength until a fuming acid of about 70 per cent SO_3 is obtained. To effect solution, the mixture is warmed to about 30°–40° in a loosely-stoppered bottle. The acid thus obtained is analyzed as above.*

4. Computation of the SO_3 Content of a Fuming Sulfuric Acid

The above titration gives not only the sulfuric anhydride present, but also the ever-present SO_2. In a separate portion, therefore, the amount of the latter should be determined by titration with a 0.1 *N* iodine solution (see Iodimetry), and an equivalent amount subtracted from the total volume of sodium hydroxide used; from the difference the total SO_3 present can be computed.

With regard to the SO_2, the following reactions take place during the titrations:

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O$$
$$H_2SO_3 + H_2O + I_2 = 2\,HI + H_2SO_4.$$

It is to be noted in the first reaction that, although sulfurous acid is a dibasic acid, the end-point is reached, with methyl orange as an indicator, when the first hydrogen atom has been neutralized. The equations show that one mole of sulfurous acid is an equivalent weight in the titration with methyl orange but represents *two* equivalents of iodine. If *T* ml. of 0.5 *N* NaOH were used to titrate all the acid and *t* ml. of 0.1 *N* iodine were used to titrate the sulfurous acid then $T - 0.1\,t$ = volume of NaOH required for all H_2SO_4 (including that formed by the reaction of SO_3 with water).

If the acidity, after deducting that corresponding to the SO_2, is computed in terms of H_2SO_4, the total of $H_2SO_4 + SO_3$ will exceed 100 per cent of the weight of sample and the excess will be H_2O equivalent to the SO_3 present.

Example. — 3.556 g. of fuming sulfuric acid (H_2SO_4, SO_3 and SO_2) were dissolved in 500 ml. of water and the solution mixed.

100 ml. of solution = 5.40 ml. of 0.1 *N* iodine = $5.40 \times 0.003203 = 0.01730$ g. SO_2 = 2.43 per cent SO_2.

100 ml. of solution = 34.40 ml. of 0.5 *N* NaOH.

$34.40 - 0.54 = 33.86$ ml. NaOH required for total H_2SO_4.

$$\frac{33.86 \times 0.5 \times 0.04904}{0.7112} = 116.7 \text{ per cent total } H_2SO_4$$

$$\frac{(116.7 + 2.43 - 100) \times SO_3}{H_2O} = \frac{19.13 \times 80.06}{18.02} = 84.99 \text{ per cent } SO_3$$

$100 - (2.43 + 84.99) = 12.58$ per cent H_2SO_4.

* G. Finch (*Chem. Ztg.*, **1910**, 297) and R. H. Vernon (*ibid.*, **1910**, 702) use a different apparatus and larger samples, thus getting more accurate results.

The original acid contains: 84.99 per cent SO_3, 12.59 per cent H_2SO_4 and 2.43 per cent SO_2.

The calculation of the H_2SO_4 and SO_3 contents can also be made algebraically as follows:

Since the sample contains 0.01730 g. of SO_2 in 100 ml. of solution, there must be $0.7112 - 0.0173 = 0.6939$ g. of SO_3 and H_2SO_4 in the corresponding weight of original sample. If x = weight of SO_3, then $0.6939 - x$ = weight of H_2SO_4 and

$$\frac{H_2SO_4}{SO_3}x + 0.6939 - x = 33.86 \times 0.5 \times 0.04904$$

$$x = 0.6058 \text{ g. } SO_3$$

$$\frac{0.6058}{0.7112} \times 100 = 85.18 \text{ per cent } SO_3.$$

Remark. — The results for SO_3 and H_2SO_4 in the above computations are only good to 3 significant figures and the third figure is doubtful because in subtracting the coefficients of x, one digit is lost. The same difficulty is encountered by any method of computing this analysis. The equivalent weights of SO_3 and H_2SO_4 are too close together and the addition of 10 per cent SO_3 to concentrated sulfuric acid only increases the total SO_3 content about 1.7 per cent.

Preparation of Concentrated Sulfuric Acid Mixtures (M. Gerster)

It is often necessary to prepare fuming sulfuric acid of definite concentration.

Given:

(*a*) Fuming sulfuric acid (*A*) with *a* per cent free SO_3.

(*b*) Sulfuric acid (*B*) with *c* per cent H_2SO_4 and $100 - c$ per cent water.

A fuming acid containing *b* per cent free SO_3 is desired.

To obtain the latter, mix 100 g. of the acid *A* with *x* g. of the acid *B*.

The final mixture $(100 + x)g$ will contain $\frac{(100 + x)\,b}{100}$ g. of free SO_3. The original *a* g. of free SO_3 will react partly with the water in the acid *B* to form H_2SO_4. Therefore, since 1 g. of H_2O reacts with 4.44 g. of SO_3 and since all the water $\left(\frac{x\,(100 - c)}{100} \text{ g.}\right)$ must be converted to H_2SO_4, we have

$$\frac{(100 + x)\,b}{100} = a - \frac{4.44\,(x)(100 - c)}{100}$$

and

$$x = \frac{100\,(a - b)}{444 + b - 4.44\,c} \text{ g. of } B.$$

Example. — How much acid containing 98.2 per cent H_2SO_4 should be mixed with 100 g. of oleum containing 25.5 per cent free SO_3 to give an acid with 19.0 per cent free SO_3? *Ans.* 24.07 g.

5. Titration of Hydroxylamine Salts

Hydroxylamine hydrochloride reacts neutral towards methyl orange and acid towards phenolphthalein. If the latter is added to an aqueous solution of the salt, and the titration is made with 0.1 *N* alkali, the end-point will be obtained when the total amount of acid present has been neutralized by the alkali. It is impossible to determine the amount of free hydrochloric acid present when phenolphthalein is used, but it can be done with methyl orange. Romijn* recommends for the titration of the acid a 0.1 *N* borax solution.

6. Hydrofluoric Acid

1000 ml. normal alkali = HF = 20.01 g. HF.

Hydrofluoric acid can be titrated with phenolphthalein as an indicator, but not with litmus or methyl orange. Measure out the acid into a platinum dish by means of a pipet which is coated with beeswax, add an excess of sodium hydroxide free from carbonate and titrate the excess of the latter in hot solution with an acid of known strength. †

A neutral fluoride can be titrated with fair accuracy by adding neutral ferrichloride solution until an end-point is obtained with KCNS.‡

$$6\ NaF + FeCl_3 = Na_3FeF_6 + 3\ NaCl.$$

Considerable sodium chloride should be added to precipitate the complex salt.

7. Fluosilicic Acid

The titration of this acid may take place according to either of the following reactions:

$$\text{I.}\quad H_2SiF_6 + 2\ KOH = K_2SiF_6 + 2\ H_2O,$$

$$\text{II.}\quad H_2SiF_6 + 6\ KOH = 6\ KF + 2\ H_2O + Si(OH)_4.$$

According to Equation I

1000 ml. normal KOH or $Ba(OH)_2$ = 72.06 g. H_2SiF_6.

Author's Method

If fluosilicic acid is titrated in the cold with caustic potash, using phenolphthalein as indicator, a red color appears after a time, but

* *Z. anal. Chem.*, **36**, 19 (1897). This method has not been tested in the author's laboratory.

† Cf. Winteler, *Z. angew. Chem.*, **1902**, 33.

‡ Greeff, *Ber.*, **36**, 2511 (1913).

disappears later on account of the excess alkali reacting according to the equation:

$$K_2SiF_6 + 4\,KOH = 6\,KF + Si(OH)_4.$$

This last reaction, however, takes place so slowly that it is impossible to obtain a distinct end-point. If, however, the solution is diluted with an equal volume of alcohol, then 2 or 3 drops of phenolphthalein added, it can be titrated with tenth-normal potassium or barium hydroxide. The insoluble potassium or barium fluosilicate separates out and is not acted upon by an excess of the alkali, so that a sharp end point is obtained. Sodium hydroxide forms a soluble salt so that the titration cannot be made with this reagent.

*Indirect Method of Penfield**

Penfield treats the solution to be titrated with an excess of KCl, dilutes with an equal volume of alcohol, and then titrates the hydrochloric acid set free in the reaction,

$$H_2SiF_6 + 2\,KCl = K_2SiF_6 + 2\,HCl,$$

with tenth-normal sodium hydroxide solution, using cochineal as indicator. Methyl red is preferable to the cochineal.

According to Equation II

1000 ml. normal NaOH = 24.05 g. H_2SiF_6.

(*a*) *Method of Sahlbom and Hinrichsen*†

Titrate the solution at the temperature of the water-bath with tenth-normal sodium hydroxide solution, using phenolphthalein as indicator.

(*b*) *Method of Schucht and Möller*‡

Treat the solution to be titrated with an excess of neutral calcium chloride solution (25 ml. of 4 *N* $CaCl_2$) and titrate with tenth-normal sodium hydroxide, using methyl orange as indicator. The following reaction takes place in the cold:

$$H_2SiF_6 + 3\,CaCl_2 + 6\,NaOH = 3\,CaF_2 + 6\,NaCl + Si(OH)_4 + 2\,H_2O.$$

During the titration the solution remains clear, for the CaF_2 and the $Si(OH)_4$ remain in colloidal solution. Phenolphthalein should not be used as indicator, as it is hard to decide upon the correct end-point.

* *Chem. News*, **39**, 179.

† *Ber.*, **39**, 2609 (1906).

‡ *Ber.*, **39**, 3693 (1906).

In the titration of salts of fluosilicic acid, however, the titration must always be carried out with phenolphthalein as indicator:

$$Na_2SiF_6 + 3\ CaCl_2 + 4\ NaOH = 3\ CaF_2 + 6\ NaCl + Si(OH)_4.$$

In this case

1000 ml. of normal NaOH = 47.03 g. of Na_2SiF_6.

8. Determination of Organic Acids

Methyl orange cannot be used for the titration of organic acids, but either phenolphthalein or litmus may be employed. If carbonic acid is present at the same time, the titration can be made in a hot solution (cf. p. 474). It is best to dilute the organic acid with water free from carbon dioxide, add phenolphthalein, and titrate with half-normal barium hydroxide in the cold.

To illustrate. — It is desired to analyze a sample of acetic anhydride. The only impurity that the distilled product is likely to contain is acetic acid, so that it is a question of determining the amount of acid and anhydride in the presence of one another. Such a problem can be solved only by an indirect analysis. Weigh out the mixture in a small glass bulb and drop it into an accurately-measured volume of standard barium hydroxide solution contained in a flask which is connected with a return-flow condenser and a soda-lime tube at the top. Heat gently until the anhydride has dissolved completely; it is thereby changed to acetic acid.

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!\rangle O + H_2O = 2\ CH_3COOH,$$

and the latter is neutralized by the base. After the reaction is complete, add a drop of phenolphthalein and titrate the excess of barium hydroxide with 0.1 N acid. Let x = weight of acetic anhydride and y the weight of acetic acid originally present. Then

$$x + y = p \text{ (original weight)};$$

$$mx + y = q \text{ (weight acetic acid after the action of water)};$$

and

$$x = \frac{1}{m-1}(q - p),$$

In these equations $m = \dfrac{2\ C_2H_4O_2}{C_4H_6O_3} = \dfrac{120.08}{102.07} = 1.176$

and

$$\frac{1}{m-1} = 5.66.$$

Example. — A sample of acetic anhydride was analyzed in this way: Weight of sample, 0.9665 g. Used 200 ml. of $Ba(OH)_2$ solution which was equivalent to 187.8 ml. of 0.1 *N* acid. After the reaction, 6.03 ml. of 0.1 *N* HCl were used. Find percentage of acetic acid and of acetic acid in the commercial preparation.

Ans. 73.04 per cent acetic anhydride and 26.96 per cent of acetic acid.

Remark. — Acetic acid anhydride is also hydrolyzed by water at the ordinary temperature. If a weighed amount of the substance is shaken with water in a flask until no more drops of anhydride are to be recognized and the acetic acid formed is then titrated with barium hydroxide, using phenolphthalein as indicator, correct results are obtained if the water used is entirely free from carbon dioxide. It is always safer, however, to carry out the determination as outlined above.

In some factories the analysis of acetic acid anhydride is carried out by the method of Menschutkin and Wasiljeff. This is based upon the fact that when acetic acid anhydride is treated with freshly distilled aniline, acetanilide is formed in accordance with the following equation.

$$\left.\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\right\rangle O + C_6H_5NH_2 = C_6H_5N(C_2H_3O)H + CH_3COOH$$

whereas acetic acid itself does not form acetanilide under the same conditions. Two or three grams of commercial acetic anhydride are shaken in a dry weighing beaker with from 4–6 ml. of freshly distilled aniline. The anhydride immediately begins to combine with the aniline, liberating considerable heat. After cooling, the solidified contents of the weighing beaker are rinsed by means of absolute alcohol into an ordinary beaker, phenolphthalein is added and the total amount of acetic acid present titrated with half-normal alkali.

We have then, using the same notation as before,

$$\begin{matrix}C_4H_6O_3 & & C_2H_4O_2 & & \\ x & + & y & = & p;\\ mx & + & y & = & q \text{ (acetic acid)};\end{matrix}$$

from which can be computed

$$x = \frac{p-q}{1-m}$$

In this equation

$$m = \frac{C_2H_4O_2}{C_4H_6O_3} = \frac{60.04}{102.07} = 0.5880,$$

and,

$$\frac{1}{1-m} = 2.428.$$

It is true that concordant results are obtained by this method, but they are much too high; in fact as much as 14–16 per cent too high. This is due to the fact that although acetic acid itself does not react with aniline in the cold, it does react very readily when heated. When, therefore, a mixture of acetic anhydride and acetic acid are allowed to remain in contact with aniline, there is so much heat liberated from the reaction between the anhydride and the aniline that a part of the acetic acid itself reacts and takes part in the formation of acetanilide:

$$CH_3CO_2H + C_6H_5NH_2 = H_2O + C_6H_5N(C_2H_3O)H,$$

so that evidently too little acetic acid is found in the subsequent titration and consequently too high values are obtained for the amount of anhydride present.

9. Determination of Sulfurous Acid

For the determination of sulfurous acid by itself, the analysis is best accomplished, as recommended by Volhard, by an iodimetric process, *i.e.*, it is oxidized to sulfuric acid. In many cases, however, it is necessary to titrate the sulfurous acid with alkali hydroxide (cf. 496). Methyl orange should be used as indicator and only one hydrogen in the H_2SO_3 is titrated:

Titration with phenolphthalein gives approximately complete neutralization but the results are reliable only when an excess of neutral hydrogen peroxide is added which oxidizes the sulfurous acid.

10. Determination of Thiosulfuric Acid*

To a large excess of mercuric chloride (20 ml. of the cold, saturated solution for each millimole of $Na_2S_2O_3$) add a measured volume of sodium thiosulfate solution. Shake several times and allow to stand 5 minutes. Then to prevent precipitation of HgO, add 30 ml. of 4 *N* ammonium chloride solution and titrate with 0.1 *N* sodium hydroxide using methyl orange as indicator,

$$(a)\ 2\,Na_2S_2O_3 + 2\,HgCl_2 = 2\,HgS_2O_3 + 4\,NaCl$$
$$(b)\ 2\,HgS_2O_3 + 2\,H_2O = 2\,HgS + 2\,H_2SO_4$$
$$(c)\ 2\,HgS + HgCl_2 = Hg_3S_2Cl_2$$

If too little $HgCl_2$ is present, black mercuric sulfide precipitates and makes the titration difficult.

Polythionates can be titrated similarly,† as the following equations show:

$$2\,K_2S_3O_6 + 3\,HgCl_2 + 4\,H_2O = Hg_3S_2Cl_2 + 4\,KCl + 4\,H_2SO_4$$
$$2\,K_2S_4O_6 + 3\,HgCl_2 + 4\,H_2O = Hg_3S_2Cl_2 + 2\,S + 4\,KCl + 4\,H_2SO_4.$$

According to Eliasberg,‡ the thiosulfates and polythionates can be determined by treatment with a measured quantity of alkali hydroxide solution and neutral hydrogen peroxide, boiling to complete the oxidation and titrating the excess of base with 0.1 *N* acid.

$$Na_2S_2O_3 + 4\,H_2O_2 + H_2O = Na_2SO_4 + 4\,H_2O + H_2SO_4$$
$$Na_2S_4O_6 + 7\,H_2O_2 + 2\,H_2O = Na_2SO_4 + 6\,H_2O + 3\,H_2SO_4.$$

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* W. Feld, *Z. angew. Chem.*, **24**, 290, 1161 (1911); A. Sander, *Ibid.*, **1915**, 9; **1916**, 16.

‡ Kessler, *J. pr. Chem.*, **47**, 42 (1849).

† *Ber.*, **19**, 322 (1866).

11. Determination of Orthophosphoric Acid

NaH_2PO_4 reacts acid toward phenolphthalein, and neutral toward methyl orange, while Na_2HPO_4 is neutral toward the former indicator and basic toward the latter.

Therefore, on titrating free phosphoric acid with alkali one of the following reactions will take place:

1. $H_3PO_4 + 2\,NaOH = Na_2HPO_4 + 2\,H_2O$ (phenolphthalein).
2. $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$ (methyl orange).

The first reaction is not altogether sharp, because pure Na_2HPO_4 is dissociated to a slight extent, so that it becomes alkaline to phenolphthalein:

$$Na_2HPO_4 + HOH \rightleftarrows NaH_2PO_4 + Na\,OH.$$

To prevent this hydrolysis, the titration is best effected in a cold, concentrated solution containing sodium chloride.

12. Alkalimetric Determination of Phosphorus in Iron and Steel*

1000 ml. normal NaOH = 1.349 g. P.

Dissolve 2.00 g. of sample in a 250 ml. Erlenmeyer flask with 100 ml. of 4 *N* nitric acid. Oxidize the phosphorus to phosphoric acid by boiling with 10 ml. of 1.5 per cent potassium permanganate solution until oxide of manganese is precipitated. Dissolve the oxide by adding sulfurous acid, or a sulfite free from phosphorus, and boil to expel the oxides of nitrogen. Add to the cold solution 40 ml. of 6 *N* ammonium hydroxide and 40 ml. of ammonium molybdate solution (see p. 384), stopper and shake for 5 minutes. The temperature of the solution should be 40°. Filter and wash 10 times with a 1 per cent potassium nitrate solution. Return the precipitate to the precipitating vessel, add a measured excess of carbonate-free 0.1 *N* sodium hydroxide and 25 ml. of water, also free from carbon dioxide, and shake or stir until the precipitate is dissolved. Dilute to 100–200 ml. with water free from carbon dioxide, add 3 drops of 0.2 per cent phenolphthalein solution, and discharge the pink color with standard acid. Finish the titration by adding standard alkali until the reappearance of the pink color.

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* The method was proposed by Hundeshagen and also by Manby but was modified by J. O. Handy. The above directions were obtained from the Bureau of Standards.

The reactions that take place in this analysis may be expressed as follows: —

$$3\,Fe_3P + 41\,HNO_3 = 9\,Fe(NO_3)_3 + 14\,NO + 3\,H_3PO_4 + 16\,H_2O$$

$$3\,H_3PO_3 + 2\,KMnO_4 + 2\,HNO_3 = 3\,H_3PO_4 + 2\,KNO_3 + 2\,MnO_2 + H_2O$$

$$MnO_2 + H_2SO_3 = MnSO_4 + H_2O$$

$$12\,(NH_4)_2MoO_4 + H_3PO_4 + 21\,HNO_3 = (NH_4)_3PO_4 \cdot 12\,MoO_3 + 21\,NH_4NO_3 + 12\,H_2O$$

$$(NH_4)_3PO_4 \cdot 12\,MoO_3 + 23\,NaOH = NaNH_4HPO_4 + (NH_4)_2MoO_4 + 11\,Na_2MoO_4 + 11\,H_2O$$

If the reaction takes place at 40° the relation of 1 P to 12 MoO_3 holds very closely. If the solution is hotter more MoO_3 is thrown down. The ammonium molybdate solution should be not over 7 days old.

If T ml. of 0.1 N NaOH and t ml. of 0.1 N HNO_3 were used in the analysis of 2 g. of steel, then

$$\frac{(T - t)\ 0.0135}{2} = \text{per cent phosphorus}$$

Modified Procedure of C. M. Johnson*

Partly because an acid solution of molybdate is not very stable and is useful only when relatively fresh, and partly because of difficulty in the analysis of alloy steels to get accurate results in the presence of vanadium, Johnson prefers to use a neutral solution of ammonium molybdate (cf. p. 381) which keeps indefinitely.

Solutions Required

Standard Sodium Hydroxide and Standard Nitric Acid. — If many analyses are to be made, it is convenient to have these solutions of equal concentration, approximately 0.125 N. Since 1 ml. of normal sodium hydroxide is equivalent to 0.001348 g. of phosphorus, if a sample of steel is taken of which the weight in grams is 13.48 times the normality of the sodium hydroxide (and nitric acid), the per cent of phosphorus in the steel can be determined by subtracting the volume of nitric acid (in millimeters) from the total volume of sodium hydroxide used and moving the decimal point two places to the left.

Dissolve 21 g. of pure sodium hydroxide and 0.1 g. of barium hydroxide in 2 liters of water. Stir the solution well, allow it to stand overnight and filter, or decant off the clear solution. Dilute the solution with 2 liters more of water and mix thoroughly.

* *J. Ind. Eng. Chem.*, 11, 113 (1919).

Dilute 83 ml. of 6-normal nitric acid (*d.* 1.2) with distilled water to a volume of 4 liters and shake well.

Titrate the 2 solutions against one another and dilute the stronger solution until both solutions are equivalent. Standardize the alkali against pure benzoic acid (cf. p. 476) using phenolphthalein as indicator.

The standardization of the alkali should take place in the cold, exactly as in the analysis of the precipitate. A slight error is introduced by the action of carbonic acid in the air, but in determining the phosphorus in steel the result is never good to more than 3 significant figures, so that this error is not serious. The barium hydroxide is added to precipitate any carbonate in the caustic soda. The sodium hydroxide solution should be protected from carbonic acid as much as possible by keeping it in a bottle as described on p. 481.

Ferrous Sulfate Solution. — Dissolve 25 g. of ferrous sulfate or 40 g. of ferrous ammonium sulfate in 180 ml. of concentrated sulfuric acid and 820 ml. of water.

Strong Permanganate. — Dissolve 5 g. of potassium permanganate in 1 liter of water.

Nitrate Wash. — Use 1 g. of potassium nitrate per liter.

Acid Wash. — Dilute 32 ml. of 6 *N* nitric acid to 1 liter.

Ammonium Molybdate. — Place 55 g. of ammonium molybdate and 50 g. of ammonium nitrate in a 400-ml. beaker, add 45 ml. of 6 *N* ammonia and 700 ml. of water. Heat with occasional stirring until nearly all the solid has dissolved. After standing overnight decant off the clear solution through a double filter but do not wash the residue.

Procedure. — Weigh out to the nearest centigram about 1.68 g. of steel and dissolve in 45 ml. of 4 *N* nitric acid heating over a low flame with the beaker covered. If much carbonaceous residue remains, filter and wash the residue 6 times with the acid wash.

Add about 3 ml. of the permanganate and boil 3 minutes to complete the oxidation of the phosphorus and dissolved carbides. Then add just enough of the ferrous sulfate solution to dissolve the precipitated manganese dioxide (3 ml. should be sufficient). Boil out the nitrous fumes and add 15 ml. of 16 *N* nitric acid. Rinse off the cover-glass and sides of the beaker with a little hot water and add to the hot solution 50 ml. of ammonium molybdate solution. Stir vigorously for 2 minutes and allow the precipitate to settle for 20 minutes or a little longer. Filter, wash the precipitate 12 times with small portions of the nitric acid wash and then with the potassium nitrate wash till all acid is removed. This may require 40 washings with a high-phosphorus steel. The washing should be done promptly without allowing

the precipitate to remain dry for any length of time. The outside fold of the filter should have no sour taste when the washing is finished.

Place the filter and precipitate in a 150-ml. beaker and add from a buret enough standard sodium hydroxide solution to cause the yellow color of the precipitate to disappear on macerating the filter to a pulp with a rubber tipped stirring rod. Dilute the solution to about 30 ml., add a drop of phenolphthalein and titrate carefully with nitric acid until the pink color disappears.

13. Determination of Boric Acid

Free boric acid has no action upon methyl orange, consequently alkali borates may be titrated with hydrochloric and nitric acids, using this indicator; with sulfuric acid the results are not as satisfactory, for there is in this case no sharp color change. If phenolphthalein is used as the indicator, the red color fades gradually and the end-point cannot be determined with certainty. If, on the other hand, sodium hydroxide is slowly run into an aqueous solution of boric acid containing phenolphthalein, after some time a pale-pink color is noticeable which becomes deeper on the addition of more alkali. The first pink color is formed before all of the boric acid has been neutralized, for sodium borate is perceptibly hydrolyzed. Free boric acid cannot be titrated by itself, but if, as proposed by Jörgensen,* a sufficient amount of glycerol† (or mannitol‡) is added to the solution, the hydrolysis is prevented, so that when 1 mole of NaOH is present for 1 mole of H_3BO_3 the solution suddenly changes from colorless to red; probably a stronger acid is formed by the addition of the glycerol, the glyceryl-boric acid $(C_3H_5O_2OH)B(OH)$.

If the solution does not contain sufficient glycerol the color change takes place too soon, as can be shown by the addition of more glycerol. If the red color disappears on adding the latter, more alkali is added until it reappears. The right end-point is reached when the red color no longer disappears on the addition of glycerol. Inasmuch as commercial glycerol reacts acid, it must be just neutralized with alkali before being used for this determination. Furthermore, in order to obtain accurate results it is necessary that the solutions should be absolutely free from carbonate.

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* *Z. Nahrungsm.* **9**, 389, and *Z. angew. Chem.*, **1897**, 5.

† *Z. angew. Chem.*, **1896**, 549.

‡ Jones, *Am. J. Sci.* [4] **7**, 147 (1899).

*Application. Determination of Boric Acid in an Alkali Borate Free from Carbonate**

Dissolve about 30 g. of the borate in water free from carbon dioxide, dilute to 1 liter, and determine the total alkali in an aliquot part by titration with 0.5 *N* hydrochloric acid, using methyl orange as an indicator. Take another aliquot part of the borate solution and exactly neutralize by the amount of hydrochloric acid found necessary by the previous titration; by this means the solution will contain free boric acid. After adding about 50 ml. of glycerol for each 1.5 g. of the borate, titrate the solution with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator. When the end-point is reached, add 10 ml. more of glycerol, and this usually causes the solution to become colorless. Again add sodium hydroxide and repeat the process until finally the addition of glycerol causes no further action upon the end-point.

If the borate contained carbonate, neutralize the portion taken for analysis with acid as before, then boil for a few minutes, taking the precaution of connecting the flask containing the solution with a return-flow condenser.† After the carbon dioxide is expelled, wash down the sides of the condenser with water and titrate with sodium hydroxide.‡

For the determination of boric acid in the presence of mineral acid,§ add an excess of potassium iodide and iodate. The mineral acid reacts with the iodide-iodate mixture and sets free iodine (cf. p. 92) but boric acid does not do this. Discharge the iodine color with dilute sodium thiosulfate, added dropwise and avoiding an excess. Then add 1–2 g. of mannitol and titrate with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator.

If considerable mineral acid is present, neutralize the most of it with caustic alkali solution before adding the iodate-iodide mixture.

Determination of Boric Acid in Insoluble Silicates

See E. T. Wherry and W. H. Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

14. Determination of Carbonic Acid

(*a*) *Determination of Free Carbonic Acid*

To determine the amount of free carbonic acid present in a dilute aqueous solution, add an excess of 0.1 *N* barium hydroxide solution,

* M. Hönig and G. Spitz, *Z. angew. Chem.*, **1896**, 549.

† The condenser serves to keep back any boric acid escaping with the steam.

‡ Instead of the glycerol, about 1 g. of mannitol can be used to advantage.

§ Jones, *loc. cit.*

and determine the excess with 0.1 *N* HCl, using phenolphthalein as an indicator:

$$H_2CO_3 + Ba(OH)_2 = BaCO_3 + 2\,H_2O$$
1 ml. of 0.1 *N* HCl = 0.0022 g. CO_2.

(*b*) *Determination of Carbon Dioxide Present as Bicarbonate*

Titrate the solution with 0.1 *N* HCl in the presence of methyl orange:

$$NaHCO_3 + HCl = NaCl + H_2CO_3$$
1 ml. of 0.1 *N* HCl = 0.0044 g. CO_2.

(*c*) *Determination of Carbon Dioxide Present as Carbonate*

Titrate with 0.1 *N* HCl and methyl orange:

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2CO_3$$
1 ml. of 0.1 *N* HCl = 0.0022 g. CO_2.

Dissolve an alkaline earth carbonate in an excess of 0.1 *N* acid and titrate back with 0.1 *N* acid.

(*d*) *Determination of Free Carbonic Acid in the Presence of Bicarbonate*

Titrate one portion with 0.1 *N* HCl, using methyl orange as indicator, and determine the amount of bicarbonate as under (*b*).

Treat a second portion with an excess of barium chloride* then with an excess of barium hydroxide, and titrate the excess of the latter with HCl, using phenolphthalein as indicator. If the volume of 0.1 *N* acid used for the first titration is deducted from the volume of 0.1 *N* barium hydroxide solution found to be necessary in the last titration, the difference multiplied by 0.0022 will give the amount of free carbonic acid.†

(*e*) *Determination of Bicarbonate in the Presence of Carbonate Method of C. Winkler*

See page 486.

15. Determination of Carbonic Acid in the Air. Method of Pettenkofer

Principle. — A large, measured volume of air is treated with an excess of titrated barium hydroxide solution whereby the carbon dioxide is quantitatively absorbed, forming insoluble barium carbonate. Phenolphthalein is added, and the excess of

* The addition of barium chloride is only necessary when free carbonic acid is titrated in the presence of alkali bicarbonates. Without it free alkali would then be formed: $NaHCO_3 + Ba(OH)_2 = BaCO_3 + H_2O + NaOH$.

† This method cannot be used when magnesium salts are present.

barium hydroxide is determined by titration with hydrochloric acid until the solution is colorless. From the amount of base used to absorb the carbon dioxide, the amount of the latter is calculated, 1 ml. of N $Ba(OH)_2$ = 0.022 g. CO_2 = 11.13 ml. of CO_2 gas at 0° and 760 mm. pressure.

Requirements. — 1. A calibrated bottle of 5 liters capacity.

2. Standard solutions of barium hydroxide and hydrochloric acid. Prepare the acid so that 1 ml. = 0.25 ml. CO_2 at 0° C. and 760 mm. pressure; this is accomplished by diluting 224.7 ml. of 0.1 N hydrochloric acid to 1 liter. The barium hydroxide solution should be of about the same strength.

Procedure. — Place the dry bottle, with its capacity etched upon it, in the space from which the air is to be taken, and by means of a bellows, which is connected with a piece of rubber tubing reaching to the bottom of the bottle, change the air in the bottle by making about 100 strokes with the bellows. Stopper the bottle with a rubber cap, and note the temperature and barometer readings.

By means of a pipet, introduce 100 ml. of barium hydroxide solution into the bottle, replace the rubber cap, and gently shake the solution back and forth in the flask for 15 minutes. Pour the turbid liquid into a dry flask, pipet out 25 ml., add phenolphthalein, and slowly run in hydrochloric acid with constant stirring until the solution is colorless. This requires n ml., so that for the 100 ml. of base, $4 \times n$ ml. would be necessary. Determine the strength of the barium hydroxide in terms of acid; 25 ml. of barium hydroxide neutralize T ml. of the standard hydrochloric acid, or 100 ml. would neutralize $4 \times T$ ml. of acid.

Calculation. — Assume the contents of the bottle to be V ml. at $T°$ C. and B mm. pressure. By the introduction of 100 ml. barium hydroxide solution the same volume of air was replaced, so that the amount of air taken for analysis amounts to $(V - 100)$ ml. at $t°$ C. and B mm. At 0° C. and 760 mm. pressure the volume is

$$V_0 = \frac{(V - 100)\ B \times 273}{760 \times (273 + t)}$$

100 ml. of barium hydroxide solution require 4 T ml. HCl, while 100 ml. of the alkali after treatment with V_0 ml. of air require 4 n ml. of the acid and this corresponds to $4\ (T - n) \cdot 0.25 = (T - n)$ ml. CO_2 at 0° C. and 760 mm. pressure.

The volume of CO_2 present in 1 liter of air measured at standard conditions amounts to $\frac{1000 \cdot (T - n)}{V_0}$ ml. of CO_2.

16. Persulfuric Acid

1000 ml. of 0.1 *N* Potassium Hydroxide = $\frac{K_2S_2O_8}{20} = \frac{270.32}{20} = 13.52$ g. $K_2S_2O_8$.

If an aqueous solution of either potassium, sodium, or barium persulfate is boiled for some time, the salt is decomposed in accordance with the equation:

$$2\,K_2S_2O_8 + 2\,H_2O = 2\,K_2SO_4 + 2\,H_2SO_4 + O_2$$

into neutral sulfate and free sulfuric acid. The latter can be titrated with 0.1 *N* potassium hydroxide solution.

Procedure. — Place about 0.25 g. of the persulfate in an Erlenmeyer flask, dissolve in about 200 ml. of water, and boil the solution for 20 minutes. Cool, add methyl orange, and titrate the solution with 0.1 *N* potassium hydroxide. Or, add an excess of the alkali and titrate with 0.1 *N* acid.

The results correspond with those obtained by the ferrous sulfate method (cf. p. 535) provided the persulfate is not contaminated with potassium bisulfate.

Remark. — Ammonium persulfate cannot be analyzed by the above method because when a solution of this salt is boiled, two reactions take place. The principal reaction, to be sure, is

$$2\,(NH_4)_2S_2O_8 + 2\,H_2O = 2\,(NH_4)_2SO_4 + 2\,H_2SO_4 + O_2,$$

but the oxygen is evolved to some extent in the form of ozone and the latter oxidizes a part of the nitrogen, so that besides sulfuric acid, the solution will contain more or less nitric acid.

$$8\,(NH_4)_2S_2O_8 + 6\,H_2O = 7\,(NH_4)_2SO_4 + 9\,H_2SO_4 + 2\,HNO_3.$$

II. OXIDATION AND REDUCTION METHODS

All processes considered under this heading are those in which the substance analyzed is either oxidized or reduced by means of the solution with which the titration is made. When hydrogen is oxidized by oxygen it is changed from the neutral condition to that of a positive valence (or polarity) of one and oxygen is reduced from the neutral condition to a negative valence (or polarity) or two. In this, and all other cases, the equivalent weight of the element used in an oxidation-reduction reaction is the atomic weight divided by the change in polarity. When an atom in any complex molecule is subjected to a change in polarity (oxidized or reduced) the equivalent weight of the molecule is the gram-molecular weight divided by the change in polarity of the oxidized or reduced element. If more than 1 atom of the reactive element is present in the molecule, the molecular weight is divided by the total change in polarity, *i.e.*, by the change in polarity multiplied by the number of atoms undergoing such change (cf. p. 458).

OXIDATION METHODS

A. The Permanganate Methods

When potassium permanganate acts as an oxidizing agent in distinctly acid solution, the manganese is reduced from a valence of +7 to +2, corresponding to a loss of 5 charges in polarity. A normal solution of permanganate, therefore, contains one-fifth mole of $KMnO_4$ = 31.61 g.

For most oxidation analyses 0.1 *N* and rarely 0.5 *N* solutions are used.

The Preparation of 0.1 *N* Potassium Permanganate Solution

was described on p. 96.

Standardization of Permanganate Solution

1. *Against Sodium Oxalate* (Sörensen).*

1000 ml. of 0.1 *N* permanganate solution = 6.701 g. $Na_2C_2O_4$.

Sodium oxalate suitable for standardizing solutions can be obtained from the Bureau of Standards at Washington, D. C. This is the most

* *Z. anal. Chem.*, **42**, 352, 512 (1903); **45**, 272 (1906).

reliable standard of all those that have been proposed. Dry the sample for an hour at 130°. For the standardization McBride recommends* the following procedure.

In a 400-ml. beaker, dissolve 0.25–0.3 g. of sodium oxalate in 200–250 ml. of hot water (80–90°) and add 10 ml. of (1: 1) sulfuric acid. Titrate at once with 0.1 N $KMnO_4$ solution, *stirring the liquid vigorously and continuously.* The permanganate must not be added more rapidly than 10–15 ml. per minute, and the last 0.5–1 ml. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color should be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° by the time the end-point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as stirring rod is most convenient in these titrations, as the variation of temperature is then easily observed.

$$2\,KMnO_4 + 5\,Na_2C_2O_4 + 8\,H_2SO_4 = \\ = K_2SO_4 + 2\,MnSO_4 + 5\,Na_2SO_4 + 10\,CO_2 + 8\,H_2O.$$

Two positive charges are required to oxidize the $C_2O_4^=$ ion to CO_2 gas.

$$C_2O_4^= + 2\oplus = 2\,CO_2.$$

It is evident, therefore, that the equivalent weight of the oxalate anion acid is one-half mole.

2. *Against Oxalic Acid*

Owing to its water of crystallization, oxalic acid, $H_2C_2O_4 \cdot 2\,H_2O$ is not as reliable a standard as the sodium salt. Its equivalent weight is one-half mole = 63.03, the same as when it acts as an acid.

It is sometimes desirable to check up the oxidimetric and alkalimetric standards and oxalic acid, potassium binoxalate, and potassium tetroxalate either as dry salt or in solution can serve for this purpose. The method of titrating is the same as in 1. The equivalent weights of these 3 substances are quite similar as reducing agents but very different as acids. Thus in a liter of aqueous solution the following relationships hold:

---

* *J. Am. Chem. Soc.*, **34**, 393 (1912).

Weight per liter	Normality as Acid	Normality as Reducer
0.5 mole = 63.03 g. $H_2C_2O_4.2\,H_2O$	1 *N*	1 *N*
0.5 mole = 64.06 g. KHC_2O_4	0.5 *N*	1 *N*
0.25 mole = 63.54 g. $KHC_2O_4.H_2C_2O_4.2\,H_2O$	0.75 *N*	1 *N*

3. *Against Metallic Iron*

It was formerly the general practice to standardize permanganate against iron wire particularly when the standard solution was to be used for the titration of iron ores. The practice is not to be recommended because of the readiness with which the material rusts and because a low carbon content influences the results, not always in the same way. If, however, a solution of permanganate is standardized against sodium oxalate and also against iron wire, then the *apparent* iron value of the wire is known and it can be used as a standard. The method is as follows:

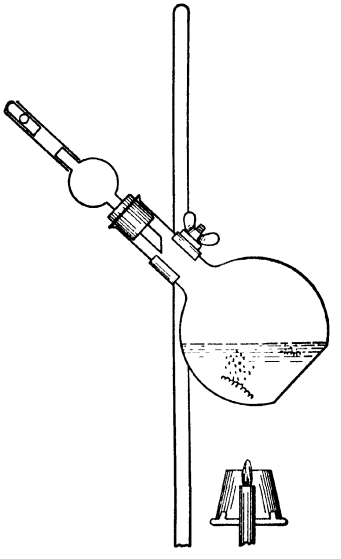


FIG. 111.

Weigh out 0.2 g. of the wire into a 200–250 ml. flask as shown in Fig. 111. Displace the air by introducing a stream of carbon dioxide, which has passed through a bottle containing water and another containing copper sulfate solution (to remove H_2S). Dissolve the wire in 55 ml. of 3.6 *N* sulfuric acid. During the dissolving of the wire, support the flask as shown in the drawing, and with the gas-exit tube closed with a rubber stopper which is connected with a Bunsen valve.* Heat the contents of the flask by means of a low flame until the wire has all dissolved, then boil the solution gently for a short time. Allow to

* A Bunsen valve consists of a short piece of rubber tubing with a cut along a few centimeters of one side, and the outer end of the tubing is closed by a glass rod. This valve prevents the entrance of air from without. A flask larger than 250 ml. capacity is likely to be so thin as to break during the cooling of the iron solution. In Fig. 111, instead of using a glass rod at the end of the valve, a glass tube is used which is sealed at one end, and has a hole on one side. This tube serves to prevent the collapse of the rubber tubing at the place where the slit is formed.

cool, remove the stopper, and titrate with permanganate until a color is obtained which is permanent for 30 seconds.

Instead of using a Bunsen valve, the Contat-Göckel valve may be used as shown in Fig. 112. The funnel contains a cold, saturated solution of sodium bicarbonate, through which the hydrogen from the flask passes. When the flame is removed sodium bicarbonate solution is drawn into the flask, and this causes the evolution of carbon dioxide, which prevents the entrance of more of the solution.

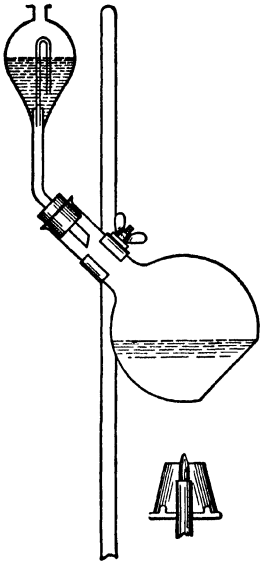


FIG. 112.

4. *Against Sodium Thiosulfate*

See Iodimetry.

5. *Against Hydrogen Peroxide*

See Gasometric Methods.

6. *Against Ferrous Ammonium Sulfate,* $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$

Mohr proposed the use of this salt as a standard and it can be purchased in a high state of purity. The equivalent weight is 392.14 or nearly 6 times as large as that of sodium oxalate. This makes it easier to weigh out a sample accurately to 4 significant figures. The substance is not as reliable a standard because of the danger of losing water of crystallization and of oxidizing. Thus a sample weighed out and allowed to stand in a moist beaker for some time is likely to undergo partial oxidation. The best way to determine whether a sample is suitable is to check up the standardization values obtained with this substance and with sodium oxalate. The gravimetric determination of the iron content is likely to lead to error; usually the values for iron are found a little too high and this gives low results in the standardization.

Procedure. — For the standardization of 0.1 *N* permanganate, weigh out samples of about 1.5 g. to 4 significant figures. Add 10 ml. of 18 *N* sulfuric acid, dilute to 100 ml. and at once titrate.

Permanence of Potassium Permanganate Solutions

A permanganate solution will keep indefinitely, provided it is kept free from dust and reducing vapors.* For very accurate work, how-

* In June, 1899, 1 ml. of a $KMnO_4$ solution = 0.005485 g. Fe; in March, 1900, 1 ml. of the $KMnO_4$ solution = 0.005476 g. Fe. See also Morse, Hopkins and Walker, *Am. Chem. Journ.*, **18**, 401.

ever, it is advisable to standardize the solution frequently. The addition of 10 g. caustic potash per liter increases the stability of the solution.

USES OF PERMANGANATE SOLUTION

1. Determination of Iron

(*a*) Method of Margueritte (1846)

1 ml. of 0.1 *N* $KMnO_4$ corresponds to $\begin{cases} 0.005584 \text{ g. Fe} \\ 0.007184 \text{ g. FeO} \\ 0.007984 \text{ g. } Fe_2O_3 \end{cases}$

In this determination the iron is oxidized from the ferrous to the ferric condition:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O$$

To each 100 ml. of the ferrous salt solution add 5 ml. of sulfuric acid, and at a volume of about 400 titrate in the cold by adding potassium permanganate from a buret with glass stop-cock until a permanent pink color is obtained.

This determination affords very accurate results and is unquestionably one of the best methods for determining iron.

TITRATION OF FERROUS SALTS IN HYDROCHLORIC ACID SOLUTION

The titration of iron in hydrochloric acid solution gives high results unless particular precautions are taken. If dilute permanganate solution is allowed to run into a cold dilute solution of ferrous chloride containing hydrochloric acid, the former is decolorized and the iron is oxidized, but there is noticeable evolution of chlorine.* More permanganate is used up than is necessary to oxidize the ferrous salt to the ferric condition.

If, however, permanganate is run into cold, dilute hydrochloric acid, in the absence of ferrous salt, there is no evolution of chlorine. Furthermore, the presence of a ferric salt does not cause evolution of chlorine. The chlorine, therefore, is not a result of the direct action of the permanganate upon the hydrochloric acid, but is probably due to the oxidation of the ferrous ion to an unstable state of oxidation corresponding to a perchloride, a peroxide, ferric acid or perferric acid.

When permanganate is run into a dilute hydrochloric acid solution containing ferrous chloride and considerable manganous salt, the fer-

* Löwenthal and Lenssen, *Z. anal. Chem.*, **1863**, 329.

rous iron is quantitatively oxidized to ferric iron and there is *no evolution of chlorine.* This was shown by Kessler* in 1863 and by Zimmermann† in 1881. It has since been confirmed by many other chemists.‡

This can be explained as follows: Permanganate ions react with manganous ions to form, as Volhard§ proved, quadrivalent manganese. In this state of oxidation, manganese is unstable in acid solution, but it is reduced more readily by ferrous ions than by chloride ions.

Zimmermann|| suspected, and Manchot's¶ experiments confirm this view, that iron like manganese has a tendency to form unstable compounds as primary oxidation products. If such a compound is formed in the presence of manganous ions, the iron will give up its excess charge to the manganese rather than to chloride ions, provided sufficient manganous ions are present.

According to Manchot there is a tendency in all oxidations to form an unstable compound as the primary oxidation product. When hydrogen burns in air, a little hydrogen peroxide is formed; when sodium burns, sodium peroxide results. In most cases, these primary products are unstable and cannot be isolated because of the readiness with which they are reduced to a more stable condition. When an *acceptor*** is present it will take up the excess charge which is lost when the primary product is reduced; in aqueous solutions in the absence of any other acceptor, free oxygen is evolved.

According to the method of oxidation, iron tends to form different primary states of oxidation. In the direct oxidation of iron by oxygen, the primary oxide appears to be FeO_2; in the oxidation by means of permanganate, chromic acid or hydrogen peroxide, the primary oxidation product appears to contain iron with a valence of 5, whereas iron with a valence of 6 is probably formed if hypochlorous acid is the oxidizer.

Potassium permanganate according to Manchot first causes the formation of quinquevalent iron. If sufficient manganese ions are

* *Pogg. Ann.*, **118**, 779, and **119**, 225.

† *Ber.*, **14**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

‡ For example, J. A. Friend, *J. Chem. Soc.*, **95**, 1228 (1909). C. C. Jones and J. H. Jeffery, *The Analyst*, **34**, 306 (1909).

§ *Ann. Chem. Pharm.*, **198**, 337.

|| *Ber.*, **11**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

¶ *Ann. Chem. Pharm.*, **325**, 105 (1902).

** An *acceptor* is a substance which is not oxidized by oxygen alone, but can be thus oxidized by the aid of some other substance present called an *auto-oxidator.* A substance which tends to be peroxidized may play the part of an acceptor. Cf. Engler, *Ber.*, **33**, 1097 (1900).

present, these play the part of acceptor, but otherwise, in hydrochloric acid solution, some chlorine is formed:

$$3\,MnO_4^- + 5\,Fe^{++} + 24\,H^+ \rightarrow 3\,Mn^{++} + 5\,\overset{+++}{Fe^{++}} + 12\,H_2O$$

$$\overset{+++}{Fe^{++}} + Mn^{++} \rightarrow \overset{++}{Mn^{++}} + Fe^{+++};$$

$$\overset{++}{Mn^{++}} + 2\,Fe^{++} \rightarrow Mn^{++} + 2\,Fe^{+++};$$

$$\overset{+++}{Fe^{++}} + 2\,Cl^- \rightarrow Cl_2 + Fe^{+++}.$$

The action of the manganous sulfate is partly to regulate the reaction between ferrous and permanganate ions, for, according to Volhard, the manganese tends to react with permanganate ions, thus slowing down the reaction between permanganate and ferrous ions. The quadrivalent manganese formed by the action of permanganate on manganous ions, at once reacts with ferrous ions; the manganous ions also act as acceptor toward any iron oxidized above the trivalent state. In both cases it is essential that manganese peroxide does not react with hydrochloric acid very rapidly, and it is necessary, too, that the amount of manganous salt shall greatly exceed the amount of iron present.

Zimmermann suggested a similar explanation, but it seemed to meet with but little approval, so that the hypothesis of Wagner* was quite generally adopted. The latter claimed that the excess of permanganate required for the titration of ferrous chloride in the absence of manganous sulfate was due to the intermediate formation and rapid oxidation of a ferrous-hydrochloric acid, $FeCl_2 \cdot 2\,HCl$.

Manchot's explanation, however, seems to be the better one.

Although it is possible, then, to titrate iron in hydrochloric acid solutions in the presence of manganous sulfate, the method possesses the disadvantage that the end-point cannot be seen so distinctly as when no chloride is present, since ferric chloride forms a much more yellow solution than does ferric sulfate. This difficulty can be overcome by the addition of phosphoric acid, as suggested by C. Reinhardt.†

(*b*) Method of Zimmermann-Reinhardt

Add from 20–25 ml. of manganese sulfate solution (prepared as described below) to a solution of ferrous chloride containing about 15 ml. of 6 *N* hydrochloric acid, dilute to 400 ml. and titrate the cold solution with potassium permanganate added so slowly that the drops can be counted.

* *Zeitschr. f. physikal. Chem.*, **28**, 33.

† *Stahl und Eisen*, **1884**, 709, and *Chem. Ztg.*, **13**, 323.

Take care toward the last not to add a drop of permanganate until the color of the preceding one has disappeared.

Prepare the manganous sulfate solution as follows: Dissolve 67 g. of crystallized manganous sulfate ($MnSO_4 + 4\,H_2O$) in 500–600 ml. of water, add 138 ml. of phosphoric acid (*d.* 1.7) and 130 ml. of concentrated sulfuric acid; dilute the mixture to 1 liter.

If the iron is present as ferric salt, it must be reduced completely to the ferrous condition before it can be titrated with potassium permanganate.

THE REDUCTION OF FERRIC SALTS TO FERROUS SALTS

can be accomplished in a number of different ways.

1. *By Hydrogen Sulfide*

This reduction has already been described on p. 99.

2. *By Sulfur Dioxide*

Nearly neutralize the solution containing the ferric salt with sodium carbonate,* add an excess of sulfurous acid, boil, and pass a current of carbon dioxide through it until the excess of the reagent is completely removed.† Test a drop of the solution with thiocyanate to make sure that the reduction is complete; cool in an atmosphere of carbon dioxide and titrate.

3. *By Metals*

Reduce the acid solution of the ferric salt, contained in a small flask fitted with a Bunsen valve, by heating on the water-bath with small pieces of chemically-pure zinc until the solution is completely colorless and a drop of it, removed by means of a piece of capillary tubing, will no longer give any color with potassium thiocyanate solution. After cooling, pour the solution through a funnel containing a platinum cone (no paper), and wash the undissolved zinc remaining in the funnel several times with boiled water.‡

---

* Ferric salts are not completely reduced by sulfurous acid in the presence of considerable hydrochloric or sulfuric acid.

† It is not advisable to depend upon the sense of smell. Test the escaping gas by passing it through dilute sulfuric acid containing a few drops of 0.1 *N* $KMnO_4$ solution. If the latter is not decolorized at the end of two or three minutes, the excess of sulfurous acid has been removed.

‡ The reduction by means of zinc may be satisfactorily accomplished with a "Jones reductor." Cf. Fig. 113, p. 540.

Remark. — Since zinc often contains iron, a blank experiment must be made by dissolving 3–5 g. in the same way and titrating the solution with permanganate. If iron is present, as shown by the fact that a measurable amount of potassium permanganate is decolorized, the reduction of the ferric salt must be effected by means of a weighed amount of zinc and a correction made for the iron. It is self-evident that in this case the titration must not take place until all of the zinc has dissolved. Instead of zinc, cadmium and aluminium are frequently used.

Remark. — Against this method objections can be raised. In the first place, the fact that a foreign metal is introduced into the solution is in many cases unfortunate. Furthermore, by means of zinc, titanic acid is reduced to Ti^{+++}, only to be oxidized again by the permanganate solution, so that more permanganate solution will then be required than corresponds to the amount of iron present. By means of H_2S or SO_2, titanic acid is not reduced and there is no foreign metal introduced into the solution. Consequently, for accurate mineral analyses, it is necessary to use one of these methods, and in fact the reduction by means of hydrogen sulfide is to be preferred but even then the presence of vanadium causes trouble.

4. *By Stannous Chloride*

This method proposed by Zimmermann and Reinhardt* is especially suited for metallurgical purposes, because it can be accomplished most rapidly.

Principle. — The method depends upon the fact that ferric chloride in hot solution is easily reduced by stannous chloride:

$$SnCl_2 + 2\ FeCl_3 + 2\ HCl = H_2SnCl_6 + 2\ FeCl_2.$$

The complete decolorization of the solution shows the end-point of reduction. The excess of stannous chloride is afterwards oxidized by means of mercuric chloride:

$$SnCl_2 + 2\ HgCl_2 + 2\ HCl = H_2SnCl_6 + Hg_2Cl_2.$$

After this treatment, which consumes but a few minutes, manganese sulfate solution is added and the solution is immediately titrated with potassium permanganate, which is added slowly.

Requirements

(*a*) Stannous chloride solution. Dissolve 50 g. of stannous chloride in 100 ml. of concentrated hydrochloric acid and dilute with water to a volume of one liter.

(*b*) 6 *N* hydrochloric acid.

(*c*) Mercuric chloride solution. A saturated solution of the pure commercial salt in water is used.

(*d*) Manganese sulfate solution. See p. 518.

Procedure. — Dissolve the ferric salt, or iron ore, in 20 ml. of the 6 *N* hydrochloric acid, heat to boiling, remove the flame, and add the stannous chloride solution, *drop by drop*, until the iron solution just becomes colorless, avoiding an excess. Cool to at least room tempera-

* *Loc. cit.*

ture and add quickly 10 ml. of mercuric chloride solution, whereby a slight silky precipitate of Hg_2Cl_2* is formed. After 5 minutes, dilute the solution to about 400 ml., add 20–25 ml. of the manganese sulfate solution and titrate the mixture (very slowly) with potassium permanganate until a pink color permanent for 15 seconds is obtained.

Example: *Determination of Iron in Hematite*, Fe_2O_3. — Weigh out 0.25–0.3 g. of the finely-powdered mineral into a beaker, add 3 ml. of the stannous chloride solution† and 25 ml. of 6 *N* hydrochloric acid. Cover the beaker with a watch-glass and heat its contents nearly to boiling until all of the iron oxide has dissolved and a white sandy residue is obtained. This operation seldom requires more than 10 minutes. Carefully treat the slightly yellow solution with stannous chloride drop by drop until it becomes colorless and analyze the reduced solution as above.

(*c*) Determination of Metallic Iron in the Presence of Iron Oxide

This method is useful for testing *ferrum reductum* which is obtained by the reduction of Fe_2O_3 in a stream of hydrogen. Usually the reduction is not complete and the preparation contains, besides the metallic iron, some oxide, usually assumed to be Fe_3O_4. The value of the preparation depends upon the free iron content.

α. Method of Wilner‡-Merck§

Principle. — The method is based upon the fact that a neutral solution of mercuric chloride dissolves iron according to the equation

$$Fe + HgCl_2 = Hg + FeCl_2$$

while the Fe_3O_4 is not attacked. The solution of ferrous chloride is titrated with permanganate solution.

Procedure. — Place about 0.5 g. of *ferrum reductum* powder.|| in a 100-ml. graduated flask, from which the air has been replaced by CO_2, add 3 g. of solid mercuric chloride and 50 ml. of water. Heat the contents of the flask to boiling, by means of a small flame, and boil gently for a minute. Then fill the flask to the mark with boiled water. Cool to 20° and again carefully bring to the mark. Shake well, and

* If the precipitate produced by mercuric chloride is at all grayish in color, the portion must be thrown away; too large an excess of stannous chloride was used. Moreover, the end-point with permanganate is difficult to see if the solution contains much precipitate.

† The stannous chloride greatly facilitates the solution of the hematite. If too much is used, add strong permanganate drop by drop until the yellow color of ferric chloride appears and then carefully decolorize again.

‡ *Farm. Tidskrift*, **1880**, 225.

§ *Z. anal. Chem.*, **41**, 710 (1902).

|| A coarse powder is not decomposed quantitatively.

allow to stand in the stoppered flask until the precipitate has settled. Pour the liquid through a dry filter, reject the first 15 ml. and catch 20 ml. of filtrate in a flask filled with carbon dioxide. To this add 20 ml. of 7 *N* sulfuric acid, add 10 ml. of manganese sulfate solution,* dilute to 200 ml., and titrate with 0.1 *N* permanganate solution.

β. The Ferric Chloride Method†

Principle. — A neutral solution of ferric chloride dissolves metallic iron with the formation of ferrous chloride:

$$Fe + 2\,FeCl_3 = 3\,FeCl_2$$

If the ferrous chloride formed is titrated with permanganate solution, one-third of the iron thus found corresponds to the weight of metallic iron present in the sample.

Proceed in exactly the same manner as in (*a*) but use 50 ml. of ferric chloride solution, obtained by dissolving 2.5 g. of anhydrous ferric chloride in cold water, instead of the 3 g. of mercuric chloride. Stopper the flask and shake 15 minutes in an atmosphere of CO_2 before diluting to the mark. The ferric chloride should give a clear solution in cold water and be perfectly free from ferrous salt.

2. Determination of Manganese. Method of Volhard‡

$$1000\text{ ml. } N\ KMnO_4 = \frac{3\,Mn}{10} = 16.48\text{ g. Mn.}$$

If an almost boiling, slightly acid solution of manganese sulfate is slowly treated with a solution of potassium permanganate, each drop will cause the formation of manganous acid (H_2MnO_3). Under ideal conditions the reaction takes place as follows:

$$2\,MnO_4^- + 3\,Mn^{++} + 7\,H_2O \rightarrow 5\,H_2MnO_3 + 4\,H^+.$$

According to this equation, therefore, 2 $KMnO_4$ will oxidize 3 g.-atoms of manganese, and as 1 liter of *N* $KMnO_4$ contains 0.2 mole of $KMnO_4$, evidently this amount of permanganate corresponds to 0.3 mole of Mn^{++} = 16.48 g. Mn. Strictly speaking, the normality of the permanganate is different when used to oxidize manganese in slightly acid or neutral solution. In this case the manganese of the permanganate is reduced to the quadrivalent form instead of to bivalent

* See page 518.

† A. Christensen, *Z. anal. Chem.*, **44**, 535 (1905); See also, E. Schmidt, *Chem. Ztg.*, **21**, 700 (1897); A. Marquardt, *Chem. Ztg.*, **25**, 743 (1901); F. Förster and V. Herold, *Z. Elektrochem.* **16**, 461 (1910).

‡ *Ann. Chem. Pharm.*, **198**, 318.

manganese, so that a normal solution should now contain one-third mole of $KMnO_4$. Inasmuch as it is customary to standardize permanganate as outlined on pp. 511–514, it is also customary to consider a *normal* $KMnO_4$ solution as one containing one-fifth of a mole per liter.

A. Guyard, who first determined manganese by this method, assumed that the oxidation took place according to the above equation.

In reality, however, instead of pure manganous acid being precipitated, different acid manganites of varying composition are formed; *e.g.*,

$$4\,KMnO_4 + 11\,MnSO_4 + 14\,H_2O = 4\,KHSO_4 + 7\,H_2SO_4 + 5\,Mn(HMnO_3)_2.$$

Volhard has shown that if calcium, barium, or, better still, zinc salts, are present, manganites of these metals are precipitated. The precipitate, although varying in composition, contains all *of the manganese in the quadrivalent form.*

Procedure. — Of manganese ores with 0–20 per cent of manganese take 3 samples of about 1 g. each for analysis; use half as much with richer ores. Weigh the samples into a large Erlenmeyer flask (800–1000 ml.) and heat with 20 ml. of concentrated hydrochloric acid and 3 g. of potassium chlorate. After all the liberated chlorine has been evolved, dilute with water to 100 ml.

If a dark residue remains which is likely to contain manganese, rinse into a casserole, evaporate to dryness and digest the residue for 10 minutes with 10 ml. of concentrated hydrochloric acid, warming gently. Dilute with hot water, heat to boiling and filter back into the Erlenmeyer flask. Ignite the residue in a platinum crucible, fuse with sodium carbonate, extract the melt with dilute hydrochloric acid, evaporate to dryness to render silica insoluble, digest with acid, dilute and filter into the main solution.

To the dilute hydrochloric acid solution add sodium carbonate solution until the greater part of the acid is neutralized but no permanent precipitate is formed. Then add in small portions, while constantly shaking the flask, a suspension of zinc oxide in water until all the iron is precipitated as shown by the sudden coagulation of the precipitate. Shake well and allow the precipitate to settle. If the supernatant solution is colored brownish, add more zinc oxide but avoid the use of too much of the reagent, which makes the solution appear milky. In that case, add a few drops of hydrochloric acid and boil until the supernatant solution is colorless. Dilute with water to about 400 ml., heat to about 80° and add to the first sample 0.1 *N* permanganate in 5 ml. portions

until, after shaking and allowing the precipitate to settle, the clear liquid appears pink. This is best observed by holding the flask in an inclined position and looking through the top of the solution against a light background. At first considerable difficulty is caused by the brown color of the suspended manganese precipitate but after a little practice the operator learns to recognize the end-point.

The first titration is rarely correct because in this method, unlike other titrations with permanganate, it is advisable to add as much as possible of the reagent at once and it is practically impossible to titrate the first portion within a drop or two of the correct point.

To the second sample, therefore, add nearly as much permanganate at once to the 400 ml. of hot solution and continue with 1 ml. portions of the reagent. In the analysis of the third sample add at the start nearly as much permanganate as was used the second time and continue with 0.2 ml. additions. Call this last titration the correct one. Allow 0.1 ml. of permanganate as a blank and do not attempt to titrate closer than to the nearest 0.1 ml. (= 0.2 mg. of Mn).

Remarks. — Standardize the permanganate solution under the same conditions against 20 ml. of pure manganese sulfate solution (7.550 g. $MnSO_4$* per liter) adding 40 ml. of 20 per cent zinc sulfate solution, 2 drops of 6 *N* hydrochloric acid and diluting to 400 ml. Use 3 samples for the standardization as in the analysis. It will be found that the manganese titer as thus determined is a little higher than the theoretical value as the reaction does not proceed quite quantitatively in the desired direction.

Large quantities of iron increase the volume of permanganate used in the titration. In that case it is best to make up the solution with precipitate to a definite volume and use an aliquot part of the filtered solution. The error produced by the volume of the iron precipitate is not a serious one; although the precipitate appears very bulky, its volume when dry is very small and it is likely to adsorb a little manganese which compensates the first error.

The presence of chromium, cobalt and vanadium also causes error. If the ore does not contain enough iron to combine with the phosphoric, arsenic and vanadic acids, and give a fair-sized precipitate with zinc oxide, add 5–10 ml. of pure ferric chloride solution, containing 6 g. to the liter, before neutralizing.

Determination of Manganese in Steel

(*a*) *Volhard Method*

Weigh out 3 separate portions of 2 g. each into a 300-ml. porcelain casserole. Cover the dish with a watch-glass and dissolve each sample by the gradual addition of 25 ml. of 6 *N* nitric acid. When the sample has dissolved, raise the cover-glass, evaporate to dryness and ignite

* Heat the pure crystals 1 hour at 400–500° before weighing.

carefully to decompose nitrates. Cool and digest the residue with 20 ml. of concentrated hydrochloric acid.

If a dark residue remains undissolved, evaporate the solution to dryness again, dehydrate silica by heating an hour at 125°, warm with 10 ml. of concentrated hydrochloric acid, dilute, filter and wash the residue thoroughly, first with a little hot 2 *N* hydrochloric acid, then with cold water and finally with hot water. If there is no dark colored residue containing graphite, this treatment is unnecessary. A carbonaceous residue is always more or less oxidizable and must beremoved.

Evaporate the hydrochloric acid to dryness. Moisten the residue with 10 ml. of 6 *N* hydrochloric acid, warm, dilute with hot water and transfer to a liter Erlenmeyer flask. Neutralize and titrate as described on p. 522.

(*b*) *The Bismuthate Method**

1000 ml. *N* $KMnO_4$ = 10.99 g. Mn.

This method originated with Schneider,† who used bismuth tetroxide as the oxidizing agent, but as the oxide is difficult to prepare free from chlorides and traces of chloride interfere with the end-point of the titration, it was abandoned by Reddrop and Ramage,‡ who proposed the use of sodium bismuthate, $NaBiO_3$. The product sold under this name is of more or less indefinite composition.

The process is based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by sodium bismuthate.

$$2\,Mn^{++} + 5\,BiO_3^- + 14\,H^+ \rightarrow 2\,MnO_4^- + 5\,Bi^{+++} + 7\,H_2O$$

The permanganic acid formed is very stable in cold solution containing 20–40 per cent of nitric acid. In hot solutions the excess of bismuthate is rapidly decomposed and then the permanganic acid breaks down; as soon as a small amount of manganous salt is formed it reacts with the permanganic acid and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt can be filtered off, an excess of ferrous sulfate added to the clear filtrate and the excess is determined by titrating with permanganate. The end-point is sharp and the method is extremely accurate. The method is inaccurate, however, in the presence of cobalt.§

* A. A. Blair, *J. Am. Chem. Soc.*, **26**, 793. W. Blum. Reprint No. 186 from *Bull. Bur. Standards*, **8** (1912).

† *Ding. poly. J.* **269**, 224.

‡ *Trans. Chem. Soc.*, **1895**, 268.

§ G. E. F. Lundell, *J. Am. Chem. Soc.*, **45**, 2600 (1923).

The following conditions are recommended by Blum. To the cold manganese solution containing 20–40 per cent nitric acid (free from nitrous acid) in a volume of 50–150 ml., add a slight excess of bismuthate (usually 0.5–1.0 g.), agitate thoroughly for about one-half minute, wash down the sides of the flask with 3 per cent nitric acid, filter through asbestos, wash with 100 ml. of 3 per cent nitric acid, add a slight excess of ferrous sulfate, and titrate at once with permanganate.

Procedure for Steels. — Dissolve 1 g. of drillings in 50 ml. of 4 *N* nitric acid and boil to expel oxides of nitrogen. Cool, add 0.5 g. of sodium bismuthate, heat until the pink color disappears and a precipitate of manganese dioxide has formed. Add more bismuthate if manganese dioxide does not precipitate. Clear the solution by adding a few drops of a saturated solution of sodium bisulfite or other suitable reducing agent free from chloride, and boil to expel oxides of nitrogen and sulfur. Cool to 15°, add an excess of sodium bismuthate, agitate and let stand for a few minutes. Add 50 ml. of 3 per cent nitric acid and filter through asbestos. Wash with 3 per cent nitric acid until the washings run through colorless. Add 3 ml. of phosphoric acid (*d.* 1.71) and titrate with ferrous sulfate and potassium permanganate, standardized against Bureau of Standards sodium oxalate.

The ratio of permanganate to ferrous sulfate solution must be determined daily. While not strictly necessary, the determination of this ratio by means of a blank affords a convenient means of testing the efficacy of the filter. The conditions found most satisfactory by Blum are as follows: To 50 ml. of nitric acid (25 per cent by volume), add a small amount of bismuthate; shake and allow to stand a few minutes, dilute with 50 ml. of 3 per cent nitric acid; filter through the asbestos filter and wash with 100 ml. of 3 per cent nitric acid. To the filtrate, which should be perfectly clear, add a volume of ferrous sulfate approximately equal to that to be used in the subsequent determinations (25–50 ml.) and titrate at once to the first visible pink. Even for the most accurate work, no end-point correction is required for this titration, provided only that the solutions are always titrated to the same color, and that about the same volumes are used in the standardization and analyses.

The analysis is accurate within 1 part in 500 if not more than 0.05 g. of manganese is present in the solution when treated with bismuthate. For the rapid solution of ores, a method recommended by Blair has been found convenient. Fuse 1 g. of the ore in a large platinum crucible with 10 g. potassium bisulfate, 1 g. of sodium sulfite and 0.5 g. sodium fluoride. The heating should be very slow till effervescence ceases. After complete fusion cool, heat carefully with 10

ml. of concentrated sulfuric acid, cool, dissolve in water, and make up to a definite volume. The slight precipitate of barium sulfate which usually forms will not influence the manganese determination. Use a suitable aliquot part for the analysis.

Ferrous sulfate and *ferrous-ammonium sulfate* were employed indiscriminately by Blum after it was found that the solutions possessed about the same stability. For use with 0.03 *N* permanganate, the solution can be prepared according to Blair, with 12.4 g. ferrous-ammonium sulfate (or 8.8 g. crystallized ferrous sulfate) and 50 ml. concentrated sulfuric acid per liter of solution. Against 0.1 *N* permanganate, use a solution containing 39.2 g. ferrous-ammonium sulfate (or 27.8 g. ferrous sulfate) and 50 ml. concentrated sulfuric acid per kilogram. If phosphoric acid is added, as recommended by Dudley, it should replace half of the sulfuric acid in the 0.03 *N* solutions, but can be added in addition to the regular amount of sulfuric acid in 0.1 *N* solutions.

Use of Weight Burets. — Simple weight burets can be made by drawing down the tips of cylindrical graduated separatory funnels (50 and 100 ml.). The increased accuracy gained by the use of weight burets is especially desirable in an operation involving a back titration, and also for determining the ratio of the two solutions used. Weighings should be made to 0.01 g., except in the case of the smaller amounts of manganese sulfate solutions, which can be weighed to 0.005 g. or in some cases 0.001 g.

(c) *Williams Method**

$$1000 \text{ ml. } 0.1\ N\ KMnO_4 = \frac{Mn}{20} = 2.747 \text{ g. Mn.}$$

Principle. — If a nitric acid solution of a manganous salt is heated with potassium chlorate, all of the manganese is precipitated as the dioxide:

$$Mn(NO_3)_2 + 2\,KClO_3 + H_2O = MnO_2 \cdot H_2O + 2\,KNO_3 + 2\,ClO_2.$$

The MnO_2 is dissolved in a measured volume of acid ferrous sulfate, and the excess is titrated with tenth-normal permanganate.

Procedure. — Weigh out 2–3 g. of an ordinary steel, about 1 g. of "spiegel" or 0.3–0.5 g. of ferromanganese into a 600 ml. Erlenmeyer flask and dissolve in 60 ml. of 6 *N* nitric acid. To prevent loss by spattering place a small funnel in the neck of the flask. After evaporating the solution to a volume of about 15 ml., add 50 ml. of concentrated nitric acid, and 3 g. of solid potassium chlorate. Boil the

* *Trans. Inst. Min. Eng.*, **10**, 100. See also W. Hampe, *Chem. Ztg.*, **7**, 73 (1883), **9**, 1478 (1885), and *Ukena, Stahl und Eisen*, **11**, 373 (1891).

solution for 15 minutes. Then remove from the source of heat to prevent violent decomposition when chlorate is added and repeat the treatment with 50 ml. concentrated nitric acid and 3 g. of potassium chlorate. Boil for 15 minutes longer. Cool the solution quickly by placing the flask in cold water, and filter off the precipitated manganese dioxide on asbestos,* wash with concentrated nitric acid till free from iron, and with water till free from acid. Transfer the asbestos pad and precipitate back to the original flask, cover with 50 ml. of standardized ferrous sulfate solution (cf. p. 526) and dilute with water to a volume of 200 ml. Shake the contents of the flask with glass beads until all the precipitate is dissolved, and titrate the solution with tenth-normal permanganate.

The amount of manganese present is computed as follows:

50 ml. of ferrous sulfate solution require T ml. 0.1 N $KMnO_4$;

50 ml. of ferrous sulfate after acting with the permanganate acid from a g. of steel require t ml. of 0.1 N $KMnO_4$. Consequently a g. of the substance = $(T - t)$ ml. 0.1 N $KMnO_4$ and

$$\frac{0.002747\,(T - t) \times 100}{a} = \text{per cent Mn.}$$

Remark. — In the analysis of cast iron, the sample should be dissolved in hydrochloric acid and the insoluble residue should be fused with sodium carbonate to see if it contains manganese. If the melt is green, showing manganese, dissolve it in hydrochloric acid and add it to the main solution. Evaporate nearly to dryness and again with nitric acid in order to remove all the hydrochloric acid.

(*d*) Persulfate Method †

In a hot solution of a manganous salt containing silver nitrate as catalyzer, ammonium persulfate causes the formation of permanganic acid (cf. p. 134).

$$2\,Mn^{++} + 5\,S_2O_8^{--} + (Ag^+) + 8\,H_2O \rightarrow 2\,MnO_4^- + 10\,SO_4^{--} + (Ag^+) + 16\,H^+$$

Without the silver salt, manganous acid, H_2MnO_3, is precipitated. In the routine analysis of steel it is customary to discharge the permanganate color by adding standard sodium arsenite. Under the

* A satisfactory filter is obtained by placing a little glass wool in a funnel, and on this a little asbestos, such as is used for Gooch crucibles.

† Walters, *Proc. Eng. Soc. Western Pa.*, **17**, 257 (1901); *Chem. News*, **84**, 239. H. P. Smith, *Chem. News*, **90**, 237 (1904). Rubricus, *Chem. Ztg. Repert.*, **1905**, 247. F. Kunze, *Chem. Ztg.*, **29**, 1017 (1905). H. Marshall, *Z. anal. Chem.*, **43**, 418; 655 (1904).

conditions that usually prevail, the arsenic is completely oxidized to the quinquevalent condition; the manganese of the permanganate is not reduced to colorless manganous salt but to a green solution which contains manganese partly tervalent and partly quinquevalent. The arsenite solution, therefore, must be standardized in exactly the same way it is used in the analysis against permanganate solution or by means of a Bureau of Standards steel.

Procedure. — Dissolve 0.1–0.3 g. of steel in 25 ml. of 4 *N* nitric acid in a small Erlenmeyer flask. Boil gently until the solution is clear and oxides of nitrogen are removed. Add 15 ml. of 0.08 *N* silver nitrate solution and 1 g. of ammonium persulfate. Continue heating 30 seconds after the oxidation begins and bubbles of oxygen rise freely. Cool, and complete the analysis either (*a*) by comparing the color with that produced with a standard steel in the same way or (*b*) by titrating with sodium arsenite solution (1 g. As_2O_3 and 5 g. of Na_2CO_3 dissolved in 15 ml. of hot water and diluted to 3 liters) till the color changes from pink to green.

If a precipitate of hydrated manganese dioxide forms after the addition of persulfate, discard the solution and start a fresh analysis with less material.

3. Determination of Uranium. Method of Belhoubek,* Zimmermann,† Hillebrand‡

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{U}{2} = 119.1 \text{ g. U.}$$

This method is especially suited for testing the purity of a precipitate of U_3O_8 obtained in the analysis of uranium minerals. It is based upon the fact that when U_3O_8 is heated in a closed tube with dilute sulfuric acid at 150°–175° it is readily decomposed according to the equation

$$U_3O_8 + 4\,H_2SO_4 = 2\,UO_2SO_4 + U(SO_4)_2 + 4\,H_2O,$$

forming uranyl and uranous sulfates. The latter compound is oxidized to the former by means of potassium permanganate,

$$2\,KMnO_4 + 5\,U(SO_4)_2 + 2\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + H_2SO_4 + 5\,UO_2SO_4.$$

If it is desired to express the results in terms of the original U_3O_8, of which two-thirds is not oxidized by the permanganate, then 1 ml. N $KMnO_4 = \frac{U_3O_8}{2000} = 0.4218$ g. U_3O_8.

Procedure. — Place 1 g. of U_3O_8 in a tube closed at one end, add 10–15 ml. of 5 *N* sulfuric acid and make the open end of the tube narrower

* *J. pr. Chem.*, **99**, 231.

† *Ann. Chem. Pharm.*, **232**, 285.

‡ *U. S. Geol. Survey*, Bulletin No. 78.

by heating in a blast-lamp and drawing it out somewhat. Remove the air in the tube by inserting a long capillary so that it reaches to the bottom of the tube containing the substance and conducting a current of carbon dioxide through it; finally seal the larger tube without removing the capillary. Heat the tube in a " bomb furnace " at 150–175° until everything has dissolved to a clear green liquid. After cooling, open the tube by making a scratch with a file and touching it with a hot glass rod. Pour the contents into a large porcelain dish, dilute with distilled water to 500–700 ml., and titrate with 0.1 *N* $KMnO_4$ solution until a permanent pink color is obtained.

Remark. — In quantitative analysis uranium is often precipitated as ammonium uranate by ammonium hydroxide (see p. 107), and the uranate dissolves in acids forming uranyl, UO_2^{++} salts. It is possible to reduce the 6-valent uranium of the uranyl salt to 4-valent uranous salt and uranium, like iron, titanium and molybdenum can be determined volumetrically by reducing in a Jones' reductor and titrating with permanganate.* Unfortunately, the oxidation and reduction of the uranium does not always proceed quantitatively in the desired manner. If the solution is passed quickly through the reductor the results are different from those obtained when the solution is added slowly but in the latter case some of the uranium is reduced too far and it is necessary to allow the air to act upon the reduced solution in order to get the uranium into the quadrivalent condition. Atmospheric oxidation, however, may cause oxidation of uranium to uranyl salt. Jander and Reeh † claim to have overcome these difficulties by using as reducing agent a piece of aluminium such as was used in 1922 as a German coin. Their procedure is as follows: —

Make a perforated glass basket of 10–15 ml. capacity from a small test tube. Bend a stout piece of pure sheet aluminium to fit the basket and attach the latter by platinum wire to a glass rod long enough to reach to the bottom of a 400 ml. Erlenmeyer flask. Insert the rod in a two-holed rubber stopper which is also provided with a Bunsen valve (see page 95). Place 100 ml. of uranyl solution, containing not more than 0.2 g. of uranium, in the 400 ml. flask, add 20 ml. of concentrated sulfuric acid and heat to boiling. Remove the flame and insert the stopper carrying the Bunsen valve and the rod with the basket and aluminium in place. Allow the reduction to take place out of contact with air for an hour.

$$3\,UO_2^{++} + 2\,Al + 12\,H^+ \rightarrow 3\,U^{++++} + 2\,Al^{+++} + 6\,H_2O.$$

Raise the stopper and add a little sodium bicarbonate solution, to fill the flask with carbon dioxide. With a stream of water from a wash bottle, rinse off the rod, the glass basket and the excess aluminium and titrate with 0.1 *N* $KMnO_4$.

$$5\,U^{++++} + 2\,MnO_4^- + 2\,H_2O \rightarrow 5\,UO_2^{++} + 2\,Mn^{++} + 4\,H^+.$$

4. Determination of Oxalic Acid

$$1000\text{ ml. } N\ KMnO_4 = \frac{H_2C_2O_4 \cdot 2\,H_2O}{2} = 63.03\text{ g. } H_2C_2O_4 \cdot 2\,H_2O.$$

The procedure is exactly the same as was described under the standardization of permanganate by means of sodium oxalate (p. 511).

* O. S. Pulman, Jr., *Am.. J. Sci.* [4] **16**, 229.
† *Z. anorg. allgem. Chem.* **129**, 293–301 (1923).

5. Determination of Calcium

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{Ca}{2} = 20.04 \text{ g. Ca.}$$

Precipitate the calcium as described on p. 81 in the form of its oxalate, filter and wash with hot water. Transfer the moist precipitate to a beaker by means of a stream of water from the wash-bottle, and dissolve the precipitate remaining on the filter, allowing hot 2 *N* sulfuric acid to pass through it several times. To the turbid solution in the beaker, add 20 ml. of 18 *N* sulfuric acid, dilute with hot water to a volume of 300–400 ml. and titrate the oxalic acid with 0.1 *N* $KMnO_4$ solution.

6. Determination of PbO_2 in Minium [Red Lead, Pb_3O_4]. Method of Lux*

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{PbO_2}{2} = 119.6 \text{ g. } PbO_2 = 342.8 \text{ g. } Pb_3O_4.$$

Principle. — If lead peroxide (PbO_2) is treated with oxalic acid or sodium oxalate in acid solution, the latter is oxidized according to the following equation:

$$PbO_2 + C_2O_4^{=} + 4\,H^+ \rightarrow Pb^{++} + 2\,CO_2 + H_2O.$$

If the decomposition takes place with a measured amount of titrated oxalic acid solution and the excess of the latter is titrated by means of potassium permanganate solution, the difference shows the amount of oxalic acid necessary to effect the reduction of the lead peroxide.

Procedure. — Weigh out about 0.25 g. of minium (red lead) into a porcelain dish and heat with 20–30 ml. of 2 *N* nitric acid. The original oxide is thereby changed into soluble lead nitrate and brown, insoluble H_2PbO_3:

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + H_2O + H_2PbO_3.$$

After the sample is dissolved, add 50 ml. of 0.2 *N* oxalic acid, heat the solution to boiling, and titrate hot with 0.2 *N* $KMnO_4$. If *t* ml. of 0.2 *N* $KMnO_4$ solution were used, then $50 - t$ ml. of 0.2 *N* $H_2C_2O_4$ were necessary for the reduction of the amount of PbO_2 contained in the minium (*a* g.) taken for analysis. There is present, therefore,

$$\frac{(50 - t) \times 2.392}{a} \text{ per cent } PbO_2 \text{ or } \frac{(50 - t) \times 6.856}{a} = \text{per cent } Pb_3O_4.$$

The Diehl-Topf iodometric method to be described later has been adopted by the American Society of Testing Materials for the analysis of red lead.

* *Z. anal. Chem.*, **19**, 153.

7. Determination of MnO_2 in Pyrolusite

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{MnO_2}{2} = 43.47 \text{ g. } MnO_2.$$

*(a) Method of Levol and Poggiale, Modified by G. Lunge**

After drying at 120° to constant weight, place 1.087 g. of the finely-powdered pyrolusite in a 250-ml. flask which is provided with a Contat valve (see p. 514). Expel the air by conducting CO_2 into the flask, and then add 75 ml. of the ferrous sulfate solution, prepared as described below, close the flask, and heat its contents over a small flame until there is no longer any dark-colored residue. Cool quickly, dilute with 200 ml. of water, and titrate the excess of ferrous sulfate with 0.5 *N* $KMnO_4$ solution. Immediately before the analysis, determine the titer of the ferrous sulfate solution by taking 25 ml. of it, diluting to 200 ml., and titrating with permanganate.

By the treatment of the pyrolusite with ferrous sulfate, the following reaction takes place:

$$MnO_2 + 2\ FeSO_4 + 2\ H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2\ H_2O.$$

The computation of the percentage of MnO_2 is as follows:

75 ml. $FeSO_4$ solution..... require T ml. 0.5 *N* $KMnO_4$
75 ml. $FeSO_4$ + 1.087 g. pyrolusite.... " t ml. 0.5 *N* $KMnO_4$
$\therefore$ 1.087 g. pyrolusite are equivalent to $T - t$ ml. 0.5 *N* $KMnO_4$

corresponding to $(T - t) \times 0.02173$ g. MnO_2 and in percentage

$$\frac{(T - t) \times 0.02173 \times 100}{1.087} = 2\ (T - t) \text{ per cent } MnO_2.$$

Prepare the ferrous sulfate solution as follows: slowly pour 200 ml. of concentrated sulfuric acid, with stirring, into 500 ml. of water and while the mixture is still hot add 100 g. of powdered $FeSO_4 \cdot 7\ H_2O$ crystals; on stirring, the salt should dissolve within a few minutes. Dilute the solution to one liter. When cold it is ready for use.

(b) The Oxalic Acid Method of Fresenius-Will, Modified by Mohr†

Heat about 0.4 g. of finely-powdered and dried pyrolusite on the water-bath with 50 ml. of 0.2 *N* oxalic acid, or the equivalent weight of pure sodium oxalate, and 20 ml. of 7 *N* sulfuric acid until no more black particles remain undissolved. Dilute the solution with 200 ml.

* *Chem.-techn. Untersuchungsmethoden.*

† Fresenius-Will carried out the analysis in an alkalimeter and determined the CO_2 evolved by loss in weight.

of hot water and titrate with 0.2 N $KMnO_4$ solution. The reaction which takes place between the manganese dioxide and the oxalic acid is expressed by the following equation:

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2\,CO_2 + 2\,H_2O.$$

1 ml. 0.2 N $KMnO_4$ = 1 ml. 0.2 N $H_2C_2O_4$ = 0.0087 g. MnO_2.

8. Determination of Formic Acid

(a) *Method of Lieben**

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{3 \times HCOOH}{10} = 13.80 \text{ g. } HCOOH.\dagger$$

In cold *acid* solutions permanganate reacts very slowly with formic acid, and in a hot solution the latter is lost by volatilization, so that the titration in open vessels is impossible; in *alkaline* solutions, on the other hand, the oxidation takes place readily and quantitatively in the cold:

$$2\,KMnO_4 + 3\,HCO_2K = 2\,K_2CO_3 + KHCO_3 + 2\,MnO_2 + H_2O.$$

In this reaction the permanganate is reduced only to the quadrivalent condition so that it has only three-fifths of its oxidizing power as determined in the standardization. Hence the weight of formic acid equivalent to 1 ml. of N permanganate (normal against sodium oxalate) is $\frac{3}{5} \times \frac{HCO_2H}{2000}$.

Procedure. — Neutralize the formic acid by an excess of sodium carbonate, and allow permanganate to run into the hot sodium formate solution until the clear liquid above the precipitate is colored pink (cf. p. 521).

(b) *Method of H. C. Jones*‡

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{HCO_2H}{2} = 23.01 \text{ g. formic acid.}$$

Add an excess of permanganate to the alkaline solution of the formate, heat 5–10 minutes on the water-bath, make acid with 6 N sulfuric acid, add an excess of 0.1 N oxalic acid solution and titrate the excess of oxalic acid with permanganate.

If T = total volume of 0.1 N permanganate used and t the volume of 0.1 N oxalic acid then

$$(T - t)\,0.002301 = \text{weight of formic acid.}$$

(c) *Method of Blackadder*§

Proceed exactly as in (*b*) but after heating on the water bath, add 2–3 g. of potassium iodide, neutralize with 6 N hydrochloric acid, add

* *Monatshefte*, **14**, 746, and **16**, 219.

† *Ber.*, **10**, 1075 (1877).

‡ *Am. Chem. J.*, **17**, 539.

§ *Dissertation*, Zürich, 1911.

15 ml. in excess and titrate the liberated iodine with 0.1 N thiosulfate. If T is the volume of 0.1 N permanganate used and t the volume of 0.1 N thiosulfate, the computation is the same as under (*b*).

9. Analysis of Nitrous Acid (Lunge)*

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{HNO_2}{2} = \frac{47.018}{2} = 23.51 \text{ g. } HNO_2.$$

On account of the volatility of nitrous acid, measure out the aqueous solution of the nitrite, or the solution of nitrous acid in concentrated sulfuric acid (nitrose), from a buret into 400 ml. of 0.75 N sulfuric acid containing a known volume of permanganate solution, warmed to 40°. Have the tip of the buret dipping below the surface of the acid permanganate solution, and stir constantly. The nitrous acid is thereby oxidized to nitric acid:

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3,$$

and the decolorization of the solution shows the end-point. Toward the end the nitrous acid must be added slowly, for the change from red to colorless requires some time.

10. Analysis of Hydrogen Peroxide

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{H_2O_2}{2} = 17.01 \text{ g. } H_2O_2.$$

Place 10 ml. of commercial 3 per cent hydrogen peroxide in a 100-ml. measuring-flask, dilute to the mark with water, and, after thoroughly mixing, transfer 10 ml. (= 1 ml. of the original solution) to a beaker, and dilute with water to a volume of 300–400 ml. After adding 20–30 ml. 7.5 N sulfuric acid, titrate the solution with 0.1 N $KMnO_4$ until a permanent pink color is obtained. The following reaction takes place:

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Frequently it happens that the first drop of the permanganate causes a permanent coloration of the solution. This shows that either not enough sulfuric acid is present, or else there is no more hydrogen peroxide left in the solution. In this case add a little more sulfuric acid, when if the coloration still remains the preparation is surely spoiled, as can be shown by the titanic or chromic acid tests (cf. Vol. I).

The amount of hydrogen peroxide is expressed either as per cent by weight or as per cent by volume.

* *Ber.*, **10**, 1075 (1877).

Example. — 10 ml. of the above-mentioned dilute solution of hydrogen peroxide (= 1 ml. of the original solution) required 17.86 ml. of 0.1 N $KMnO_4$ solution, corresponding to $17.86 \times 0.001701 = 0.03038$ g. H_2O_2. As the specific gravity of the original hydrogen peroxide solution can be assumed to be 1, it therefore contains 3.04 per cent H_2O_2.

When expressed in "per cent by volume" the result shows how many cubic centimeters of oxygen can be obtained from 100 ml. of the solution.

In this case 100 ml. of the hydrogen peroxide solution contain 3.04 g. of H_2O_2 and, on being decomposed, 2 moles of H_2O_2 sets free 1 mole of O_2.

$$2\,H_2O_2 = 2\,H_2O + O_2,$$

or 22.39 liters of oxygen at 0° C. and 760 mm. pressure; consequently 3.04 g. H_2O_2 will evolve $x = \frac{3.04 \times 11200}{34.02} = 1000$ ml. oxygen measured under standard conditions of temperature and pressure.

100 ml. of the commercial hydrogen peroxide, therefore, will evolve 1000 ml. of oxygen, *i.e.*, 10 times its own volume. This is sometimes designated as 10 volume hydrogen peroxide.

11. Analysis of Barium Peroxide

$$1000 \text{ ml. } N\ KMnO_4 = \frac{BaO_2}{2} = 84.685 \text{ g. } BaO_2.$$

Weigh 0.2 g. of the substance into a 400-ml. beaker, cover with 300 ml. of cold water, and add with constant stirring, 20–30 ml. of 2 N hydrochloric acid. When all the BaO_2 has dissolved, titrate the solution with 0.1 N $KMnO_4$. The addition of H_2SO_4 is not advisable, as the precipitated $BaSO_4$ is likely to enclose some BaO_2 which will then escape the titration.

Another method for the analysis of BaO_2 has been proposed by Kassner.*

12. Analysis of Potassium Percarbonate

$$1000 \text{ ml. } N\ KMnO_4 = \frac{K_2C_2O_6}{2} = 99.10 \text{ g. } K_2C_2O_6.$$

Weigh 0.25 g. of potassium percarbonate into 300 ml. of cold, N sulfuric acid, in which it dissolves with vigorous evolution of carbon dioxide and formation of an equivalent amount of hydrogen peroxide:

$$K_2C_2O_6 + 2\,H_2SO_4 = 2\,KHSO_4 + 2\,CO_2 + H_2O_2.$$

Titrate the latter with 0.1 N potassium permanganate.

13. Analysis of Persulfates (Persulfuric Acid, $H_2S_2O_8$)

$$1000 \text{ ml. } N\ KMnO_4 = \frac{R_2S_2O_8}{2} \begin{cases} 97.07 \text{ g. } H_2S_2O_8 \\ 114.1 \text{ g. } (NH_4)_2S_2O_8 \\ 135.2 \text{ g. } K_2S_2O_8 \end{cases}$$

* *Arch. Pharm.*, **228**, 432.

A solution of persulfuric acid does not reduce permanganate, nor does it react with titanic acid; on the other hand it oxidizes ferrous salts immediately in the cold to ferric salts, and by means of this behavior it can be easily determined. The ammonium and potassium salts are now commercial products, and are analyzed as follows: Weigh 0.3 g. of the salt into a flask fitted with a Bunsen valve, replace the air by carbon dioxide, add 30 ml. of a freshly titrated solution of ferrous sulfate, and then 200 ml. of hot water. Close the flask and rotate its contents. The salt dissolves without difficulty, and the ferrous sulfate is oxidized:

$$H_2S_2O_8 + 2\ FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4.$$

After all of the salt has dissolved, cool the contents of the flask by placing the flask in cold water, and titrate the excess of ferrous salt with 0.1 *N* $KMnO_4$.

The ferrous sulfate must be added to the persulfate, and then the hot water. If the hot water is added first, the persulfate is decomposed somewhat and the results obtained will be low. In this way it is found that:

30 ml. ferrous sulfate solution require *T* ml. 0.1 *N* $KMnO_4$ solution.

30 ml. ferrous sulfate + *a* g. persulfate require *t* ml. 0.1 *N* $KMnO_4$ solution.

Consequently *a* g. of persulfate correspond to $(T - t)$ ml. 0.1 *N* $KMnO_4$.

In the case of the potassium salt, since 1000 ml. *N* $KMnO_4$ = 135.2 g. $K_2S_2O_8$, and 1 ml. 0.1 *N* $KMnO_4$ = 0.01352 g. $K_2S_2O_8$, we have: $(T - t) \times 0.01352$ g. $K_2S_2O_8$ in *a* g. of the commercial salt, or in per cent: $\frac{1.352\ (T - t)}{a}$ = per cent $K_2S_2O_8$.

With the ammonium salt the factor becomes 0.01141 instead of 0.01352.

The ferrous sulfate necessary for this determination is prepared as described on p. 531.

Persulfates may also be analyzed very satisfactorily by means of oxalic acid.* When a sulfuric acid solution of a persulfate is treated with oxalic acid alone, there is no perceptible reaction. On adding a small amount of silver sulfate as catalyzer, however, a lively evolution of carbon dioxide takes place, and at the water-bath temperature the reaction is soon completed.

$$H_2S_2O_8 + H_2C_2O_4 = 2\ H_2SO_4 + 2\ CO_2.$$

The excess of the oxalic acid can be titrated with permanganate.

Procedure. — Place 0.5 g. of the persulfate in a 400-ml. Erlenmeyer flask, add 50 ml. of 0.1 *N* oxalic acid solution, and 0.2 g. of silver sulfate dissolved in 20 ml. of 10 per cent sulfuric acid. Heat the mixture on the water-bath until the evolution of carbon dioxide ceases; this requires not more than 15 or 20 minutes. Dilute the solution to about 100 ml. with water at about 40° and titrate with 0.1 *N* permanganate.

14. Determination of Hydroxylamine (Raschig)†

$$1000\text{ ml. } N\ KMnO_4 = \frac{NH_2OH}{2} = 16.52\text{ g. } NH_2OH.$$

Principle. — Hydroxylamine is oxidized in hot acid solution by means of ferric salts to form nitrous oxide and an equivalent amount of ferrous salt:

$$2\ NH_2OH + 4\ Fe^{+++} \rightarrow 4\ Fe^{++} + N_2O + 4\ H^+ + H_2O.$$

* R. Kempf, *Ber.*, **38**, 3965 (1905).

† *Ann. Chem. Pharm.*, **241**, 318.

The quantity of ferrous salt is determined by titration with 0.1 *N* potassium permanganate.

Procedure. — Place 0.1 g. of the hydroxylamine salt in a 500-ml. flask and dissolve in a little water. Add 30 ml. of a cold, saturated solution of ferric-ammonium alum and 10 ml. of 7.5 *N* sulfuric acid. Heat the contents of the flask to boiling and keep at this temperature for 5 minutes. Then dilute the solution with distilled water to a volume of about 300 ml. and immediately titrate with permanganate solution.

Remark. — If only slightly more than the theoretical amount of the ferric salt is added, the oxidation of the hydroxylamine does not take place entirely in accordance with the above equation, but part of the substance is oxidized to nitric oxide:

$$2\ NH_2OH + 6\ Fe^{+++} \rightarrow 6\ Fe^{++} + 2\ NO + 6\ H^+,$$

and it is then impossible to obtain exact results.

15. Determination of Ferrocyanic Acid (de Haën)*

1000 ml. *N* $KMnO_4$ = 1 mole $K_4Fe(CN)_6$ = 368.3 g. $K_4Fe(CN)_6$.

Principle. — By oxidation in acid solution, ferricyanic acid is formed from ferrocyanic acid:

$$5\ H_4Fe(CN)_6 + MnO_4^- + 3\ H^+ \rightarrow 5\ H_3Fe(CN)_6 + Mn^{++} + 4\ H_2O.$$

Good results are obtained only when the solution is dilute and contains considerable acid. If too much ferrocyanide is present, a precipitate of $K_2Mn[Fe(CN)_6]_2$ is likely to form. In this case it is necessary to make sure that sufficient acid is present and to dilute the solution. The end-point is a change from greenish yellow to yellowish pink.

Procedure. — Dissolve 10 g. of potassium salt in 1 liter of water. Mix and transfer 50 ml. to a white porcelain dish. Add 100–150 ml. of water and 10–20 ml. of 7.5 *N* sulfuric acid and titrate with 0.1 *N* permanganate.

16. Determination of Ferricyanic Acid

1000 ml. *N* $KMnO_4$ = 1 mole $K_3Fe(CN)_6$ = 329.2 g. $K_3Fe(CN)_3$.

Principle. — The potassium ferricyanide is reduced in alkaline solution to potassium ferrocyanide, and the latter is titrated with permanganate.

Procedure. — In a 300-ml. measuring flask dissolve 6.0 g. of the ferricyanide in water, make the solution alkaline with potassium hydroxide, heat to boiling, and add an excess of a concentrated ferrous sulfate solution. At first brown ferric hydroxide is precipitated, later black ferrous-ferric hydroxide is formed, and this shows the completion of the reaction.

* *Ann. Chem. Pharm.*, **90**, 160.

Cool, dilute the contents of the flask with water to the mark, filter through a dry filter (after mixing), reject the first runnings and take 50 ml. of the filtrate (= 1 g. of the substance) for the titration with 0.1 N $KMnO_4$ solution.

17. Determination of Chloric Acid

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{RClO_3}{6} = \begin{cases} 20.43 \text{ g. } KClO_3 \\ 17.74 \text{ g. } NaClO_3 \end{cases}$$

Dissolve 5 g. of potassium chlorate, or 4 g. of the sodium salt, in water, and dilute the solution to 1 liter. After thoroughly mixing, transfer 10 ml. to a flask fitted with a Bunsen valve and expel the air from the flask by a current of carbon dioxide. After this add 50 ml. of a freshly-standardized solution of ferrous sulfate (see p. 531) and boil the solution 10 minutes. The following reaction takes place:

$$KClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 = KCl + 3\,Fe_2(SO_4)_3 + 3\,H_2O.$$

After cooling, dilute the solution with cold distilled water to 200 ml., add 10 ml. of manganous sulfate solution (cf. p. 518), and titrate the excess of the ferrous sulfate with potassium permanganate.

If 50 ml. ferrous sulfate..... required T ml. 0.1 N $KMnO_4$ sol.
and 50 ml. " " + 10 ml. chlorate sol. " t ml. 0.1 N " "
then 10 ml. of chlorate solution = $0.01a$ g. substance = $(T - t)$ ml. 0.1 N $KMnO_4$ "

$$\text{The substance contains } \frac{20.43 \times (T - t)}{a} \text{ per cent of } KClO_3.$$

18. Determination of Nitric Acid (Pelouze-Fresenius)

$$1000 \text{ ml. } N \text{ } KMnO_4 = \frac{RNO_3}{3} = \begin{cases} 21.01 \text{ g. } HNO_3 \\ 28.34 \text{ g. } NaNO_3 \\ 33.71 \text{ g. } KNO_3 \end{cases}$$

This method depends upon the fact that on heating a nitrate with an acid ferrous chloride solution the nitric acid is reduced to nitric oxide:

$$2\,KNO_3 + 6\,FeCl_2 + 8\,HCl = 2\,KCl + 2\,NO + 4\,H_2O + 6\,FeCl_3.$$

As a measure for the amount of nitrate reduced we have:
(1) The excess of ferrous salt. (2) The ferric salt produced. (3) The nitric oxide formed.

The method of Schlösing-Grandeau described on p. 393 is based upon the measurement of the nitric oxide formed. C. D. Braun* estimates the amount of ferric salt formed, while Pelouze and Fresenius determine the amount of ferrous salt not used up in the reduction of the nitric acid.

* *J. prakt. Chem.*, **81**, 421 (1860).

Procedure. — Place 1.5 g. of pure iron wire in a long-necked flask, and expel the air by passing a current of pure carbon dioxide through it for 2–3 minutes. Then add 30–40 ml. of concentrated hydrochloric acid and place the flask in an inclined position and close by means of a rubber stopper through which tubes pass so that a current of carbon dioxide can be introduced. Heat the solution on the water-bath in this atmosphere of carbon dioxide until the iron has completely dissolved, and allow the solution to cool in a current of the gas. Meanwhile weigh 0.25–0.3 g. of the nitrate into a small glass tube closed at one end. Drop this into the acid solution of the ferrous sulfate and quickly close the flask again. Heat as before for 15 minutes, while continuing the stream of carbon dioxide. Have the exit tube through from the flask dipping into a beaker filled with water so that there is no chance of any air getting back into the flask. Finally heat the solution to boiling and keep hot there until the dark color disappears and the yellow color of the ferric chloride becomes apparent. To make sure that the nitric oxide is entirely removed boil 5 minutes longer and then allow to cool in the atmosphere of carbon dioxide. When cold pour the solution into a beaker, rinse the flask with a little boiled water, and dilute to about 400 ml. Add 10 ml. of manganese sulfate solution (p. 518), and titrate the unoxidized ferrous salt with 0.5 N $KMnO_4$ solution.

Determine the purity of the iron wire by titrating 1 g. of the wire after similar treatment with acid and manganese sulfate solution.

If a g. of potassium nitrate and p g. of the wire were taken for the analysis, t ml. of 0.5 $KMnO_4$ were required to oxidize the excess of iron, and p g. of the wire require T ml. of 0.5 $KMnO_4$, then:

$$\frac{(T - t) \times 1.685}{a} = \text{per cent } KNO_3.$$

Remark. — This method gives results just as accurate as those obtained by the method of Devarda (p. 392), but the latter determination is much easier to carry out.

19. Determination of Vanadic Acid

$$1000 \text{ ml. of } 0.1\ N\ KMnO_4 = \frac{V_2O_5}{20} = 9.10 \text{ g. } V_2O_5.$$

Conduct sulfur dioxide into the boiling acid solution of an alkali vanadate until the solution is clear blue in color; by this means the vanadic acid is reduced to vanadyl salt:

$$2\,H_3VO_4 + H_2SO_3 + H_2SO_4 \rightarrow V_2O_2(SO_4)_2 + 5\,H_2O$$

$$5\,V_2O_2^{++++} + 2\,MnO_4^- + 22\,H_2O \rightarrow 10\,H_3VO_4 + 2\,Mn^{++} + 14\,H^+.$$

Continue boiling and introduce a current of carbon dioxide through the solution until the escaping gas will no longer decolorize a solution of potassium permanganate, showing that the excess of the sulfur dioxide has been expelled. Titrate the hot solution with potassium permanganate until a permanent pink color is obtained. The end-point is easily recognized only when the solution is hot. This accurate determination is used for the analysis of vanadium in iron and steel, or in ores. (Cf. p. 283.)

20. Blair Method for Determining Phosphorus in Steel*

$$1000 \text{ ml. of } 0.1\ N\ KMnO_4 = \frac{P}{360} = 0.0862 \text{ g. P.}$$

Principle. — The substance is dissolved in nitric acid, all carbonaceous matter is destroyed and the phosphorus is oxidized completely to phosphoric acid by the action of strong permanganate solution, any precipitated manganese dioxide is redissolved, and the phosphorus is precipitated in slightly acid solution as ammonium phosphomolybdate. The precipitate contains 1 P : 12 Mo if the precipitation takes place under the prescribed conditions with fresh molybdate solutions and the solution is not allowed to stand too long before filtering. Vanadium and titanium are likely to precipitate with the phosphorus and arsenic will cause trouble if the solution is too hot or stands too long.

The ammonium phosphomolybdate precipitate is dissolved in ammonia, the solution made acid with sulfuric acid and the molybdenum reduced by means of a so-called *Jones reductor*. The reduced solution is titrated with permanganate.

The Jones reductor (Fig. 113) is made by placing glass beads in the bottom of a glass-stoppered tube which is 30 cm. long and has an inside diameter of 18 mm. Upon the beads place a plug of glass wool and then a thin layer of asbestos such as is used for Gooch crucibles. This asbestos layer must be thick enough to prevent zinc powder to run through but not so thick that the flow of solution will be retarded too much. Water should run slowly through the filled reductor without the application of suction. Fill the tube with amalgamated zinc to within 5 cm. of the top. This zinc can be prepared by taking some 20- to 30-mesh zinc, cleaning it with a little hydrochloric acid, and adding mercuric chloride until hydrogen ceases to be evolved. In this condition the zinc is scarcely acted upon at all by dilute acid, but is capable of reducing an iron or molybdenum solution just as effectively as if it were not amalgamated. On top of the column of zinc place a little glass wool to serve as filter.

Procedure. — Weigh 2 g. of steel into a 250-ml. Erlenmeyer flask, add 100 ml. of 4 *N* nitric acid and insert a small, short-stemmed funnel into the neck of the flask. Heat until the sample is all dissolved and oxides of nitrogen are no longer visible in the neck of the flask. Add 10 ml. of 1.5 per cent permanganate, or more if necessary to impart a pink color to the solution. The purpose of the permanganate

* Andrew Blair. *The Chemical Analysis of Iron.*

is to oxidize the dissolved carbide and to make sure that all of the phosphorus is fully oxidized to phosphoric acid. Boil until the pink color disappears and manganese dioxide is precipitated. Continue boiling for several minutes and add a few drops of sulfurous acid, a small crystal of ferrous sulfate or 5 per cent sodium thiosulfate solution. Add very little of the reducing agent at a time but continue adding it, at short intervals, until the manganese dioxide is dissolved. If there is any appreciable silicious residue at this point it should be removed by filtration. Boil 2 minutes after the manganese dioxide has dissolved and then cool to 40°. Add 40 ml. of 6 *N* ammonium hydroxide in portions of 25, 10 and 5 ml., and rotate the flask until the precipitated ferric hydroxide redissolves. It is important that the solution should now assume a pale straw color and not appear at all red from colloidal ferric hydroxide. A red solution shows that too much ammonia was added and the precipitation of the phosphorus will be incomplete. With the solution at 35–40° add 40 ml. of ammonium molybdate solution (p. 384). Stopper the flask with a rubber stopper and shake vigorously for 5 minutes, allow the precipitate to settle for 15 minutes and then filter. Wash it promptly with acid ammonium sulfate solution (1 liter of water, 25 ml. concentrated H_2SO_4, and 15 ml. strong ammonia), until the washings give no test for molybdenum when treated with a drop of yellow ammonium sulfide solution. Compare the color obtained in the test with a blank test of the wash water treated with ammonium sulfide in the same way.

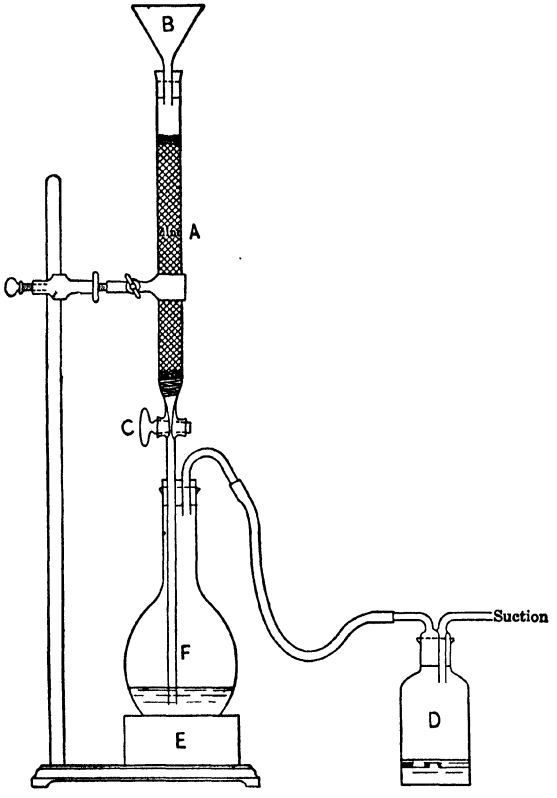


FIG. 113.

Dissolve the ammonium phosphomolybdate precipitate in 25 ml. of 3 *N* ammonium hydroxide, wash the filter with hot water and treat the filtrate with 10 ml. of concentrated sulfuric acid. It is now ready for reduction. A blank is run with the reductor before each series of determinations, and whenever the reductor has stood idle for 3 hours. After a reductor has stood over night, it should be well washed with dilute sulfuric acid, before even running a blank test.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml. of normal sulfuric acid through the funnel, *B*, with the stop-cock *C* open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, in the case of blanks, 50 ml. of 1.5 *N* sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml. of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml. of water through the reductor. At no time, however, should any air be allowed to enter the reductor tube, which should be kept full of water at all times when idle. Run blanks until two successive tests require less than 0.2 ml. of 0.1 *N* permanganate to give a pink color to the acid solution.

In the original Blair method, the reduced solution was caught in an empty flask and it was assumed that the MoO_3 of the phosphomolybdate precipitate is reduced to $Mo_{24}O_{37}$ and 1 ml. of 0.1 *N* $KMnO_4$ = 0.0000886 g. P. The molybdenum is reduced completely to the tervalent condition by the amalgamated zinc:

$$(NH_4)_3PO_4 \cdot 12\,MoO_3 + 23\,NH_4OH = 12\,(NH_4)_2MoO_4 + (NH_4)_2HPO_4 + 11\,H_2O.$$

$$2\,MoO_4^{--} + 3\,Zn + 16\,H^+ \rightarrow 2\,Mo^{+++} + 3\,Zn^{++} + 8\,H_2O.$$

The tervalent molybdenum is slowly oxidized by the air in the flask and by that shaken into the solution during the titration. A practiced manipulator usually titrates so that about 3 per cent of the total oxidation is accomplished by the air. The only safe way to avoid this error is to catch the reduced solution, before it comes in contact with air, in 50 ml. of 10 per cent ferric alum solution dissolved in water containing 25 ml. of concentrated sulfuric acid and 40 ml. of sirupy phosphoric acid per liter.

This ferric alum solution does not change the reduced molybdenum entirely back to the 6-valent condition but it does oxidize it sufficiently to prevent the effect of the atmosphere, and for every equivalent of molybdenum oxidized an equivalent of reduced iron is formed so that the solution titrates exactly as if a perfect reduction was obtained without the use of the ferric salt. Since the precipitate contains 1 P : 12

Mo, and the valence change of the Mo is 3, it is clear how the normal weight is computed.

To illustrate the computation assume that the ammonium phosphomolybdate precipitate from 2 g. of steel required by the above method 12 ml. of 0.1 *N* permanganate solution. The blank on the reductor was 0.18 ml. The phosphorus present in the steel is then: $(12 - 0.18) \times 0.00431$ per cent.

If 2.16 g. of steel is taken then for analysis, the percentage of phosphorus will be 0.4 times the net volume of permanganate in milliliters.

21. The Determination of Chromium in Steel

A small quantity of chromium is a common constituent of iron and steel and in some of the alloy steels it is present to the extent of several per cent. The simplest and most rapid method for determining this element consists in oxidizing it to chromate, adding a known quantity of ferrous salt and determining the excess of the latter by titrating with standard potassium permanganate. A great many different methods have been proposed for carrying out the oxidation.

(*a*) *The Barba Method**

Principle. — The steel is dissolved in dilute sulfuric acid, the iron is oxidized to the ferric state by means of nitric acid, and the chromium is oxidized by the addition of strong permanganate solution. The excess of the latter is destroyed by boiling in ammoniacal solution, the solution is acidified again, the precipitated manganese dioxide filtered off, a known volume of standard ferrous sulfate solution is added to an aliquot part of the filtrate, and the excess of the latter is titrated with permanganate.

Procedure. — Dissolve exactly 1.25 g. of steel in 20 ml. of 6 *N* sulfuric acid, and when the solution is complete, add concentrated nitric acid, drop by drop, until the iron is all oxidized to the ferric state. Boil the solution to remove nitrous fumes, dilute to 150 ml., add 5 ml. of 6 per cent potassium permanganate solution and boil briskly for 15–20 minutes. Remove from the hot plate, wash the sides of the beaker with water and pour 25 ml. of concentrated ammonium hydroxide down the sides of the beaker. Stir the liquid vigorously and place on the cooler part of the hot plate, for if it is heated too rapidly there is likely to be loss by " bumping." Digest with occasional stirring for 15 minutes, or until the permanganate is all decomposed as shown by the disappearance of the pink color. Then carefully add 20 ml. of 16 *N* sulfuric acid and heat the solution to boiling. Transfer to a 250-ml. measuring flask, cool to room temperature, and dilute to the mark.

* *J. Iron and Steel Institute*, **1893**, ii, 536; *The Iron Age*, **52**, 153.

After thoroughly mixing by pouring back and forth several times into a dry beaker, filter the solution and use exactly 200 ml. (1 g. of metal) for the rest of the analysis. Add 50 ml. of standard ferrous sulfate solution (see p. 531), and titrate the excess with 0.1 N permanganate.

Computation. — When the ferrous sulfate solution is added, the chromium is reduced from chromic acid to chromic salt in accordance with the following equation:

$$2\,H_2CrO_4 + 6\,FeSO_4 + 6\,H_2SO_4 = Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 8\,H_2O.$$

The ferrous sulfate solution is not very stable and should be titrated against the permanganate at the same time the analysis is made. If 50 ml. of the ferrous sulfate solution are equivalent to T_1 ml. of permanganate, of which 1 ml. = a g. of pure sodium oxalate, and T_2 ml. of permanganate were used in titrating the excess of ferrous sulfate in the analysis of 1 g. of steel, then

$$\frac{2\,Cr \cdot a\,(T_1 - T_2) \cdot 100}{3\,Na_2C_2O_4} = 25.86\,a\,(T_1 - T_2) = \text{per cent Cr.}$$

(*b*) *Sodium Bismuthate Method*

1000 ml. of 0.1 N $KMnO_4$ = 1.733 g. Cr.

Principle. — Sodium bismuthate, $NaBiO_3$, is often used for oxidizing manganese from the bivalent to septavalent condition (cf. p. 524). This oxidation takes place best in a *cold* solution containing 20–40 per cent of nitric acid (free from nitrous acid) in a volume of 50–100 ml.* Moreover, an excess of sodium bismuthate should be present and the solution must not stand long. Under these conditions scarcely any chromium is oxidized so that the manganese may be determined by the bismuthate method even when chromium is present.† If the solution is heated to boiling, the permanganate is decomposed and the manganese is precipitated as manganese dioxide. Chromium, on the other hand, is oxidized in *hot* solutions from the trivalent to the sexavalent condition and the chromic acid is not decomposed by boiling, unless some reducing agent is present. In hot solutions, therefore, it is possible to oxidize the chromium by sodium bismuthate, to filter off the precipitated manganese dioxide and to determine the chromium in the filtrate by adding a known volume of standard ferrous sulfate solution and titrating the excess as in (*a*).

* William Blum, *J. Am. Chem. Soc.*, **34**, 1395.

† This statement has been made by several writers, but considerable evidence has accumulated to prove that, as ordinarily carried out in the laboratory, the bismuthate method for the determination of manganese in a steel containing chromium is likely to give high results due to a partial oxidation of chromium by the bismuthate. If the essential conditions with regard to temperature, acidity and time allowed for the completion of the reaction are adjusted very carefully it is probably possible to get accurate results in the manganese determination but in ordinary practice it is advisable to separate the manganese and chromium by precipitating the latter. This can be accomplished satisfactorily by means of zinc oxide (cf. Volhard method, p. 522). The manganese can then be determined by the bismuthate method in an aliquot part of the filtrate.

Procedure. — Dissolve 2 g. of steel in a 250-ml. Erlenmeyer flask in 50 ml. of 4 *N* nitric acid. If there is any carbonaceous residue, as in the analysis of cast irons, it must be removed and should be filtered off and examined for chromium by fusion with an alkaline oxidizing flux. If the metal is difficultly soluble in nitric acid, it is sometimes necessary to add sulfuric acid to hasten the solution.

When the sample is all dissolved, cool the solution to between 65° and 75° and add 2 g. of sodium bismuthate. Agitate the contents of the flask for a few minutes and then wash down the sides of the flask with a little water. Heat the solution and gently boil until the permanganate formed from the manganese in the steel is all decomposed as shown by the color. This usually requires about 15 minutes. Add 50 ml. of 0.5 *N* nitric acid, and filter off any precipitated manganese dioxide or undissolved sodium bismuthate on an asbestos filter. Wash the residue 3 times with 50 ml. portions of the dilute nitric acid. Cool to room temperature by running tap water over the flask and finally dilute with distilled water to 500 ml. Add a measured volume of ferrous sulfate solution and titrate the excess with permanganate as in (*a*).

(*c*) *Chromium in Chrome-nickel Steel**

Dissolve 2 g. of the steel in 70 ml. of 7.5 *N* sulfuric acid and add 3 ml. of concentrated nitric acid to oxidize the iron. Boil 5 minutes, dilute to about 300 ml. and again heat to boiling. Add 10 ml. of silver nitrate solution (2.5 g. per liter) and 20 ml. of 10 per cent ammonium persulfate solution. Boil 8 minutes and then add enough 1.5 *N* hydrochloric acid to dissolve the precipitated oxide of manganese. Boil 5 minutes longer to drive out chlorine. A few drops of the acid are enough for manganese steels but sometimes 5 ml. are required. Cool to 20° C. and titrate the chromium with ferrous sulfate and potassium permanganate in the presence of 5 ml. of sirupy phosphoric acid.

(*d*) *Determination of Chromium and Vanadium in Chrome-nickel Steels*†

Dissolve 2 g. of sample in a 300-ml. Erlenmeyer flask in 30 ml. of 3.3 *N* sulfuric acid. Dilute to 200 ml. with boiling water and add sodium bicarbonate solution (80 g. per liter) from a buret until a permanent precipitate first appears, and then 4 *ml. more.* Boil *one minute,* allow to settle and filter *rapidly.* Wash 4–5 times with boiling water.

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* Directions furnished by the Bureau of Standards. Cf. Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 719 (1916).

† Directions furnished by the Bureau of Standards.

(The filtrate may be used for the determination of the manganese.)* Ignite the residue in an iron or nickel crucible and fuse with 10–12 times as much sodium peroxide. Dissolve the melt by immersing in 100 ml. of water, remove the crucible and destroy any remaining peroxide by heating for one-half hour on the steam bath. Filter into a 200-ml. graduated flask and fill to the mark with water. Take 100 ml. of this solution, make acid with sulfuric acid, add 10 ml. of silver nitrate solution (2.5 g. per liter) and 20 ml. of a 10 per cent solution of ammonium persulfate solution. Boil for 8 minutes and then add 5 ml. of 3 *N* hydrochloric acid and boil 5 minutes longer. Cool to 20° and titrate the chromium with ferrous sulfate and permanganate as in (*a*).

Neutralize the remaining 100 ml. of solution with sulfuric acid and then add 6 ml. more of 18 *N* sulfuric acid. Heat the solution to boiling and reduce in a Jones reductor allowing the reduced solution to flow into a ferric alum solution contained in the receiving flask (see pp. 540, 541). Remove the receiving flask, decolorize the solution if necessary by adding a little phosphoric acid and titrate hot with potassium permanganate. Subtract from the permanganate used one-third the number of ml. of permanganate equivalent to the chromium reduction in the first 100 ml. aliquot. The remainder represents the amount of permanganate required to oxidize the vanadium from the valence of 4 to 5, 1 ml. of 0.1 *N* $KMnO_4$ = 0.001831 g. V.

In passing through the Jones reductor the chromium is reduced to chromous salt and the vanadium to a state corresponding to V_2O_2. These react with the ferric alum more or less completely with the formation of an equivalent amount of ferrous sulfate. The permanganate oxidizes the chromium to the tervalent, the vanadium to the quinquevalent and the iron to the ferric condition.

Note. A blank determination should be run in the reductor using equivalent amounts of peroxide and reagents (cf. p. 541).

22. Determination of Molybdenum in Wulfenite and Molybdenite†

1. *Method of Dissolving Wulfenite*

Dissolve 1 g. of the powdered ore by treatment with 15 ml. of concentrated nitric acid and 7 ml. of concentrated sulfuric acid in a 150-ml. covered beaker at a temperature just short of boiling. When practically complete decomposition has been effected, evaporate until

* This procedure is satisfactory if carefully carried out and separates manganese from interfering chromium.

† Method furnished by the Bureau of Standards and based upon the work of J. A. Holladay and A. M. Smoot.

fumes of sulfur trioxide are expelled freely. Cool, add 40 ml. of water, boil to dissolve the bulk of the molybdenum, cool to tap water temperature, and filter into a 150-ml. beaker; the residue consists of lead sulfate, silica, and possible small amounts of undecomposed ore, and tungstic and molybdic acids. Save both the residue and the filtrate.

Dissolve the lead sulfate in hot ammonium acetate solution (see p. 178), washing until the ammonium acetate filtrate gives no test for lead with ammonium sulfide solution. Ignite the silicious residue in a platinum crucible and remove silica by treating it with sulfuric and hydrofluoric acids. Evaporate till the excess acid is all expelled. If an appreciable residue remains after this treatment, fuse it with potassium pyrosulfate and test for molybdenum by means of tartaric acid and ammonium sulfide as further described. The residue, however, seldom contains any molybdenum.

2. *Method of Dissolving Molybdenite*

Treat 0.5–5 g. of the finely-pulverized sample with from 10–35 ml. of concentrated nitric acid and 7–10 ml. of concentrated sulfuric acid in a 250-ml. beaker, covered with a watch-glass. Digest at a temperature somewhat below the boiling point until most of the molybdenite appears to have been decomposed, and then evaporate until strong fumes of sulfur trioxide are evolved. When the beaker and its contents have cooled, add 50 ml. of water and boil briskly for a few minutes. Filter into a 150-ml. beaker. Wash the residue with hot water, then 6 or 8 times with 4 *N* ammonium hydroxide, and finally with hot water, allowing the washings to run into the main filtrate.

Treat the siliceous residue (which will also contain nearly all lead and barium present in the ore) with ammonium acetate solution (cf. p. 178) and ignite the remainder at a very low red heat in a porcelain crucible, cool, transfer to a platinum crucible, treat with 2 or 3 drops of concentrated sulfuric acid and several ml. of hydrofluoric acid, and evaporate until sulfuric acid has been completely expelled. Fuse the small residue remaining with sodium carbonate, extract with water, and add the water extract to the main solution.

3. *Method of Analysis*

To the solution containing all of the molybdenum, add sufficient ferric sulfate to provide 10 times as much iron as there is arsenic present; from 0.3–0.4 g. is usually ample. Nearly neutralize the acid with ammonia (do not add enough to impart a red tint to the solution), heat nearly to boiling and pour slowly and with vigorous stirring into

75 ml. of nearly boiling 9 *N* ammonium hydroxide contained in a 250-ml. beaker. When the precipitate has settled, filter and wash thoroughly with hot water. Dissolve the precipitate in a slight excess of hot 7.5 *N* sulfuric acid, heat to boiling and pour again into 75 ml. of boiling 9 *N* ammonium hydroxide. Collect the 2 filtrates, containing all of the molybdenum, in a 500-ml. beaker. It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. The addition of ferric sulfate should be omitted only in case arsenic is known to be absent.

To the combined ammoniacal filtrates, add 3 g. of tartaric acid and when the acid has dissolved, saturate the warm solution with hydrogen sulfide. The presence of tartaric acid is necessary to prevent the subsequent precipitation of vanadium and tungsten sulfides. If these elements are known to be absent its use may be dispensed with. Under these conditions the molybdenum remains in solution as ammonium thiomolybdate, $(NH_4)_2MoS_4$, which imparts a deep red color to the solution. If a small precipitate of insoluble sulfides separates out, filter and wash with hydrogen sulfide water. Make the thiomolybdate solution *slightly acid* with sulfuric acid (cf. p. 265).

Heat for a short time, allow the precipitate to settle, filter and wash thoroughly with hydrogen sulfide water containing a little of sulfuric and tartaric acids.

The filtrate from the molybdenum sulfide sometimes contains appreciable amounts of molybdenum.

Boil off the hydrogen sulfide, add an excess of bromine water to oxidize molybdenum, expel the excess by boiling, make ammoniacal as before and treat with hydrogen sulfide and acid as outlined on p. 265. If any more molybdenum sulfide is formed, recover it.

Place the molybdenum sulfide precipitate and filter paper in a 250-ml. flask and treat with 6 ml. of concentrated sulfuric acid and 10 ml. of concentrated nitric acid. Evaporate to fumes and repeat the nitric acid treatment, evaporating until the filter paper has been completely destroyed and every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, allow the solution to fume strongly for a short while, cool, add 5 ml. of water, and again evaporate to fumes to insure the expulsion of every trace of nitric acid. Cool, add 75 ml. of water and boil for a few minutes, which should give a pefectly clear solution. Add 5 g. of pure, shot zinc (0.002 per cent iron or under) and boil the solution until most of the zinc has dissolved; this results in partial reduction of the molybdenum and complete precipitation of the traces of copper which are usually pres-

ent. Filter on an asbestos or 'alundum' filter to remove the undissolved zinc and the copper.

Reduce the molybdenum completely as described on p. 541 and titrate with 0.1 *N* permanganate. 1 ml. 0.1 *N* permanganate solution = 0.003200 g. of molybdenum.

23. Determination of Titanium*

1000 ml. 0.1 *N* $KMnO_4$ = 1 g.-at. Ti = 48.1 g. Ti.

Principle. — The reduction of titanium from the quadrivalent to tervalent condition proceeds rapidly and quantitatively in 1.1 to 1.8 *N* H_2SO_4 solution by passage through a Jones reductor. Organic compounds, nitric acid, tin, arsenic, antimony, molybdenum, iron, chromium, vanadium, tungsten, uranium and columbium must be absent but, with the exception of the rare element columbium, all of these can be easily separated from titanium. Nitric acid can be removed by repeated evaporation with sulfuric acid. Arsenic, antimony and tin can be removed as sulfides from a solution sufficiently acid to prevent hydrolysis of the titanium. Iron can be precipitated as sulfide from an alkaline tartrate solution (see page 109) and the organic matter then removed by treatment with nitric and sulfuric acids. Chromium, vanadium, tungsten and uranium can be removed by oxidation in alkaline solution with sodium peroxide and boiling to precipitate titanium hydroxide.

Procedure. — Carry out the reduction as described on page 541 for molybdenum taking the precaution to wash out the reductor with dilute sulfuric acid before each run which is carried out in the following order, — 25–50 ml. of 1.1–1.8 *N* sulfuric acid, 150 ml. of the same strength acid containing 0.12 g. of titanium or less, 100 ml. more of acid and finally 100 ml. of water. Catch the solution in 3 times the theoretical quantity of ferric sulfate dissolved in 3 *N* sulfuric acid. The reduction takes place at any temperature between 25° and 100° and it is not necessary to expel air from the solutions used in the reductor.

$$2\ Ti^{++++} + Zn \rightarrow 2\ Ti^{+++} + Zn^{++}.$$

$$Ti^{+++} + Fe^{+++} \rightarrow Fe^{++} + Ti^{++++}.$$

B. Potassium Dichromate Methods

1. Determination of Iron according to the Method of Penny

1000 ml. *N* $K_2Cr_2O_7$ = 1 g.-at. Fe = 55.84 g. Fe.

Principle. — If a solution of a ferrous salt, in either hydrochloric or sulfuric acid, is treated with an alkali dichromate solution, the dichromate is at once reduced in the cold and the ferrous salt is oxidized quantitatively:

$$Cr_2O_7^{--} + 6\ Fe^{++} + 14\ H^+ = 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O.$$

On account of the formation of the chromic salt the solution becomes emerald-green in color.

* G. E. F. Lundell and H. B. Knowles. · *J. Am. Chem. Soc.* **45**, 2620 (1923).

The end-point of the reaction is determined by removing a drop of the solution and testing it with a freshly-prepared solution of potassium ferricyanide; if no blue coloration is formed, the ferrous salt has been completely oxidized.

The 0.1 *N* potassium dichromate solution necessary for this titration may be prepared by dissolving one-sixtieth mole of $K_2Cr_2O_7$ = 4.903 g. of the pure, dry, recrystallized salt. Do not heat over 130° in drying. The potassium dichromate is less susceptible than permanganate to reduction by hydrochloric acid.

Method of Titration. — To the solution of the ferrous salt in 0.2–0.4 *N* acid (with 0.1–0.15 g. iron in each 100 ml.), add the 0.1 *N* $K_2Cr_2O_7$, from a buret.

From time to time remove a drop of the solution on the end of a glass stirring-rod to a white porcelain plate, and place beside a drop of a 1 per cent solution of potassium ferricyanide.* By means of a stirring-rod cause one solution to run into the other. If considerable ferrous salt remains in the solution, the blue color will be formed immediately, but finally a bluish-green color is obtained, perceptible at the junction of the two solutions. As soon as no more bluish-green coloration is to be detected the reaction is complete. In all cases carry out the analysis in duplicate, and, other things being equal, the second determination should be the more accurate. This time it is possible to add almost the whole of the required amount of bichromate at once, and for the testing not more than 2 or 3 drops of the dilute solution of ferrous salt are required. The loss of ferrous solution will then be inappreciable. Make sure that the end-point is not overstepped by adding a drop of 0.1 *N* ferrous solution to see if the solution will give a blue test with the indicator.

Remark. — The dichromate method is slightly less accurate than the permanganate method, but it possesses the advantage that a solution of a ferrous salt containing hydrochloric acid can be titrated without the addition of manganese sulfate, even when the solution is turbid with suspended insoluble salts, fibers of filter-paper, etc. In turbid solutions it is difficult to recognize the permanganate end-point. A further advantage lies in the fact that the normal dichromate solution can be readily prepared by simply weighing out the required amount of the pure, dry salt, and diluting the aqueous solution to a volume of 1 liter. It is then unnecessary to test the concentration in any other way.

2. Determination of Manganese in Iron and Steel

Method of J. Pattinson†

Principle. — If a solution containing iron, manganese, and calcium salts is treated with " chloride of lime " solution and calcium carbonate, all of the iron and man-

* The potassium ferricyanide must be absolutely free from ferrocyanide; as the former is readily reduced by the dust of the air, the surface of the salt should be washed off several times with water before dissolving it for the test solution.

† *J. Chem. Soc.* **1879**, 365.

ganese are precipitated, the latter in the form of its hydrated dioxide. The entire precipitate can be dissolved in an acid ferrous sulfate solution of known strength, and the excess of the latter titrated with dichromate solution:

$$MnO_2 + 2\,Fe^{++} + 4\,H^+ \rightarrow Mn^{++} + 2\,Fe^{+++} + 2\,H_2O.$$

$$1000 \text{ ml. } N\ K_2Cr_2O_7 = \frac{Mn}{2} = 27.47 \text{ g. Mn.}$$

Procedure. — Dissolve 5 g. of the iron or steel (or 1 g. of ferromanganese) in hydrochloric acid, oxidize the solution with nitric acid, evaporate to a small volume, pour into a 100-ml. measuring-flask, and dilute up to the mark with water. After thoroughly mixing, transfer 20 ml. of the solution to a large beaker (of about 1 liter capacity) and neutralize with pure calcium carbonate. Add the carbonate in small portions until the solution finally becomes a dark brown but still remains clear. After this add 50 ml. of " chloride of lime " solution,* and more calcium carbonate with constant stirring until finally a little of the latter remains undissolved. To the slimy contents of the beaker, add 700 ml. of hot water, and, after stirring, allow the insoluble residue to settle. If the supernatant liquid is violet, on account of the formation of calcium permanganate, add 1 or 2 drops of alcohol, boil and again allow the precipitate to settle; in this case the upper liquid should be colorless. Decant the clear solution through a funnel containing a hardened filter-paper and connected with suction. Wash the precipitate 4 times by decantation with 300 ml. of hot water, then transfer to the filter without making any attempt to remove the last portions of the precipitate from the sides of the beaker, and wash with the aid of suction until the filtrate will no longer turn iodo-starch paper blue. Place the precipitate and filter in the original beaker, add 50 ml. of a freshly-standardized ferrous sulfate solution (cf. p. 531) and stir the liquid until the precipitate has entirely dissolved,† leaving behind the filter-paper and sometimes small amounts of undissolved calcium sulfate. Titrate the excess of ferrous sulfate with potassium dichromate solution.

Assume that a g. of steel are dissolved in 100 ml. of the solution and of this 20 ml. were taken for the analysis. Assume that 50 ml. of ferrous sulfate solution = T ml. 0.1 N $K_2Cr_2O_7$ and 50 ml. ferrous sulfate + 0.2 a g. substance = t ml. 0.1 N $K_2Cr_2O_7$. Then

$$\frac{(T - t) \times 1.374}{a} = \text{per cent Mn.}$$

---

* Prepared by shaking 15 g. of fresh bleaching powder with 1 liter of water and allowing the mixture to stand until the supernatant solution is clear.

† If the precipitate should not completely dissolve, add a little 18 N sulfuric acid until the brown color entirely disappears.

C. Iodimetry

The fundamental reaction of iodimetry is the following:

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6.$$

or

$$S_2O_3^{--} + I_2 \rightarrow 2\,I^- + S_4O_6^{--}$$

If to a solution containing an unknown amount of iodine a little starch solution is added, and sodium thiosulfate solution is run in from a buret, the blue color will disappear from the solution as soon as the iodine has all been reduced to iodide in accordance with the above equation. This reaction is one of the most sensitive reactions used in analytical chemistry. If, therefore, a sodium thiosulfate solution of known strength is at hand, we have a means of determining not only iodine itself, but all of those substances (oxidizing agents) which when treated with potassium iodide set free iodine, or evolve chlorine when acted upon by hydrochloric acid. Consequently, iodimetric processes are not only accurate but capable of most general application. For most analyses 0.1 *N* sodium thiosulfate solution and 0.1 *N* iodine solution are required, and starch solution as indicator. In some few cases 0.01 *N* solutions are used.

Preparation of Sodium Thiosulfate Solution

From the above equation it is evident that an equivalent weight of iodine, the atomic weight in grams, is equal to 1 mole of $Na_2S_2O_3$. Hence, exactly 0.1 mole of crystallized sodium thiosulfate ($Na_2S_2O_3 + 5\,H_2O$) are required to make 1 liter of tenth-normal solution.

A solution of pure sodium thiosulfate in "best" water will keep very well but solutions of commercial thiosulfate usually deposits sulfur on standing and the titer changes until the decomposition brought about by impurities is complete.

Prepare a large amount of the thiosulfate solution (about 5 liters) by roughly weighing out the required amount of the commercial salt and after standing for from 8–14 days, standardize the solution by one of the following methods.

The molecular weight of $Na_2S_2O_3 + 5\,H_2O$ is 248.32. To prepare 1 liter of 0.1 *N* solution 24.83 g. of the salt are necessary, or, in round numbers, 25 g. For 5 liters, 125 g. should be weighed out.

Standardization of Sodium Thiosulfate Solution

1. *With Pure Iodine*

Commercial iodine is contaminated with chlorine, bromine, water, and sometimes cyanogen; it must be purified. For this purpose grind 5 or 6 g. of the commercial product with 2 g. of potassium iodide;

any chlorine or bromine present forms potassium chloride or bromide, setting free an equivalent amount of iodine. Place the mixture in a dry casserole (Fig. 114)* which rests in a muffle. Upon the casserole place a flask filled with cold water. Have a wire gauze at the bottom of the muffle and a Bunsen flame beneath this. The iodine sublimes rapidly and collects as a crystalline crust on the bottom of the flask, and practically none of it is lost. As soon as the evolution of violet vapors from the bottom of the casserole has practically ceased, the sublimation is complete. Remove the flame, and after allowing to cool, take away the flask with the iodine adhering to it. To remove the latter, pass a current of cold water through the tube *a* into the flask and out at *b*. This causes the glass to contract somewhat and the whole of the iodine crust can be removed by lightly scraping with a clean glass rod. Catch it upon a watch-glass; break up into large pieces, and repeat the sublimation without the addition of potassium iodide at as low a temperature as possible; in this way a product free from potassium iodide is obtained. Grind the iodine somewhat in an agate mortar and dry in a desiccator containing calcium chloride. If dried over sulfuric acid, some of the latter is likely to be present in the iodine. Furthermore, the cover of the desiccator must not be greased, for grease is attacked by iodine vapors, forming hydriodic acid, which might cause contamination.

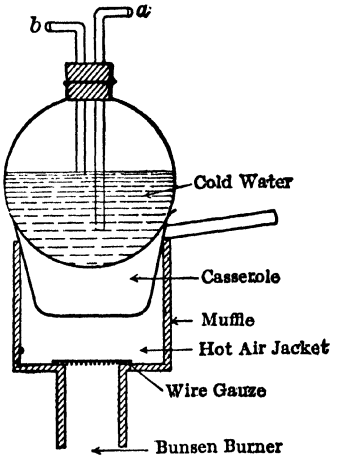


FIG. 114.

The Weighing Out of the Iodine. — In each of 2 or 3 small weighing-tubes with tightly-fitting glass stoppers place 2–2.5 g. of pure potassium iodide free from iodate and 0.5 ml. of water (not more); stopper the tubes and accurately weigh. Then open the tubes and add 0.4–0.5 g. of pure iodine to each. Quickly insert the stopper and again weigh; the difference shows the amount of iodine. As the tubes are cooled by the dissolving of the iodine, moisture sometimes collects on the outside and must be wiped off before weighing. The iodine dissolves almost instantly in the concentrated potassium iodide solution. Place one of the tubes in the neck of a 500-ml. Erlenmeyer flask which is held in an inclined position and contains 200 ml. of water and about

* C. R. McCrosky, *J. Am. Chem. Soc.*, **40**, 1664 (1918).

1 g. of potassium iodide. Drop the tube to the bottom of the flask, but just as it begins to fall remove the stopper and allow it to follow. In this way there is no iodine lost, which will be the case if the contents of a tube are washed into the water. A solution is thus prepared containing a known amount of iodine. To it add the sodium thiosulfate solution to be standardized from a buret until the liquid is pale yellow in color. Then add 2 or 3 ml. of starch solution and carefully titrate until colorless. From the mean of 2 or 3 determinations, the strength of the thiosulfate solution is calculated.

If the weight of iodine equivalent to 1 ml. of sodium thiosulfate solution is divided by 0.12685 (the milliequivalent of iodine) the *normality* of the solution will be obtained.

2. *With Potassium Biiodate (C. Than)**

If a solution of potassium biiodate is added to a solution of potassium iodide containing hydrochloric acid, the following reaction takes place:

$$\underbrace{KIO_3 \cdot HIO_3}_{389.95} + 10\,KI + 11\,HCl = 11\,KCl + 6\,H_2O + \underbrace{6\,I_2}_{1523.}$$

If, therefore, 3.250 g. of pure potassium biiodate are contained in one liter of the aqueous solution, 10 ml. of such a solution on being treated with an excess of potassium iodide and hydrochloric acid will set free exactly as much iodine as would be contained in 10 ml. of 0.1 *N* iodine solution. By means of such a solution a known amount of iodine may be obtained at any time and in this way the solution of sodium thiosulfate may be standardized. At present it is possible to obtain commercially very pure potassium biiodate, but it is best to prepare a solution by weighing out 3.250 g. per liter and determine the concentration accurately by titrating it against a solution of thiosulfate which has been freshly standardized against pure iodine. In this way a solution is obtained which can be conveniently used from time to time for testing the concentration of the thiosulfate solution.

Method of Titrating. Place 1–2 g. of pure potassium iodide in a beaker, dissolve in as little water as possible, and to this add 5 ml. of 6 *N* hydrochloric acid, and then 20–25 ml. of the biiodate solution (never in the reverse order). Iodine is liberated, immediately and quantitatively. Dilute with 200 ml. of distilled water, and titrate the iodine as under 1.

Remark. — Instead of a solution of potassium biiodate, solid potassium iodate or potassium bromate can be used. One mole of each of these last two salts liberates 3 moles of I_2 when treated with potassium iodide and dilute acid.

* *Z. anal. Chem.*, **16**, 477, (1877).

3. *With Potassium Permanganate (Volhard)**

On adding potassium permanganate solution to an acid solution containing potassium iodide, the permanganate is reduced to manganous salt, while an equivalent amount of iodine is set free from the iodide:

$$2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 2\,MnCl_2 + 8\,H_2O + 5\,I_2.$$

If an accurately-standardized solution of potassium permanganate is at hand, it can, therefore, be used advantageously for the standardization of the sodium thiosulfate solution. The procedure is the same as was described with the potassium biiodate solution.

4. *With Potassium Dichromate*

Similarly a 0.4 *N* hydrochloric acid solution of potassium iodide will, in the cold, quantitatively reduce chromic acid to green chromic salt, setting free an equivalent amount of iodine.

$$K_2Cr_2O_7 + 6\,KI + 14\,HCl = 8\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,I_2.$$

Weigh out 4.903 gs. of pure, dry potassium dichromate into a liter measuring flask. Dissolve in water and dilute to the mark at 20°. In this way a 0.1 *N* solution is obtained. Measure out 25–40 ml. of 0.1 *N* dichromate solution into a 500-ml. beaker containing 10 ml. of concentrated hydrochloric acid and 3 g. of potassium iodide in 50 ml. of water. Allow the reaction to proceed in the dark for at least 5 minutes, dilute to 400 ml. and titrate with 0.1 *N* thiosulfate solution using starch as indicator. Some difficulty is encountered owing to the green color of the chromic solution. The solution must be 0.2–0.4 *N* in acid or the reduction is incomplete.

Permanence of 0.1 *N* Sodium Thiosulfate Solutions

A two-months-old sodium thiosulfate solution was standardized against pure iodine and its concentration found to be −1 ml. = 0.01167 g. I. Eight months later, the same solution of thiosulfate was again standardized and found to be of the same strength.

Preparation of 0.1 *N* Iodine Solution

There is no advantage to be obtained by dissolving the theoretical amount of sublimed iodine in a definite volume of solution, for the latter cannot be kept very long unchanged. It is more practical to prepare the iodine solution by placing 20–25 g. of pure potassium iodide

* *Ann. Chem. Pharm.*, **242**, 98.

in a liter bottle dissolving it in as little water as possible and then adding about 12.7 g. of commercial iodine, weighed out roughly on a watch-glass. Shake the contents of the flask until the iodine is all dissolved. When this is accomplished, dilute the solution to about one liter and standardize according to one of the following methods.

(*a*) *With* 0.1 *N Sodium Thiosulfate Solution*

Take 25 ml. of the well-mixed iodine solution in a 250-ml. Erlenmeyer flask and introduce 0.1 *N* $Na_2S_2O_3$ solution until nearly all of the iodine has reacted as shown by the color. Add 5 ml. of starch paste and titrate slowly until colorless.

Remark. — To titrate a solution of iodine obtained from a solution of iodide-iodate mixture, titrate in the same way but in the presence of 20 millimoles of free hydrochloric acid.

(*b*) *With* 0.1 *N Arsenious Acid Solution*

If iodine is allowed to act upon a neutral solution of arsenious acid the reaction which takes place may be expressed as follows:

$$H_2AsO_3^- + I_2 + 2\,HCO_3^- = H_2AsO_4^- + 2\,I^- + H_2O + 2\,CO_2.$$

It is necessary to keep the solution neutral or the opposite reaction will take place.

$$H_2AsO_4^- + 2\,I^- + 6\,H^+ = As^{+++} + I_2 + 4\,H_2O.$$

In a neutral solution arsenite can be oxidized quantitatively by means of free iodine but in strongly acid solution arsenic acid can be reduced quantitatively to the tervalent condition by means of iodide. To accomplish a complete oxidation of the arsenic by iodine, it is necessary to keep the solution approximately neutral to phenolphthalein. This is usually accomplished by providing an excess of sodium bicarbonate, by adding normal sodium carbonate to the cold, acid solution, or by adding some disodium phosphate. Caustic alkali cannot be used because it reacts with iodine to form hypo-iodite and iodide. A little neutral sodium carbonate does no harm if added to an acid solution because the liberated carbon dioxide neutralizes the hydroxyl iron formed by hydrolysis of the carbonate.

From the above equation, and the fact that the valence change of arsenic is two, it follows that the equivalent weight of arsenic is one-half the atomic weight. Ordinarily, the arsenite solution is prepared by weighing out pure As_2O_3. As the molecule contains two atoms of arsenic, it is evident that one-fourth the molecular weight in grams is the equivalent weight of As_2O_3.

To prepare 0.1 *N* arsenious acid solution, dissolve 4.95 g. of the pure sublimed oxide and 15 g. of sodium carbonate by warming with 150 ml. of water. Transfer the solution to a liter measuring flask, add 25 ml. of normal acid and dilute at 20° to the mark.

To prepare pure arsenious oxide from the commercial product, sublime by heating in a porcelain dish and collect the sublimate on a watch-glass. If a yellow sublimate of sulfide is noticed, dissolve the sample in hot 4 *N* hydrochloric acid, filter off the undissolved sulfide and cool the filtrate to cause crystals to deposit. Filter, wash with water and then sublime. Dry over calcium chloride in a desiccator.

Titrate the arsenite against the iodine solution in the usual way. Deiss,* however, finds that iodine gradually changes to iodate on standing and the iodate does not react with arsenic in the presence of sodium bicarbonate. He proceeds as follows:

Add 25 ml. of the iodine solution to 200 ml. of water. Add 2 ml. of 6 *N* hydrochloric acid and then 2 g. of sodium bicarbonate. As soon as it has dissolved titrate with sodium arsenite.

A solution of sodium arsenite gradually oxidizes on long standing.†

(c) *With Anhydrous Sodium Thiosulfate*‡

Anhydrous sodium thiosulfate may be prepared in a state of sufficient purity to permit its use for standardizing iodine solutions. Prepare a saturated filtered solution of the commercial salt at 30° to 35° and then cool while stirring constantly. Collect the salt that deposits, dry over sulfuric acid until it falls to a powder and a little of it in a test-tube shows no sign of fusion when heated to 50°. Effect the final dehydration by heating at 80° with repeated stirring of the powder.

Young standardized a solution of iodine by this method and obtained the same value as by titrating against a thiosulfate solution which had been standardized against pure iodine.

The Starch Solution

Triturate 5 g. of powdered starch into a paste with a little cold water, and slowly add to a liter of boiling water. Boil 1 or 2 minutes so that an almost clear solution is obtained. Cool by placing the dish in cold water, and after standing overnight filter the clear liquid into small 50-ml. medicine bottles. Place these in a water-bath and fill up to the neck with the starch solution, heat 2 hours, and close by means of

* *Chem. Ztg.*, **38**, 413 (1914).

† *Ibid.*, **36**, 713 (1912).

‡ S. W. Young, *J. Am. Chem. Soc.*, **26**, 1028 (1904).

soft stoppers before removing from the hot-water bath. The solution thus sterilized can be kept almost indefinitely without the slightest trace of mould formation. Such a solution prepared according to the above directions by H. N. Stokes remained perfectly clear after standing 18 months and was as sensitive then as when first made up. After opening the bottle, mould begins to form within one week, which explains why the solution is poured into small bottles; it may then be used before it becomes spoiled.

It is quicker to use a *soluble starch*. In this case triturate 6 g. with cold water to a thin paste and rinse this into a liter of boiling water. Add a solution of 6 g. zinc chloride in 50 ml. of water.

Sensitiveness of the Iodo-Starch Reaction

As already mentioned in Vol. I, iodine produces a blue color with starch only when hydriodic acid or a soluble iodide is present, and further the formation of the blue color depends not only upon the presence of iodide but is largely influenced by the concentration of the iodide solution. With the same amount of iodide and different volumes of liquid quite different amounts of iodine are necessary to produce the blue color. From this it is evident that in any iodimetric analysis about the same concentration should be maintained as in the case of the standardization of the solutions used for the analysis. When 0.1 *N* solutions are used, the error produced by not following this rule is a small one and for most purposes can be neglected. On the other hand, when an analysis is made with 0.01 *N* solutions, a large error may be introduced and a blank should always be made to determine how much iodine solution is required to give an end-point. The results of a series of experiments show that the amount of iodine solution necessary to produce the blue color in the absence of potassium iodide is directly proportioned to the dilution. If the solution contains 1 g. of potassium iodide, a blue color will be produced by the same amount of iodine solution as long as not more than 150 ml. of solution are present, but with a greater volume than that, more iodine is necessary independent of whether the solution contains 1 g. or more of potassium iodide.

ANALYSES BY IODIMETRIC METHODS

1. Determination of Free Iodine

1000 ml. of 0.1 *N* thiosulfate solution = 12.69 g. I.

Dissolve the iodine in a solution of potassium iodide and titrate either with sodium thiosulfate or with arsenious acid exactly as described under the standardization of an iodine solution.

2. Determination of Chlorine in Chlorine Water

1000 ml. of 0.1 N thiosulfate solution = 3.546 g. Cl.

Add a measured amount of chlorine water to a solution containing an excess of potassium iodide. Hold the point of the pipet just above the surface of the iodide solution contained in a glass-stoppered bottle. After the chlorine water has been added, stopper the bottle, vigorously shake the contents, and titrate the liberated iodine with sodium thiosulfate as above:

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

3. Determination of Bromine in Bromine Water

1000 ml. of 0.1 N thiosulfate solution = 7.992 g. Br.

The procedure is the same as under 2:

$$2\,KI + Br_2 = 2\,KBr + I_2.$$

4. Determination of Hypochlorous Acid in the Presence of Chlorine

The determination is based upon the following reactions:

$$HOCl + 2\,KI = KCl + KOH + I_2;$$
$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

1 mole of hypochlorous acid liberates 1 mole of iodine, but produces at the same time 1 mole of potassium hydroxide, while the chlorine simply sets free an equivalent amount of iodine. After neutralizing the alkali by means of an excess of hydrochloric acid and determining the iodine by titration with sodium thiosulfate, the excess of hydrochloric acid is titrated with standard alkali solution.

Procedure. — Add a measured excess of 0.1 N hydrochloric acid to a potassium iodide solution, and to this add a known amount of the mixture of chlorine and hypochlorous acid. Titrate the iodine set free with 0.1 thiosulfate solution. Then add methyl orange to the colorless solution and titrate the excess of hydrochloric acid with 0.1 N NaOH. The alkali hydroxide produced by the action of the hypochlorous acid upon the iodide requires half as much 0.1 N acid for neutralization as are required of 0.1 N $Na_2S_2O_3$ solution to react with the iodine set free by the action of the hypochlorous acid.

Example. — If V ml. of chlorine + hypochlorous acid were taken fo analysis, t ml. 0.1 N HCl were added at the start, T ml. 0.1 N $Na_2S_2O_3$ used for titrating the iodine, and t_1 ml. 0.1 N NaOH for titrating the excess of acid, then $t - t_1$ ml. of 0.1 N acid were required to neutralize the alkali hydroxide and $2\,(t - t_1)$ ml. of 0.1 N $Na_2S_2O_3$ to react with the iodine formed from the hypochlorite.

Hence $(t - t_1)\ 0.005247^*$ = g. HOCl in V ml. solution

and

$$T - 2\,(t - t_1)\ 0.003546 = \text{g. Cl in } V \text{ ml. solution.}$$

5. Determination of Iodine in Soluble Iodides†

(*a*) *By Decomposition with Ferric Salts*

If a solution of a soluble iodide is treated with an excess of ferric-ammonium alum and acidified with sulfuric acid, the ferric salt will be reduced to ferrous salt with separation of iodine:

$$Fe_2(SO_4)_3 + 2\,HI = H_2SO_4 + 2\,FeSO_4 + I_2$$

If the solution is heated to boiling, the iodine escapes with the steam and can be collected in a solution of potassium iodide and then titrated with sodium thiosulfate or arsenious acid. This method is suited for separating iodine from bromine, for bromides do not reduce ferric salts. The bromide will be found in the residue obtained after the distillation, and is best determined gravimetrically.

(*b*) *By Decomposition with Nitrous Acid (Fresenius)*

This excellent method, which is especially suited for determining small amounts of iodine in the presence of bromine and chlorine in mineral waters, depends upon the easy oxidation of hydriodic acid by means of nitrous acid.

$$2\,HI + 2\,HNO_2 = 2\,H_2O + 2\,NO + I_2.$$

Hydrochloric and hydrobromic acids are not attacked by nitrous acid.

Procedure. — To the small apparatus shown in Fig. 115 transfer the neutral or slightly alkaline solution of the iodide; make slightly acid with dilute sulfuric acid, and add a little freshly-distilled, colorless carbon bisulfide (carbon tetrachloride or chloroform), so that it does not quite reach to the stop-cock, near the bottom of the tube. Then introduce 2, or at the most 3, drops of "nitrose,"‡ stopper the tube, shake vigorously, and then allow the carbon bisulfide to settle once more. The small amount of the latter which at first adheres to the glass sides can be made to fall to the bottom by revolving and inclining the tube. On the upper surface of the liquid there will still remain a few tiny drops

* HOCl = 52.47; 1 ml. 0.1 N solution = 0.005247 g. HOCl (against NaOH).

† In the case of insoluble iodides, the metal must first be removed if the iodine is to be determined volumetrically. This can be accomplished by the method of Mensel (*Z. anal. Chem.*, **12**, 137). It may be said, however, that the volumetric method offers no advantages over the gravimetric one.

‡ Cf. Vol. I.

of carbon bisulfide. To obtain these, moisten a filter with water and place the funnel under the glass stop-cock, remove the stopper from the tube and allow the aqueous solution to run through the filter; the carbon bisulfide will remain behind on the paper. Shake the carbon bisulfide remaining in the tube 3 times with successive portions of distilled water, and each time allow the latter to run off through the same filter. Then place the funnel at the top of the tube, puncture the filter with a pointed glass rod, and wash the carbon bisulfide into the tube by means of about 0.5 ml. of water. After this add 1 or 2 drops of sodium bicarbonate solution and thoroughly shake with the carbon bisulfide, then add standard sodium thiosulfate solution until the reddish-violet carbon bisulfide solution becomes colorless.

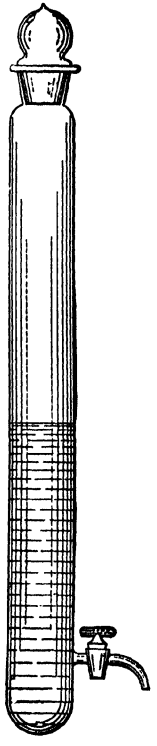


FIG. 115.

The value of the sodium thiosulfate solution is not determined as ordinarily, but by means of a potassium iodide solution treated as above described.

Remark. — This method is useful for determining small amounts of iodide in the presence of relatively large amounts of chloride and bromide, as in the analysis of mineral waters. For the standardization of the sodium thiosulfate solution, as nearly as possible the same amount of potassium iodide should be used as is present in the unknown solution; this is determined by the color of the carbon bisulfide. Pure potassium iodide must be used for this purpose, and its purity tested by means of a gravimetric determination of the iodine present in the salt after it has been dried at 170°–180°.

The reason the sodium thiosulfate solution must be standardized in this way is as follows:

When an aqueous solution containing iodine is shaken with carbon bisulfide, not all of the iodine but the greater part of it will pass into the latter solvent. The error is compensated, however, by standardizing the solution in the same way.

If the solution of a substance is shaken with another solvent in which the former does not mix, the original amount of the substance divides itself between the two solvents, and in fact the concentration of one solution (amount of the dissolved substance present per milliliter) always bears a constant relation to that of the other.

Thus if x_0 g. of iodine are dissolved in V ml. of water, and the solution is shaken with V_1 ml. of carbon bisulfide, then x_1 g. of iodine will remain in the aqueous solution and $x_0 - x_1$ g. will pass into the carbon bisulfide.

The amount x_1 is found by the following equation:

$$(1) \quad \frac{x_1}{V} = \frac{x_0 - x_1}{V_1} k, \qquad \text{and} \qquad x_1 = x_0 \frac{kV}{V_1 + Vk}.$$

$\frac{x_1}{V}$ and $\frac{x_0 - x_1}{V_1}$ are the concentrations in each of the solutions and k is the *distribution*

coefficient, which is $\frac{1}{400}$ for iodine.* If the aqueous solution is now shaken with the same amount of fresh carbon bisulfide, then x_2 g. of iodine will remain in the water and $x_1 - x_2$ will be extracted by the carbon bisulfide. In this case, however,

$$(2) \quad x_2 = x_0\left(\frac{kV}{V_1 + Vk}\right)^2 \text{ g. iodine,}$$

so that after shaking n times with fresh portions of carbon bisulfide, the amount of iodine remaining in the water would be:

$$(3) \quad x_n = x_0\left(\frac{kV}{V_1 + Vx}\right)^n \text{ g. iodine.}$$

Assuming that in the analysis 0.005 g. of iodine was dissolved in 10 ml. of water and that this solution was shaken once with 1 ml. of carbon bisulfide, then according to equation (1)

$$x_1 = 0.005\frac{\frac{1}{400} \times 10}{1 + \frac{10}{400}} = 0.005 \cdot \frac{1}{41} = 0.0001 \text{ g. iodine}$$

would remain dissolved in the water, or an amount that can be neglected. The distribution coefficient, as used above, holds when the same molecular species is present in each solvent. When potassium iodide is added to the aqueous solution, KI_3 is formed and it is much harder to dissolve out the iodine. As some potassium iodide is present, the above calculation is inexact.

If, after shaking with carbon bisulfide, the aqueous solution still appears yellow, it must be treated a second, and perhaps a third, time with fresh amounts of carbon bisulfide.

6. Determination of Bromine in Soluble Bromides (Bunsen)

If chlorine water is added to a colorless bromide solution in a porcelain dish, the solution becomes yellow:

$$2\,KBr + Cl_2 = 2\,KCl + Br_2.$$

If it is heated to boiling, the bromine is expelled and the solution becomes colorless again. The addition of the chlorine water is continued until finally no yellow coloration is produced.

Preparation and Standardization of the Chlorine Water

Dilute 100 ml. of a saturated chlorine water to 500 ml. and titrate against a weighed amount of pure potassium bromide which has been dried at 170°, taking about the same amount of bromide for the standardization as is supposed to be present in the solution to be analyzed. During the titration, wrap the buret containing the chlorine water in black paper to protect its contents from the light, and hold the tip of the buret just above the surface of the hot bromide solution, so that as little chlorine as possible is lost by evaporation.

* Berthelot and Jungfleisch, *Comptes rend.*, **69**, 338.

7. Determination of Iodine and Bromine in Mineral Waters

According to the amount of halogen present, take 5–60 liters of water for the analysis.

The amount of bromine and iodine present is usually small compared with the chlorine, so that the residue obtained by the evaporation of a large amount of water cannot be used directly for the analysis, but by partial crystallization a mother-liquor rich in bromide and iodide must first be obtained.

Procedure. — Pour the water into a large evaporating-dish, a liter at a time, and if not already alkaline,* add enough pure sodium carbonate solution to make it distinctly so, and evaporate to about one-fourth of its original volume. This causes the separation of some calcium and magnesium carbonates, as well as hydroxides of iron and manganese, but all of the halogen salts remain in solution. Filter off the residue and thoroughly wash with water. Concentrate the filtrate further until salts begin to crystallize out, and pour the hot solution into three times its volume of absolute alcohol; this causes the greater part of the sodium chloride and other undesired salts to precipitate. After standing 12 hours, filter the alcoholic liquid and wash the residue 5 or 6 times with 95 per cent alcohol.

To the alcoholic solution, which contains all of the iodine and bromine with considerable chlorine in the form of the alkali salts, add 5 drops of concentrated potassium hydroxide solution and distil off most of the alcohol, while passing a current of air through the solution by means of a capillary tube reaching to the bottom of the liquid in the distilling-flask.

Evaporate the residue from the distillation until salts again begin to crystallize out and repeat the precipitation with alcohol. Again distil off the alcohol, but this time with the addition of only 1 or 2 drops of potassium hydroxide solution. According to the amount of salts present in solution repeat this operation 3–6 times. Place the final filtrate, after the alcohol has been distilled off, in a platinum dish, evaporate to dryness, cover the dish with a watch-glass, and gently ignite the residue to destroy organic matter. Dissolve the residue from the ignition in a little water, filter off the carbonaceous material,† make the solution slightly acid with dilute sulfuric acid, titrate the iodine liberated by the addition of 1 or 2 drops of " nitrose," and with sodium thiosulfate, after shaking with chloroform, as described on p. 559.‡ Determine bromine in the aqueous solution obtained after the

* The solution is alkaline if after the addition of phenolphthalein the solution turns red on boiling.

† If the filtrate is not completely colorless, evaporate and again ignite.

‡ Lecco determines the iodine colorimetrically (*Z. anal. Chem.*, **35**, 318).

extraction of the iodine with chloroform. Make the acid solution alkaline by the addition of sodium carbonate solution, add 2 drops of a saturated sugar solution, and evaporate the solution to dryness in a platinum dish. With a watch-glass upon the dish, gently ignite the residue to destroy the sugar and the excess of nitrite.* After this has been accomplished dissolve the residue in water, filter, make slightly acid with sulfuric acid, and titrate the bromine with chlorine water as described on p. 561.

Remark. — If sufficient mineral water is available it is better to divide the mother-liquor containing the bromide and iodide into two portions; in one portion determine the iodine as above, and in the other determine bromine and iodine by titration with chlorine water.†

8. Analysis of Peroxides (Bunsen)

All peroxides of the heavy metals which evolve chlorine on treatment with hydrochloric acid, can be determined with great accuracy by conducting the chlorine

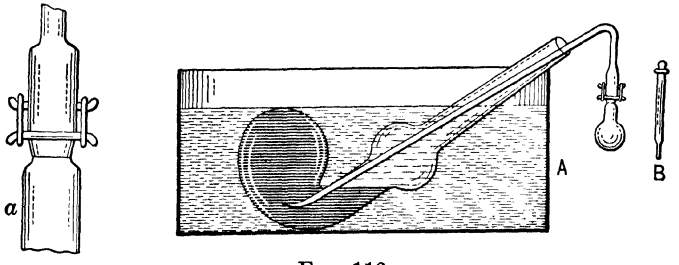


FIG. 116.

into potassium iodide solution and titrating the liberated iodine with sodium thiosulfate or arsenious acid solution. It is only necessary to make sure that the chlorine is allowed to act upon the potassium iodide without loss. For all such determinations, Bunsen employed the apparatus shown in Fig. 116. The small decomposition-flask of about 40 ml. capacity has a ground-glass connection with the delivery-tube‡ and is held firmly in place by means of rubber rings, as at *a*. The lower end of the bent delivery-tube is drawn out into a not-too-small capillary.

Procedure. — Place the finely-powdered substance in the small glass-stoppered weighing-tube (Fig. 116 *B*), which has a small piece of glass

* The addition of the sugar causes the nitrite to be destroyed at a lower temperature than would otherwise be the case, and the danger of losing bromine by volatilization is avoided.

† As the chlorine water was standardized against bromine, an amount of the latter equivalent to the iodine present should be deducted from the amount represented by the chlorine water used; the difference shows the bromine present.

‡ Instead of the ground-flask connection, Bunsen used a tube of the same size as the neck of the flask and connected them with rubber tubing, the two glass tubes being against one another.

fused on the end, and weigh. Take hold of the tube by the glass at the bottom,* introduce it into the neck of an absolutely dry decomposition-flask, and allow the required amount of the substance to fall into it by carefully revolving the weighing-tube. Again weigh the tube, to determine the amount of substance taken. Add hydrochloric acid (its concentration depends upon the nature of the substance), at once connect the delivery tubing with the flask and introduce it into the retort containing potassium iodide solution. By means of a tiny flame, heat the contents of the flask to boiling and distil half to two-thirds of the liquid over into the retort. To prevent the iodide solution from sucking back into the flask, take out the delivery-tube from the retort before removing the flame, and wash the contents of the tube into the retort.

Pour the potassium iodide solution into a large beaker, rinse out the retort several times with a little water, and then with potassium iodide solution to remove any iodine which may remain adhering to the glass. Titrate with 0.1 *N* sodium thiosulfate solution using starch as indicator. In this way pyrolusite, chromates, lead peroxide, minium, ceric oxide, selenic, telluric, and molybdic acids may be analyzed.

(*a*) Determination of Manganese Dioxide in Pyrolusite

$$1000 \text{ ml. of } 0.1\ N\ Na_2S_2O_3 \text{ solution} = \frac{MnO_2}{20} = 4.347 \text{ g. } MnO_2.$$

Weigh out about 0.2 g. of the substance which has been dried at 120°. To this add 25 ml. of 4 *N* hydrochloric acid and carry out the analysis as described above.

$$MnO_2 + 4\,HCl = 2\,H_2O + MnCl_2 + Cl_2$$
$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

If t ml. of 0.1 *N* $Na_2S_2O_3$ were used in titrating a g. of MnO_2, then

$$\frac{0.4347\,t}{a} = \text{per cent } MnO_2.$$

The determination of chromates, lead peroxide, and selenic acid is carried out in the same way, except that 12 *N* hydrochloric acid is used for the decomposition.

(*b*) Determination of Telluric Acid

If the telluric acid is present as the hydrous acid ($H_2TeO_4 + 2\,H_2O$) or as tellurate, the analysis is performed in the same way as with selenic and chromic acids. If, however, the tellurium is present as the an-

* By holding the tube in this way, deviations of weight, due to unequal warming, are avoided.

hydrous acid or as the anhydride, the method must be modified, for these substances are scarcely attacked by concentrated hydrochloric acid. They are placed in the decomposition-flask, dissolved in a little concentrated potassium hydroxide,* and to the tellurate solution thus obtained the concentrated hydrochloric acid is added; the reduction then is accomplished without difficulty:

$$K_2TeO_4 + 4\,HCl = 2\,KCl + H_2TeO_3 + H_2O + Cl_2.$$

According to this equation, 1 liter of 0.1 N $Na_2S_2O_3$ = 6.375 g. Te = 6.535 g. TeO_2.

(*c*) Determination of Ceric Oxide

$$1000 \text{ ml. of } 0.1\ N \text{ iodine solution} = \frac{CeO_2}{10} = 17.225 \text{ g. } CeO_2.$$

Ceric oxide when mixed with considerable lanthanum and didymium oxides is reduced by distillation with concentrated hydrochloric acid: $2\,CeO_2 + 8\,HCl = 4\,H_2O + 2\,CeCl_3 + Cl_2$.

If, however, the mixture contains but little of the two last substances, or if it is pure ceric oxide, the heating with concentrated hydrochloric acid is of no avail; the ceric oxide will not dissolve.

In the presence of hydriodic acid, however, the reduction takes place readily, so that it is only necessary to add 2 g. of potassium iodide to a weighed amount of the substance (0.67–0.68 g.) in the decomposition-flask, and then, after the addition of hydrochloric acid, violet vapors of iodine can be distilled from the solution:

$$2\,CeO_2 + 2\,KI + 8\,HCl = 2\,KCl + 2\,CeCl_3 + 4\,H_2O + I_2.$$

Often there will be so much iodine given off that the solid is likely to stop up the tube and the flask may explode. To prevent this, do not draw out the end of the delivery-tube into a capillary, but at the bottom leave an opening of about 4 mm. in diameter. During the operation, the flame must be protected from air-currents, for otherwise there is danger of liquid sucking back from the retort.

(*d*) Determination of Vanadic Acid†

$$1000 \text{ ml. of } 0.1\ N \text{ iodine solution} = \frac{V_2O_5}{20} = 9.12 \text{ g. } V_2O_5.$$

By boiling vanadic acid, or one of its salts, with concentrated hydrochloric acid, the vanadium is reduced with evolution of chlorine. Unfortunately, this reaction cannot be used for the determination of

* The solution could not be effected by using *sodium* hydroxide.

† Friedheim and Euler, *Ber.*, **28**, 2067 (1895), and **29**, 2981 (1896).

vanadic acid, for the amount of chlorine evolved depends upon the concentration of the vanadium solution; the vanadium is not reduced to a definite oxide. On the other hand, by means of *hydrobromic* acid,* vanadic acid is reduced to a blue vanadyl salt:

$$2\,H_3VO_4 + 2\,HBr + 4\,HCl = V_2O_2Cl_4 + 6\,H_2O + Br_2.$$

If the free bromine is absorbed in potassium iodide, and the liberated iodine titrated with sodium thiosulfate, a sharp determination of the vanadium will be obtained. To carry out this analysis, place 0.3–0.5 g. of the vanadate, together with 1.5–2 g. of potassium bromide in the decomposition-flask of the Bunsen apparatus (Fig. 116, p. 563), add 30 ml. of concentrated hydrochloric acid, and distil as before. The decomposition is always complete when the liquid in the flask is a pure blue.

If hydriodic acid is used instead of hydrobromic acid, the vanadic acid is reduced still further, almost to VCl_3.† In fact, a complete reduction to the latter can be accomplished if potassium iodide, concentrated hydrochloric acid, and 1 or 2 ml. of sirupy phosphoric acid are added and the liquid distilled until no more vapors of iodine are evolved. According to Steffan, this will always be the case when the liquid is reduced to one-third of its original volume.

(*e*) Determination of Molybdic Acid

$$1000 \text{ ml. of } 0.1\ N\ Na_2S_2O_3 = \frac{MoO_3}{10} = 14.4 \text{ g. } MoO_3.$$

The determination depends upon the fact that molybdic acid is reduced to the quinquevalent state by means of hydriodic acid with liberation of iodine:

$$2\,MoO_3 + 2\,HI + 10\,HCl = 2\,MoCl_5 + 6\,H_2O + I_2.$$

Remark. — This method finds no practical application on account of the fact that it is difficult to obtain a quantitative reduction in accordance with the above equation. Gooch and Fairbanks‡ found that if a solution containing molybdic acid is distilled in the Bunsen apparatus with potassium iodide and hydrochloric acid until iodine vapors are no longer visible and the solution is a light green, too little iodine is obtained. On the other hand, if the distillation is continued still further, they found that the reduction goes on and more iodine is obtained than corresponds to the above equation. Steffan,§ who tested the method in the author's laboratory, obtained results agreeing with those published by Gooch and Fairbanks. By means of *hydrobromic* acid, molybdic acid is not reduced.

* Holverscheidt, *Dissertation*, Berlin, 1890.

† Friedheim and Euler, *Ber.*, **28**, 2067 (1895).

‡ *Z. anorg. Chem.*, **13**, 101 (1897), and **14**, 317.

§ Steffan, *Inaug. Dissertation*, Zürich, 1902.

(*f*) Determination of Vanadic and Molybdic Acids in the Presence of One Another

According to Steffan, these two acids may be determined very accurately when present together. The vanadic acid is determined, according to Holverscheidt, by distillation with potassium bromide and concentrated hydrochloric acid, absorption of the bromine in potassium iodide solution, and titration of the liberated iodine (cf. p. 566). The contents of the distillation flask, in which the vanadium is present as vanadyl salt and the molybdenum as molybdic acid, are treated with hydrogen sulfide in a pressure-flask, and the precipitated molybdenum sulfide is filtered through a Gooch crucible, and weighed as MoO_3, as described on p. 264. The results obtained by this method are perfectly satisfactory.

As molybdic acid is unattacked by hydrobromic acid, but is reduced to the quinquevalent state with separation of iodine by means of hydriodic acid, Friedheim and Euler proposed the following method for the determination of vanadic and molybdic acids when present together:

Distil the mixture of the two acids as usual with potassium bromide and hydrochloric acid; the vanadium is thereby reduced to the quadrivalent condition (p. 566) with separation of two atoms of bromine which are determined iodimetrically. To the cold solution remaining in the distilling-flask, add potassium iodide, hydrochloric acid, and sirupy phosphoric acid and continue distilling until no more iodine is given off and the solution is a light green.

By means of this second reduction the vanadium tetroxide is supposed to be reduced to VCl_3, and consequently more iodine is liberated by the vanadium. Furthermore, according to Friedheim and Euler, the molybdenum is reduced to $MoCl_5$.

If, therefore, the amount of iodine corresponding to the first titration is deducted from the amount obtained in the second, the difference should correspond to the amount of molybdenum present. But Gooch and Fairbanks have shown that this is not the case.*

The error in the method lies in the fact that the vanadic acid is only reduced completely to V_2O_3 when the solution is distilled to one-third of its original volume. In this case, however, the molybdenum is reduced further than corresponds to the formation of $MoCl_5$; too much iodine is liberated and too high a value is obtained for the molybdic acid present. On the other hand, if after the addition of the potassium

* The results of Gooch and Fairbanks have been confirmed in every respect by Steffan.

iodide the liquid is only distilled until the iodine vapors cease to appear and the solution is a light green, the vanadium is not completely reduced to VCl_3, and a too low value for the molybdenum is obtained.

9. Analysis of Chlorates

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{KClO_3}{60} = 2.043 \text{ g. } KClO_3.$$

This is carried out the same way as the analysis of pyrolusite (cf. p. 563): $KClO_3 + 6\,HCl = KCl + 3\,H_2O + 3\,Cl_2$.

Many oxidizing agents can be determined iodimetrically without previous distillation with hydrochloric acid.

For other methods of analyzing chlorates iodimetrically, consult H. Dietz, *Chem.-Ztg.* **1901**, 727 and Luther and Rutter, Z. *anal. Chem.* **46**, 521 (1907).

10. Determination of Hypochlorous Acid

This determination is used in the analysis of chloride of lime.

Procedure. — Into a tared weighing-tube introduce about 5 g. of "chloride of lime," and weigh the stoppered tube. Wash into a porcelain dish, rub to a paste with a pestle, and transfer without loss to a 500-ml. measuring-flask. Dilute to the mark with water and shake well. Of this turbid solution, pipet off 20 ml. into 10 ml. of 10 per cent potassium iodide solution, make acid with hydrochloric acid, titrate the liberated iodine with 0.1 N $Na_2S_2O_3$. Express the result in per cent of *available chlorine.*

Remark. — If the "chloride of lime" contained calcium chlorate it will be partially reduced by hydrochloric acid and potassium iodide with liberation of iodine, and consequently the results obtained for hypochlorite chlorine (bleaching chlorine) will be too high. In this case the hypochlorite is best determined by a chlorimetric process with arsenious acid (see p. 598).

11. The Analysis of Iodates

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{HIO_3}{60} = 2.932 \text{ g. } HIO_3.$$

Allow the solution of the iodate to run into an acid solution containing an excess of potassium iodide. Iodine is set free according to the equation, $KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2$. Titrate the iodine with thiosulfate solution as described on p. 553.

12. The Analysis of Periodates

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{HIO_4}{80} = 2.399 \text{ g. } HIO_4.$$

The analysis of periodates is carried out exactly as with iodates; the reaction that takes place is

$$KIO_4 + 7\ KI + 8\ HCl = 8\ KCl + 4\ H_2O + 4\ I_2.$$

13. Analysis of a Mixture of Iodate and Periodate*

If a neutral or slightly alkaline solution of an alkali periodate is treated with a solution of potassium iodide, the following reaction takes place:

$$KIO_4 + 2\ KI + H_2O = 2\ KOH + KIO_3 + I_2.$$

The liberated iodine is titrated with tenth-normal arsenious acid (not with sodium thiosulfate); in a neutral solution the *iodate* does not react with potassium iodide. For the analysis of a mixture of iodate and periodate, the following procedure is used:

In one sample determine the iodate + periodate by adding the solution of the substance to an acid solution containing an excess of potassium iodide and titrate the liberated iodine with sodium thiosulfate solution.

Dissolve a second sample in water, add a drop of phenolphthalein indicator, and make the solution alkaline enough to give the pink color with phenolphthalein, adding alkali if the solution is acid and hydrochloric acid if the solution is strongly alkaline. To the barely alkaline solution, add 10 ml. of a cold, saturated solution of sodium bicarbonate and then an excess of potassium iodide; titrate the liberated iodine at once with 0.1 N arsenious acid.†

Example. — In a mixture of KIO_3 and KIO_4 weighing a g., the iodine liberated on treatment with an acid solution of KI reacts with T ml. of 0.1 N $Na_2S_2O_3$ and the same weight of sample liberates in alkaline solution only enough iodine to react with t ml. of 0.1 N As_2O_3 solution. By comparing the equations given under **12** and **13**, it is evident that the periodate alone would react with $4\,t$ ml. of 0.1 N $Na_2S_2O_3$ in acid solution. The amount of KIO_4 and KIO_3 present will be

$$t \times 0.01150 \text{ g.} = \frac{t \times 1.150}{a} \text{ per cent } KIO_4,$$

$$(T - 4\,t) \times 0.003567 \text{ g.} = \frac{(T - 4\,t) \times 0.3567}{a} \text{ per cent } KIO_3.$$

* E. Müller and O. Friedberger, *Ber.*, **1902**, 2655.

† The iodine cannot be titrated in the alkaline solution with sodium thiosulfate, and the iodine in the acid solution cannot be titrated with the arsenious acid.

14. Analysis of Iodides*

Method of H. Dietz and B. M. Margosches

$$1 \text{ liter of } 0.1\ N\ KIO_3 = \frac{5\ I}{60} = 10.58 \text{ g. iodine.}$$

Treat the solution of the iodide with an excess of 0.1 N potassium iodate solution, make acid with sulfuric acid, add a piece of calcite, as suggested by Prince,† and boil until all the iodine is expelled. Allow the solution to cool, then add an excess of potassium iodide, and titrate the iodine now liberated, which corresponds to the excess of potassium iodate used, with 0.1 N $Na_2S_2O_3$ solution.

From the equation

$$KIO_3 + 5\ KI + 6\ HCl = 6\ KCl + 3\ H_2O + 3\ I_2.$$

it is evident that five-sixths of the iodine liberated comes from the iodide. If, therefore, T ml. of 0.1 N KIO_3 solution were added and t ml. of 0.1 N Na_2S_2O were used for titrating the excess of KIO_3, then there is present

$$(T - t) \times 0.01058 \text{ g. iodine as iodide.}$$

15. Determination of Copper with Potassium Iodate‡

Potassium iodate in dilute hydrochloric acid solution is reduced by potassium iodide to free iodine (cf. p. 568):

$$KIO_3 + 5\ KI + 6\ HCl = 6\ KCl + 3\ I_2 + 3\ H_2O,$$

but if the solution is strongly acid with hydrochloric acid and an excess of the iodate is added, the iodine is oxidized to ICl:

$$2\ I_2 + KIO_3 + 6\ HCl = KCl + 5\ ICl + 3\ H_2O,$$

and in this case the whole reaction may be expressed by the equation:

$$KIO_3 + 2\ KI + 6\ HCl = 3\ KCl + 3\ ICl + 3\ H_2O.$$

The ICl is not very stable, and is at once reduced to free iodine in the presence of any oxidizable substance.

L. W. Andrew§ has shown that quite a number of reducing substances, such as free iodine, iodides, arsenites, and antimonites, can be titrated with potassium iodate very exactly, by taking advantage of the fact that when the reducing agent is present in excess free iodine is formed, which is oxidized quantitatively by more iodate, provided the proper amount of hydrochloric acid is present. Copper solutions are precipitated quantitatively by potassium thiocyanate and sulfurous acid as cuprous thiocyanate, CuSCN, and Parr|| has estimated copper quantitatively by titrating

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* *Chem. Ztg.*, **1904**, II, 1191.

† *Inaug. Dissert.*, Zürich, 1910.

‡ Jamieson, Levy, and Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

§ *Ibid.*, **25**, 756 (1903).

|| *J. Am. Chem. Soc.*, **22**, 685 (1900).

this precipitate with permanganate. The oxidation is, however, simpler and more accurate when the titration is effected by potassium iodate, or biiodate. The reaction goes through the stage in which iodine is set free, but the latter is oxidized completely to iodine chloride upon the addition of more iodate:

(*a*) $10\,CuSCN + 14\,KIO_3 + 14\,HCl = 10\,CuSO_4 + 7\,I_2 + 10\,HCN + 14\,KCl + 2\,H_2O$.

(*b*) $2\,I_2 + KIO_3 + 6\,HCl = KCl + 5\,ICl + 3\,H_2O$,

and the whole reaction is

(*c*) $4\,CuSCN + 7\,KIO_3 + 14\,HCl = 4\,CuSO_4 + 7\,ICl + 4\,HCN + 7\,KCl + 5\,H_2O$.

The potassium iodate solution is very stable and can be preserved for years if protected from evaporation. The standard solution used can be prepared by weighing out a known amount of the pure salt and dissolving to a definite volume, or the solution may be standardized against pure copper, carrying out the process as in an analysis. A convenient concentration is one-fifth mole KIO_3 per liter.

Procedure. — To 0.5 g. of the ore in a 200-ml. flask, add 6–10 ml. of strong nitric acid, and boil gently, best over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 ml. of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 ml. Now add gradually and carefully, best after cooling somewhat, 12 ml. of 18 *N* sulfuric acid and continue the boiling until sulfuric acid fumes are evolved copiously. Allow to cool, add 25 ml. of cold water, heat to boiling, and keep hot until the soluble sulfates have dissolved. Filter into a beaker, and wash the flask and filter thoroughly with cold water.* Nearly neutralize the filtrate with ammonia and add 10–15 ml. of strong sulfur dioxide water. Heat just to boiling and add 5–10 ml. of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 or 10 minutes, filter on paper, and wash with hot water until the ammonium thiocyanate is completely removed.

Place the filter with its contents in a glass-stoppered bottle of about 250 ml. capacity, and by means of a piece of moist filter-paper transfer into the bottle any precipitate adhering to the stirring-rod and beaker. Add to the bottle about 5 ml. of chloroform, 20 ml. of water and 30 ml. of concentrated hydrochloric acid (the two latter liquids may be previously mixed). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then

* With substances containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulfate or antimonic oxide that may be present.

diminishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

In order to make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 ml. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference in the results of the titration.

16. Analysis of Soluble Chromates

A concentrated, acid solution of potassium iodide is treated with a weighed amount of the chromate, diluted with water, and the liberated iodine titrated. (Cf. standardization of sodium thiosulfate against potassium dichromate, p. 554.)

17. Determination of Chromium in Chromite

1 ml. of 0.1 N $Na_2S_2O_3$ = 0.001733 g. Cr.

Mix about 0.2 g. of the finely-powdered chromite with 4 g. of sodium peroxide in a nickel or iron crucible. Heat carefully until the flux melts and keep at this temperature for 15 or 20 minutes, using a small flame. At the end of this time, all the chromium will be converted into soluble sodium chromate. Place the crucible and its contents in 100–200 ml. of water, heat to boiling and digest at this temperature until the melt is completely disintegrated and the excess of peroxide is decomposed. Filter off the ferric oxide, boil the filtrate to make sure that all peroxide is destroyed and evaporate to a small volume. Neutralize with hydrochloric acid, and titrate as described on p. 554.

Remark. — By the fusion with sodium peroxide, chromite is converted into sodium chromate and probably sodium ferrite; the former is soluble in water but the latter undergoes hydrolysis;

$$2\ FeCr_2O_4 + 7\ Na_2O_2 = 4\ Na_2CrO_4 + 2\ NaFeO_2 + 2\ Na_2O.$$
$$NaFeO_2 + 2\ H_2O = NaOH + Fe(OH)_3.$$

If the chromite or the crucible contains manganese sometimes the aqueous solution is colored with permanganate. In that case, cool and decompose the permanganate by adding sodium peroxide to the solution.

Little and Costa* have modified the procedure so that it is not necessary to filter off the insoluble ferric hydroxide by adding ammonium fluoride to the acid solution.

* *J. Ind. Eng. Chem.* **13**, 228 (1921).

This forms a complex anion, $Fe^{+++} + 6\ F^- \rightarrow FeF_6^{---}$, with ferric ions and thus prevents the reduction of the tervalent iron upon treatment with potassium iodide. Their procedure is briefly as follows:

Carry out the fusion of the chromite with sodium peroxide as outlined above. Allow the contents of the crucible to cool and then digest with 150 ml. of water. When the fused mass has disintegrated, remove the crucible and add 0.5 g. more of sodium peroxide to make sure that the oxidation of the chromium is complete. Heat carefully to boiling and keep at this temperature long enough to decompose the excess peroxide. Cool, add hydrochloric acid till the precipitated ferric hydroxide dissolves and add 5 ml. of concentrated acid in excess for each 100 ml. of solution. Add ammonium fluoride until a small drop of the solution fails to give the Prussian blue test for ferric iron by treatment with a drop of ferrocyanide solution on a spot plate. Add 1 g. of fluoride in excess. Add 3 g. of pure potassium iodide, wait three minutes and then titrate the liberated iodine with sodium thiosulfate solution.

18. Determination of Lead Peroxide

*Method of Diehl, modified by Topf**

The analysis depends upon the fact that lead peroxide is reduced by means of potassium iodide in acetic acid solution when considerable alkali acetate is present:

$$PbO_2 + 4\ HI = PbI_2 + 2\ H_2O + I_2.$$

After diluting with water the iodine is titrated with 0.1 *N* $Na_2S_2O_3$ solution.

Procedure. — Dissolve about 0.5 g. of the substance with 1.2 g. of potassium iodide and 10 g. of sodium acetate in 5 ml. of 5 per cent acetic acid. Dilute the solution with water to a volume of 25 ml. and titrate with sodium thiosulfate.

Remark. — Moist lead peroxide reacts almost instantly on undergoing the above treatment; thoroughly dried material, on the other hand, dissolves after a few minutes provided it is finely ground. If, however, the dry peroxide is in the form of coarse grains, it may be several hours before the reaction is finished, or the decomposition may be incomplete.

Furthermore, too much potassium iodide should not be used, as otherwise lead iodide will separate out. In that case add 3–5 g. more of sodium acetate and a few milliliters of water. Shake until the lead iodide has dissolved completely and then dilute to a volume of 25 ml. The solution must remain perfectly clear and there should not be a trace of lead iodide precipitate.

This excellent method may also be used for the analysis of minium (red lead) or pyrolusite.

19. Determination of Ozone in Ozonized Oxygen

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{O_3}{20} = 2.4 \text{ g. } O_3.$$

(*a*) *Schönbein's Method*

The most accurate method for estimating ozone consists in allowing the ozonized oxygen to act upon potassium iodide solution whereby free iodine is formed:

$$2\ KI + O_3 + H_2O = 2\ KOH + I_2 + O_2,$$

* Diehl, *Dingl. polyt. J.*, **246**, 196, and Topf, *Z. anal. Chem.*, **26**, 296 (1887).

and the iodine may be titrated, after acidifying the solution with dilute sulfuric acid, by means of 0.1 *N* sodium thiosulfate.

It is not, however, immaterial whether the ozone reacts with a *neutral* or with an *acid* solution. In the latter case far too much iodine is liberated, although in the former case exactly the right amount is set free. Sir B. C. Brodie* called attention to this fact in his classic researches on ozone. Brodie confirmed the results obtained in his titrations by weighing the amount of ozone used in the experiments. This work of Brodie's appears to have been forgotten,† for many other chemists have since that time attempted to work out an iodimetric method for estimating ozone, some using acid solutions of potassium and iodide and some neutral solutions to absorb the gas, although for a long time it occurred to no one else that the results could be checked by weighing out a definite amount of ozone for test experiments. In 1901, however, this was done in a very simple way by R. Ladenburg and R. Quasig,‡ who were without knowledge of Brodie's work. Their method consisted in weighing a glass bulb of known capacity which was provided with glass stop-cocks, filling it with oxygen and then weighing. The oxygen was then replaced by ozone, so that *the gain in weight multiplied by three represented the amount of ozone present.*

In order, now, to titrate the ozone, Ladenburg and Quasig expelled the gas from the bulb by distilled water, and conducted it slowly through a *neutral* solution of potassium iodide which was subsequently treated with an equivalent amount of sulfuric acid and the liberated iodine titrated with *N* sodium thiosulfate.

The results of Ladenburg and Quasig have been carefully tested in the author's laboratory§ and the method improved somewhat by absorbing the ozonized oxygen by potassium iodide solution in the glass bulb itself rather than expelling the gas from the bulb and passing it into the iodide solution.

The estimation of ozone by weighing is a much too round-about process to permit a practical application, particularly on account of the fact that the measurement and weighing of the gas must take place in a room at constant temperature, a condition which cannot in many cases be readily fulfilled. Consequently the volumetric titration of the gas is far more practical.

Procedure. — Procure a glass bulb of about 300–400 ml. capacity, of the form shown in Fig. 117, and determine its volume accurately by weighing it empty and then fill with water, applying the correction for temperature as described on p. 443 *et seq.* Connect the bulb with a gas delivery tube, making use of Babo flanged joints (Fig. 117, *c* and *d*) pressing them together by means of a steel clamp, lined with cork (Fig. 118). Connect the delivery tube with the supply of ozone and oxygen, and replace the water in the bulb with the gas. During the filling of the bulb, but little of the ozone is absorbed by the water. When the tube is filled, close the lower stop-cock first and the upper one a few seconds later. Then disconnect the bulb with the gas delivery tube, invert, open the upper stop-cock quickly for an instant to establish atmospheric

* *Phil. Trans.*, **162**, 435–484 (1872).

† Luther and Inglis, *Z. phys. Chem.*, **48**, 208 (1903).

‡ *Ber.*, **34**, 1184 (1901).

§ Treadwell and Anneler, *Z. anorg. Chem.*, **48**, 86 (1905).

pressure in the bulb, and connect by means of rubber tubing with the gas reservoir N which is filled with 2 N potassium iodide solution (Fig. 119). Allow the air imprisoned in the rubber tubing to escape through the three-way stop-cock b and after properly setting the cock, introduce 20–30 ml. of the iodide solution into the bulb. Finally close the stop-cock b and disconnect the rubber tubing. Shake the contents of the bulb vigorously and allow to stand for half an hour; at the end of this time the absorption of the ozone will be complete.

Place an Erlenmeyer flask under the stop-cock b'; open this and immediately afterwards the upper stop-cock also. Wash out the bulb

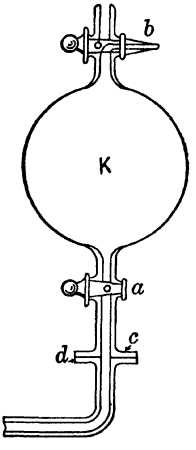


FIG. 117.

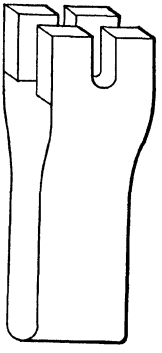


FIG. 118.

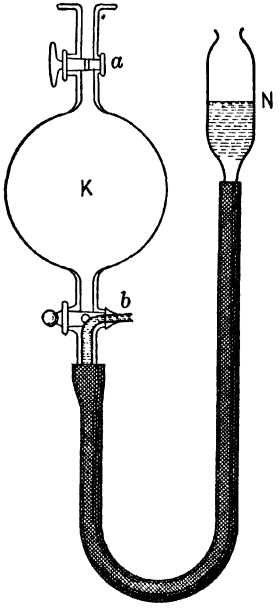


FIG. 119.

first by introducing some potassium iodide solution through a and finally with pure water. Make the contents of the flask acid with dilute sulfuric acid and titrate the liberated iodine with 0.1 N sodium thiosulfate.

The computation takes place as follows: Assume the bulb to hold V ml.; the weight of ozone found by titration = p g.; the temperature = $t°$, the barometer reading = B mm., and the tension of water vapor = w.

The volume of the bulb at 0° and 760 mm. pressure is

$$V_0 = \frac{V\,(B - w)\,273}{760\,(273 + t)}.$$

When filled with oxygen this would weigh:

$$\frac{0.032\ V_0}{22.41}\text{ g.}$$

Therefore the weight of oxygen and ozone in the bulb is

$$\frac{0.032\ V_0}{22.41} + \frac{p}{3},$$

and the per cent of ozone in the mixture is

$$\frac{100\ p}{\frac{0.032\ V_0}{22.41} + \frac{p}{3}} = \frac{6720\ p}{0.096\ V_0 + 22.41\ p} = \text{per cent ozone.}$$

*(b) Method of Soret-Thenard**

Ozone is absorbed quantitatively by means of sodium arsenite solution in accordance with the following equation:

$$Na_2HAsO_3 + O_3 = Na_2HAsO_4 + O_2,$$

although A. Ladenburg† finds that the absorption takes place much more slowly than by means of potassium iodide. When, therefore, the ozone is passed through the arsenite solution, there is danger of getting to low results. If the absorption takes place in a glass bulb, however, the results are good.

Ozone is also absorbed by alkali bisulfite‡ solutions and may be estimated in this way, by titrating the excess of bisulfite with iodine. Ladenburg,§ however, has shown that the method is not as accurate as the potassium iodide one, so that it will not be considered further here.

20. Determination of Hydrogen Peroxide. Kingzett's Method||

$$1\text{ liter of }0.1\ N\ Na_2S_2O_3\text{ solution} = \frac{H_2O_2}{20} = 1.7008\text{ g. } H_2O_2.$$

The hydrogen peroxide solution is diluted until its H_2O_2 content corresponds to about 0.6 per cent by weight and of this solution 10 ml. are used in the analysis.

Procedure. — Place about 2 g. of potassium iodide in an Erlenmeyer flask and dissolve in 200 ml. of water. Add 30 ml. of 18 *N* sulfuric

* *Compt. rend.*, **38**, 445 (1854), **75**, 174 (1872).

† *Ber.*, **36**, 115 (1903).

‡ Neutral alkali sulfite is not suitable here, because it is not oxidized quickly by pure oxygen alone.

§ *Loc. cit.*

|| *J. Chem. Soc.*, **1880**, 792.

acid, and then, with constant stirring, introduce 10 ml. of the hydrogen peroxide solution from a pipet. After standing 5 minutes, titrate the iodine liberated with 0.1 *N* thiosulfate solution.

$$H_2O_2 + 2\,KI + H_2SO_4 = K_2SO_4 + 2\,H_2O + I_2.$$

Remark. — This method is rather better than that described on p. 553 because the titration can take place in the presence of glycerol, salicylic acid, etc., which are sometimes used as preservatives in commercial hydrogen peroxide preparations. These substances will render the results obtained by the permanganate titration less accurate.

21. Determination of Iron

This method was first proposed by Carl Mohr* and is based upon the following reaction:

$$2\,FeCl_3 + 2\,HI \rightleftarrows 2\,HCl + 2\,FeCl_2 + I_2.$$

As the reaction is reversible, it is necessary to have an excess of hydriodic acid present in order that it may take place quantitatively in the direction from left to right.

Procedure. — Place the hydrochloric acid solution containing a weighed amount of the ferric salt in a 300-ml. glass-stoppered bottle, neutralize the greater part of the acid with sodium hydroxide, and remove the air by means of a current of carbon dioxide. After this add about 5 g. of potassium iodide, close the bottle, shake and allow to stand in the cold for 20 minutes. Then titrate the liberated iodine with 0.1 *N* sodium thiosulfate solution. As soon as the blue color has disappeared† conduct more carbon dioxide through the solution, stopper the bottle and allow to stand for a few minutes to see whether the blue color will reappear. Should this be the case, add more thiosulfate, again stopper the flask and allow to stand. If a blue color again appears, the solution contains too little potassium iodide, so that it is necessary to repeat the entire analysis, using 1–2 g. more of it. With sufficient potassium iodide and only little free hydrochloric acid, the reaction is always complete at the end of 20 minutes. The results obtained are satisfactory.

22. Determination of Copper. Method of Haën‡-Low§

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 \text{ solution} = \frac{Cu}{10} = 6.357 \text{ g. Cu.}$$

Principle. — If a solution of a cupric salt at a suitable concentration is treated with an excess of potassium iodide, all the copper is precipitated as cuprous iodide,

* *Ann. d. Chem. u. Pharm.*, **105**, 53.

† Starch is added in all these titrations.

‡ *Ann. Chem. Pharm.*, **91**, 237 (1854).

§ Technical Methods of Ore Analysis.

and there is liberated one atom of iodine for each atom of copper present, $2\,Cu^{++} + 4\,I^- \rightarrow Cu_2I_2 + I_2$. The iodine is titrated with sodium thiosulfate solution. The method has been studied by Gooch and Heath* who find that the quantity of potassium iodide used, the concentration of the solution, and the quantity of acid present are three factors which must be taken into consideration. In a volume of 50 ml. an excess of 0.6–1 g. of potassium iodide is sufficient to cause the complete precipitation of 0.0020 g. of copper but in a volume of 100 ml. an excess of 3–5 g. is desirable. In general, the more dilute the solution, the greater the quantity of potassium iodide required. A larger excess of potassium iodide does no harm.

A little free acid does no harm, but not more than 2 ml. of concentrated mineral acid may be present in 50 ml. of solution.

If an appreciable amount of arsenic is present, mineral acids must not be present on account of their tendency to bring about the reduction of the higher salts of arsenic and antimony when an excess of potassium iodide is used. Obviously the solution must not contain ferric iron or any other oxidizing agent.

Standardization of the Thiosulfate Solution

In technical work it is customary to standardize the thiosulfate solution against pure copper. Weigh out 0.2 g. of pure Cu into a 200-ml. Erlenmeyer flask and dissolve in 5 ml. of 8 N HNO_3. Dilute with 25 ml. water and boil a few minutes to remove oxides of nitrogen. To remove the last of the nitrous oxides, add 5 ml. of bromine water and boil until the excess bromine is expelled. Remove the flask from the flame and add strong ammonia until a slight excess is present. After boiling off the excess of ammonia, add 7 ml. of strong acetic acid, which dissolves any copper oxide that has deposited. Cool to room temperature, add 3 g. of potassium iodide and titrate the brown solution with sodium thiosulfate until nearly colorless, then add starch solution, and complete the titration. In making the titration for the first time, one is bothered somewhat by the fact that the cuprous iodide is not pure white in color. If t ml. of the solution were used in titrating a g. of copper then 1 ml. of thiosulfate $= \frac{a}{t}$ g. Cu.

Determination of Copper in Ores. Low's Method

Principle. — The ore is dissolved in acid, the copper separated from iron, etc. by precipitating it upon metallic aluminium, the deposit dissolved in nitric acid and treated as in the standardization

Procedure. — To 0.25–0.50 g. of fine ore weighed into a 250-ml. Erlenmeyer flask, add 6 ml. of 16 N HNO_3, and boil gently until nearly dry. Add 5 ml. of 12 N HCl and heat again. As soon as the

* F. A. Gooch and F. H. Heath, *Am. J. Sci.*, **4**, 25, 67; F. H. Heath, *ibid.*, 25, 153.

incrusted matter has dissolved add 12 ml. of 18 N H_2SO_4 and heat until the acid fumes freely. Cool and add 25 ml. of water. Then heat until any anhydrous ferric sulfate is dissolved, and filter to remove insoluble sulfates and silica. Wash the flask and filter-paper until the volume of the filtrate amounts to about 75 ml., receiving it in a No. 2 beaker. Take a strip of aluminium, about 2.5 cm. wide and 14 cm. long, bend it into a triangle and place it in the beaker resting on its edge. Cover the beaker and boil gently for 7–10 minutes, which will be sufficient to precipitate all the copper, provided the solution does not much exceed 75 ml. Avoid boiling to a very small volume. The aluminium should now appear clean, the copper being detached or loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with hydrogen sulfide water. This will prevent oxidation and will also serve to precipitate the last traces of copper. If the hydrogen sulfide shows that there was more than a very little copper remaining in solution, it is best to dilute the solution to 75 ml. again and to boil a short time longer. This will coagulate the sulfide. Finally, decant through a filter and then, without delay, transfer the precipitate to the filter with the aid of a stream of hydrogen sulfide water from a wash bottle. Let the strip of aluminium remain in the beaker, but wash it as clean as possible with the hydrogen sulfide water. Wash the filter and precipitate at least 6 times with this hydrogen sulfide water, but take care not to let the filter remain empty for any length of time. Moist copper sulfide oxidizes very rapidly when in contact with the air with the formation of a little copper sulfate which will dissolve and pass through the filter only to precipitate again when it comes in contact with the filtrate containing hydrogen sulfide.

Now place the original clean flask under the funnel, perforate the filter and rinse the precipitate into the flask with hot water, using as little as possible. Lift the fold of the filter and rinse down any precipitate found beneath the fold. Using a small pipet, allow 5 ml. of strong nitric acid to run over the aluminium in the beaker and pour it from the beaker through the filter into the flask, but do not wash the beaker or filter at this stage. Remove the flask and replace it with the beaker. Heat the contents of the flask to dissolve the copper and expel the red fumes, then again place the flask under the funnel. Now pour over the filter 5 ml. or more of bromine water, using enough to impart a strong color to the solution in the flask. Next wash the beaker and aluminium, pouring the washings through the filter. Finally wash the filter 6 times with hot water. Boil till the solution is reduced to about 25 ml., cool somewhat and add a slight excess of strong ammonia (about 7 ml.). Boil off the excess of ammonia, add an excess of acetic acid,

and boil a minute longer. Cool to room temperature, add 3 g. of potassium iodide and titrate with sodium thiosulfate solution, adding starch toward the last.

23. Analysis of Arsenious Acid

The titration can take place in exactly the same way as in the standardization of 0.1 *N* iodine solution (see p. 553).

Determination of Arsenious Acid in Acid Solution

$$1 \text{ liter of } 0.1\ N\ KBrO_3 = \frac{KBrO_3}{60} = 2.784 \text{ g. } KBrO_3 = 4.948 \text{ g. } As_2O_3.$$

Principle. — If a hydrochloric acid solution of arsenious acid is treated with potassium bromate, the arsenic is completely oxidized to arsenate. As soon as the arsenic is all oxidized, the next drop of potassium bromate solution causes separation of bromine.

$$3\ Na_2HAsO_3 + KBrO_3 + 6\ HCl = 6\ NaCl + KBr + 3\ H_3AsO_4$$
$$KBrO_3 + 5\ KBr + 6\ HCl = 6\ KCl + 3\ H_2O + 3\ Br_2$$

If the solution contains methyl orange it will show an acid reaction as long as arsenic is present but free bromine destroys the indicator and the solution becomes colorless at the end-point.

Procedure. — Make the solution of the arsenite strongly acid with hydrochloric acid, add a drop of methy orange indicator solution and titrate with 0.1 *N* potassium bromate until the red solution is decolorized, adding the reagent very slowly toward the last, and stirring constantly.

24. Determination of Antimony Trioxide Compounds

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{Sb_2O_3}{40} = 7.21 \text{ g. } Sb_2O_3 = 6.01 \text{ g. Sb.}$$

The titration is carried out exactly as in the case of arsenious acid (cf. p. 553) except that tartaric acid, or Rochelle salt, must be added to the solution in order to prevent the precipitation of antimonous acid, or antimony oxychloride, as a result of hydrolysis.

Examples:

(*a*) *Determination of Antimony in Tartar Emetic*

If an aqueous solution of tartar emetic is treated with iodine in the presence of starch, the first few drops of reagent will impart a permanent blue color to the solution. If, however, a little sodium bicarbonate is added to the solution, the tervalent antimony is oxidized quantitatively to the quinquevalent condition.

$$K(SbO)C_4H_4O_6 + 6\,NaHCO_3 + I_2 = Na_3SbO_4 + 2\,NaI + KNaC_4H_4O_6 + 3\,H_2O + 6\,CO_2.$$

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{K(SbO)C_4H_4O_6 + \frac{1}{2}\,H_2O}{20} = 16.62 \text{ g.}$$

Dissolve 8.309 g. of tartar emetic in water, dilute the solution to exactly 500 ml. and mix well. Of this solution, transfer 20 ml. with a pipet into 100 ml. of water containing 0.5 g. of sodium bicarbonate. Titrate with 0.1 N iodine solution, using starch as an indicator. If t ml. are used for the titration, the salt contains:

$$\frac{1.662 \times 25 \times t}{8.309} = 5\,t = \text{per cent tartar emetic, or, } 1.809\,t = \text{per cent antimony.}$$

(*b*) *Determination of Antimony in Stibnite*

Weigh out 0.2–0.3 g. of stibnite into a 150-ml. beaker, cover with a watch-glass, and add 10 ml. of concentrated hydrochloric acid. Allow the acid to act in the cold for 10 minutes, add 0.3 g. of solid potassium chloride and heat gently on the water-bath for another 10 minutes. Add 3 g. of powdered tartaric acid and heat a little longer, but take care not to allow the liquid to evaporate sufficiently to expose any part of the bottom of the beaker. When this precaution is taken, there is no volatilization of the antimony, and all of the hydrogen sulfide is expelled.

$$Sb_2S_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2S.$$

Remove the solution from the water-bath, allow to cool to the room temperature, and very cautiously dilute with water to 100 ml., adding it drop by drop until 5 ml. have been added. If, in the meantime, a red coloration due to antimony sulfide appears during the dilution, the solution should be at once heated until it disappears, and the diluting then continued.

Nearly neutralize the diluted solution with sodium hydroxide and pour the cold, slightly acid solution into a 700-ml. beaker containing 3 g. of sodium bicarbonate dissolved in 200 ml. of water. Add starch paste, and titrate with iodine to the appearance of a permanent blue.

Remarks. — Antimony chloride is volatile with steam from its concentrated solutions, so that the solution should not be boiled until it has been diluted, the addition of potassium chloride forms less volatile $KSbCl_4$. The heating on the water-bath can be carried out, however, without fear of losing antimony provided the acid is not allowed to evaporate to any extent. This heating serves to remove all the hydrogen sulfide which would otherwise precipitate the antimony as trisulfide upon diluting the solution. If insufficient tartaric acid is present, antimony oxychloride, SbOCl, precipitates and if the solution is titrated in this condition it is impossible to obtain a permanent end-point. Such a precipitate may be filtered off, dissolved in concentrated hydrochloric acid and the solution treated by itself as above described. The value of the iodine solution in terms of Sb is given in the previous process (*a*).

(*c*) Determination of Antimonous Acid with Potassium Bromate*

$$1 \text{ liter of } N\ KBrO_3 = \frac{Sb_2O_3}{40} = 7.210 \text{ g. } Sb_2O_3 \text{ or } 6.010 \text{ g. Sb.}$$

The procedure is the same as that described on p. 580. Enough hydrochloric acid must be used to prevent the precipitation of SbOCl.

* Method of H. Zschokke. Cf. Fiechter and Mueller, *Chem. Ztg.*, **37**, 309 (1913).

25. Determination of Antimony Pentoxide Compounds (A. Weller)*

By heating a quinquevalent antimony compound with concentrated hydrochloric acid and potassium iodide in the Bunsen apparatus (Fig. 116, p. 563), the antimonic acid is reduced to antimonous acid with separation of iodine:

$$Sb_2O_5 + 4\,HI = Sb_2O_3 + 2\,H_2O + 2\,I_2.$$

The iodine is distilled over into potassium iodide solution and titrated with 0.1 N $Na_2S_2O_3$ solution. The results are a little low.

26. Determination of Tin with Potassium Bromate†

1 liter of 0.1 N $KBrO_3 = \frac{Sn}{20} = 5.935$ g. Sn.

Place 20 ml. of faintly acid stannous or stannic solution (about 6 g. of Sn per liter) in a 200-ml. flask, add 0.15 g. of Al wire in short pieces and allow the reaction to proceed in the cold until all the Sn is precipitated. Add 30 ml. of concentrated hydrochloric acid and 20 ml. of water and stopper the flask with a Bunsen valve (p. 95). Heat gently till all the tin has dissolved. Cool and titrate with 0.1 N potassium bromate solution (2.784 g. per liter) until a permanent yellow color is obtained.

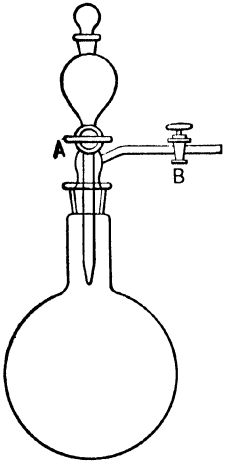


FIG. 120.

$$3\,Sn^{++} + BrO_3^- + 6\,H^+ = 3\,H_2O + Br^- + 3\,Sn^{++++}$$
$$BrO_3^- + 5\,Br^- + 6\,H^+ = 3\,Br_2 + 3\,H_2O.$$

Remark. — Boller obtained low results when testing pure tin. He has improved the method by adding a slight excess of bromate, then some potassium iodide and finally titrating with sodium thiosulfate. The results are about 1 per cent too low if air is present in the solution. Boller proceeds as follows:

Place 100 ml. of 7 N hydrochloric acid in the 500-ml. flask shown in Fig. 120, and boil 5 minutes to expel air, with stop-cock A open and B closed. Remove the flame and quickly introduce the weighed sample of metallic tin and a little piece of calcite to furnish carbon dioxide gas. Replace the top piece and with B open, boil gently until the tin is all dissolved. Then close B and cool the contents of the flask with cold water. This produces a partial vacuum in the flask.

While the tin is dissolving prepare a mixture of 50 ml. of 0.1 N $KBrO_3$ solution, 1 g. of potassium bromide and a little water. Boil 5 minutes

* *Ann. Chem. Pharm.*, **213**, 364.

† St. Györy, *Z. anal. Chem.*, **32**, 415 (1893).

to expel air. Pour this solution into the funnel of the above-mentioned flask and allow it to flow into the stannous solution by carefully opening the stop-cock *A*. The stannous chloride is oxidized instantly to stannic salt. Rinse out the contents of the funnel with boiled water, add 10 ml. of 5 per cent potassium iodide solution and titrate with 0.1 *N* thiosulfate.

The tin determination as originally given by Zschokke gives good results if the bromate solution is standardized against tin in the same way that the analysis is made.

27. Determination of Hydrogen Sulfide

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_5 \text{ solution} = \frac{H_2S}{20} = 1.704 \text{ g. } H_2S.$$

If a solution of hydrogen sulfide is treated with iodine, it is oxidized with separation of sulfur: $H_2S + I_2 = 2\,HI + S$.

For the determination of the amount of the gas present in hydrogen sulfide water, transfer a measured amount by means of a pipet to a known volume of 0.1 *N* iodine solution and titrate the excess of the latter with thiosulfate solution.*

If the amount of hydrogen sulfide present is not very large, correct results are obtained without difficulty. With considerable hydrogen sulfide, on the other hand, the deposited sulfur is likely to enclose some of the iodine solution, as shown by its brown color; this iodine escapes the titration with thiosulfate. In such a case, remove the film of sulfur floating on the surface of the liquid with a glass rod after the completion of the thiosulfate titration, transfer it to a glass-stoppered cylinder, and shake with 1–2 ml. of carbon bisulfide. The latter dissolves the iodine with a violet color and the color can be discharged with sodium thiosulfate solution.† In this way the total amount of the iodine that remains can be titrated.

Remark. — This method can be used to advantage for determining the sulfur present in soluble sulfides.

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* Correct results cannot be obtained by titrating directly with iodine, cf. O. Brunck, *Z. anal. Chem.*, **45**, 541 (1906).

† The separation of the sulfur into a coherent film can be prevented by sufficiently diluting the solution with boiled water. O. Brunck (*Z. anal. Chem.*, **45**, 541) therefore, recommends using 0.01 *N* iodine instead of 0.1 *N* solution, and this is certainly advisable in the case of small quantities of hydrogen sulfide as, for example, in a mineral water. On the other hand, when a relatively large volume of hydrogen sulfide is liberated from a sulfide by means of acid (see p. 311) it is advisable to use 0.1 *N* iodine, as otherwise the volume of solution will be too large unless a very small weight of substance is used in the analysis.

Determination of Hydrogen Sulfide in Mineral Waters

Place a measured amount of 0.01 *N* iodine solution and 2 g. of potassium iodide in a tall liter cylinder, add 1 liter of the water to be analyzed, and, after thoroughly shaking, titrate the excess of the iodine with 0.01 *N* thiosulfate. The standardization of the iodine solution used is accomplished by measuring off 10 ml. of the solution, adding 2 g. of potassium iodide, diluting to 1 liter with boiled water, and titrating with 0.01 *N* thiosulfate solution.

Remark. — The hydrogen sulfide in a water is not always present as free gas but may be present as hydrosulfide, *i.e.*, as HS^- anions. The mineral water will also contain free carbonic acid and HCO_3^- anions. According to the mass action law,

$$(1)\quad \frac{[H^+] \times [HS^-]}{[H_2S]} = 0.91 \times 10^{-7}, \quad \text{and} \quad (2)\quad \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3.04 \times 10^{-7}.$$

Since the two equilibria are both satisfied in the solution, the hydrogen ion concentrated is the same in each expression. $[H^+] = \frac{0.91 \times 10^{-7} \times [H_2S]}{[HS^-]}$ and inserting this value in equation (2) we have

$$(3)\quad \frac{[HS^-]}{[H_2S]} = 0.3\,\frac{[HCO_3^-].}{[H_2CO_3]}$$

In all these equations the symbols in brackets represent moles per liter of the substance.

With the aid of equation (3) it is possible to compute the quantity of free hydrogen sulfide present in a sample of mineral provided a complete analysis of the water has been made.

Let C = the total millimoles per liter of non-ionized H_2CO_3 and HCO_3^-, let S = the total millimoles per liter of HS^- and non-ionized H_2S and let d = the difference between the total milli-equivalents of cations per liter and of the anions with the exception of HCO_3^- and HS^-. Then $d = [HS^-] + [HCO_3^-]$, $S = [HS^- + H_2S]$ and $C = d + [H_2CO_3] - [HS^-]$.

From this it follows: —

$$[HS^-] = S - [H_2S]$$
$$[HCO_3^-] = d - [HS^-] = d - S + [H_2S]$$
$$[H_2CO_3] = C - d + [HS^-] = C - d + S - [H_2S]$$

Substituting these values in equation (3) we get, —

$$\frac{S - [H_2S]}{[H_2S]} = 0.3\,\frac{d - S + [H_2S]}{C - d + S - [H_2S]}$$

and by solving the equation

$$(4)\quad [H_2S] = \frac{(1.7\,S - C - 0.7\,d) \pm \sqrt{(1.7\,S + C - 0.7\,d)^2 - 2.8\,S\,(S + C - d)}}{1.4}$$

= millimoles of free H_2S per liter.

This value multiplied by 34.09 gives the weight of free H_2S in grams.

28. Analysis of Alkali Sulfides

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{R_2S}{20} \text{ or } \frac{S}{20} = 1.603 \text{ g. S.}$$

Allow a measured volume of the alkali sulfide solution to run slowly, with constant stirring, into 300–400 ml. of water, an excess of iodine and hydrochloric acid.* Titrate the excess of iodine with sodium thiosulfate solution.

Remark. — It does not work to titrate directly with the solution of sulfide.

29. Determination of Alkali Sulfides with Potassium Bromate†

$$1 \text{ liter of } 0.1\ N\ KBrO_3 = \frac{H_2S}{80} = 0.4260 \text{ g. } H_2S.$$

$$H_2S + 4\,H_2O + 4\,Br_2 = 8\,HBr + H_2SO_4.$$

Place the measured sample of solution in the liter bottle shown in Fig. 121 which is provided with a ground glass stopper carrying a dropping funnel. Add a considerable excess of 0.1 N potassium bromate solution and 3–4 g. of potassium bromide. Evacuate the bottle with a water-suction pump and close the stop-cock. Pour hydrochloric acid in the funnel and allow it to flow into the bottle by carefully opening the stop-cock. When the solution is distinctly acid, close the stop-cock and shake the contents of the bottle. To effect a good oxidation, the solution should contain 25 per cent of concentrated hydrochloric acid by volume. At first the solution assumes a brown color, then the color fades but should remain distinctly yellow. A slight turbidity of sulfur disappears in 10–15 minutes, being oxidized to sulfuric acid.

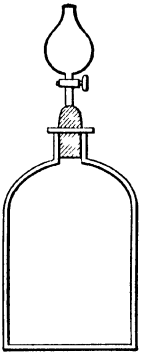


FIG. 121.

When the solution is perfectly clear, wash out the funnel with a little water but avoid letting air enter. Add 2–3 g. of potassium iodide dissolved in a little water and shake. Rinse out the funnel and titrate with sodium thiosulfate solution.

If T is the volume of 0.1 N bromate solution used and t the volume of 0.1 N thiosulfate, then $(T - t)$ 0.0004260 g. H_2S is present.

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* To determine how much acid is necessary, titrate a trial sample with methyl orange as indicator with 6 N hydrochloric acid.

† Treadwell and Mayr, *Z. anorg. Chem.*, **92**, 127 (1915).

This method is a little more complicated than direct titration with iodine but as the oxidation of the sulfur is from sulfide to sulfate, 4 times as much oxidizing agent is required. The method is suitable for the titration of hydrogen sulfide in the presence of thiocyanate.

30. Titration of Alkali Sulfide in the Presence of Alkali Thiocyanate

The reactions involved in the method are illustrated by the following equations:

(*a*) $\begin{cases} H_2S + 4\,H_2O + 4\,Br_2 = 8\,HBr + H_2SO_4 \\ HCNS + 4\,H_2O + 3\,Br_2 = H_2SO_4 + HCN + 6\,HBr. \end{cases}$

(*b*) $H_2S + I_2 = 2\,HI + S.$

In one sample determine the total sulfur content by the method just described and in another sample determine the sulfide iodometrically according to 27, p. 583. If the total 0.1 *N* potassium bromate solution used was *T* ml. and *t* ml. of thiosulfate were used for titrating the excess and t_1 ml. of 0.1 *N* iodine solution were used for the direct titration of sulfide in the same weight of substance, *a* g., then

$$\frac{[(T - t) - 4\,t_1]\,0.0968}{a} = \text{per cent CNS}$$

and

$$\frac{t \times 0.1603}{a} = \text{per cent S (as sulfide).}$$

31. Analysis of a Mixture of Alkali Sulfide and Alkali Hydrosulfide

If a solution of alkali sulfide and alkali hydrosulfide is treated with an acid solution of iodine, the following reactions take place:

(*a*) $Na_2S + 2\,HCl = 2\,NaCl + H_2S,$

(*b*) $NaSH + HCl = NaCl + H_2S,$

(*c*) $H_2S + I_2 = 2\,HI + S.$

It is evident from these equations that in the case of the sulfide, the quantity of hydriodic acid formed by the oxidation of the hydrogen sulfide is equivalent to the quantity of hydrochloric acid required to decompose the sulfide; in this case, therefore, the acidity of the solution remains unchanged. In the case of the hydrosulfide, however, which is the acid salt of hydrogen sulfide, the quantity of hydriodic acid formed is equivalent to twice the quantity of hydrochloric acid required to decompose the hydrosulfide. Thus the acidity of the solution is a measure of the quantity of hydrosulfide present. Moreover, if *t* ml. of tenth-normal alkali are required to titrate this acid, then 2 *t* ml. of tenth-normal iodine must have been required to oxidize the hydrogen sulfide from the hydrosulfide.

Procedure. — Dilute a known volume of 0.1 *N* iodine together with a known volume of 0.1 *N* hydrochloric acid* in a beaker to a volume of about 400 ml. and slowly add the solution containing the sulfide and hydrosulfide from a buret with constant stirring, until the solution becomes pale yellow. Add starch indicator and titrate the excess of iodine with tenth-normal thiosulfate solution. Finally, titrate the acid in the solution with 0.1 *N* sodium hydroxide solution, using lacmoid or phenolphthalein. Carbonate must be absent.

Computation. — In the analysis, the volumes of standard solutions used were: T ml. 0.1 *N* iodine; t_1 ml. 0.1 *N* thiosulfate; t_2 ml. 0.1 *N* hydrochloric acid; t_3 ml. of 0.1 *N* sodium hydroxide: and V ml. of the sulfide mixture.

Then $(T - t_1)$ ml. = total volume of iodine required, and $(t_3 - t_2)$ ml. = the volume of sodium hydroxide required to neutralize the acid formed by the reaction with the hydrosulfide. Therefore,

$$(t_3 - t_2)\frac{\text{NaSH}}{10{,}000} = (t_3 - t_2) \times 0.005607 \text{ g. NaSH},$$

and

$$[(T - t_1) - 2(t_3 - t_2)]\frac{\text{Na}_2\text{S}}{20{,}000} = [(T - t_1) - 2(t_3 - t_2)] \times 0.003903 \text{ g. Na}_2\text{S}$$

are present in V ml. of solution.

32. Analysis of a Mixture of Hydrogen Sulfide and Alkali Hydrosulfide

The analysis is carried out exactly as in the case just described and the computation is similar.

Let T = ml. 0.1 iodine, t_1 = ml. 0.1 *N* thiosulfate, t_2 = ml. 0.1 *N* acid, and t_3 = ml. 0.1 *N* alkali. Then

$$[(T - t_1) - (t_3 - t_2)] \times 0.005607 \text{ g. NaSH}$$

and

$$[t_1 + 2t_3 - (T + 2t_2)] \times 0.001701 \text{ g. } H_2S.$$

Remark. — The last two methods of analysis are applicable only to solutions containing no other compounds decomposable by hydrochloric acid than sulfide and hydrosulfide, and no other substance that will react with iodine. The analysis may be carried out without the addition of any hydrochloric acid. In this case the solution of sulfides is diluted to about 400 ml., starch added, and the titration with

* The quantity of hydrochloric acid present must be sufficient to decompose all the sulfide and sulphydrate; an excess does no harm.

iodine carried out directly. The hydriodic acid formed is titrated with caustic soda, using lacmoid* as indicator. The reactions are

$$NaSH + I_2 = NaI + HI + S.$$
$$H_2S + I_2 = 2\,HI + S.$$

33. Determination of Thiosulfate in the Presence of Sulfide and Hydrosulfide

Treat a measured volume of the solution in a 200-ml. measuring-flask with an excess of freshly-precipitated cadmium carbonate. Shake well and dilute the liquid to the mark. Filter through a dry filter, reject the first 20 ml. of filtrate and titrate 100 ml. with iodine solution. By shaking with cadmium carbonate, the sulfide and hydrosulfide are removed and the thiosulfate remains in solution.

34. Determination of Sulfurous Acid

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{SO_2}{20} = 3.203 \text{ g. } SO_2.$$

The determination is based upon the following reaction:

$$SO_2 + 2\,H_2O + I_2 = 2\,HI + H_2SO_4,$$

the sulfurous acid being oxidized to sulfuric acid. If starch is added to a solution of sulfurous acid, and a titrated iodine solution is run into it from a buret, the blue color will not be obtained until all of the sulfurous acid has been acted upon. Bunsen, however, in 1854 showed that this sensitive reaction, which was first used by Dupasquier, will only take place quantitatively according to the above equation when the solution does not contain more than 0.04 per cent by weight of SO_2. With greater concentrations uniform results are not obtained. This irregularity was ascribed to the reversibility of the reaction, so that it was suggested that the titration be performed in alkaline solution,† thus removing the hydriodic acid as fast as it is formed. But the results then obtained are still inaccurate.‡ Finkener,§ on the other hand,

* Methyl orange can be used, but it is not so easy to distinguish the end-point. Phenolphthalein works well but no better than the lacmoid. Care should be taken to titrate the acid against the alkali during the standardization at the same dilution as to be used in the analysis and an appreciable amount of carbonate should not be present.

† Addition of $MgCO_3$ or $NaHCO_3$ (Fordos and Gelis).

‡ E. Rupp, *Ber.*, **35**, 3694 (1902), states that it is possible to obtain good results by the method of Fordos and Gelis if the sulfurous acid is allowed to act for at least half an hour upon an excess of iodine in the presence of sodium bicarbonate. The solution is then titrated with sodium thiosulfate. According to E. Müller and O. Diefenthäler, however, this is theoretically incorrect, for the iodine tends to form a little hypoiodite: $I_2 + H_2O \rightleftarrows HI + HIO$, and the latter reacts with sodium thiosulfate: $Na_2S_2O_3 + 4\,HIO + H_2O = Na_2SO_4 + H_2SO_4 + 4\,HI$.

§ Finkener-Rose, *Quantitative Analyse*, p. 937, (1871).

states that correct values will be obtained if the sulfurous acid is allowed to run into the iodine solution.

J. Volhard* has confirmed the results of Finkener and shown that the anomalous results obtained on titrating sulfurous acid with iodine are not due to the reversibility of the reaction, for the direct addition of 20 per cent sulfuric acid is without influence. The incomplete oxidation of the sulfurous acid is caused by the fact that the hydriodic acid reduces a part of the sulfurous acid to free sulfur:†

$$(1) \quad SO_2 + 4\,HI = 2\,I_2 + 2\,H_2O + S.$$

If sulfurous acid, whether dilute or concentrated, is allowed to run into a solution of iodine with constant stirring, there is complete oxidation of the SO_2:

$$(2) \quad SO_2 + I_2 + 2\,H_2O = 2\,HI + H_2SO_4.$$

If, on the contrary, iodine solution is run into the solution of sulfurous acid, both reactions will take place:

$$(3) \quad 3\,SO_2 + 4\,HI + 2\,H_2O = 2\,H_2SO_4 + 4\,HI‡ + S.$$

According to Raschig,§ however, Volhard's explanation is also incorrect, for he finds that no separation of free sulfur takes place if the iodine is allowed to act upon sulfur dioxide in a *dilute* solution. Raschig believes that the error that results when iodine is added to the sulfurous acid solution is due to a loss of SO_2 by evaporation.

Correct results are always obtained if the sulfurous acid is added slowly, with constant stirring, to the iodine solution until the latter is decolorized.

In the analysis of sulfites, add the sulfite solution from a buret to the solution of iodine and hydrochloric acid.

35. Determination of Formaldehyde (Formalin). Method of G. Romijn||

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{HCHO}{2} = 15.01 \text{ g. formaldehyde.}$$

Principle. — Formaldehyde is quantitatively oxidized to formic acid by remaining in contact with iodine for a short time in alkaline solution:

$$HCHO + H_2O + I_2 = 2\,HI + HCOOH.$$

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* *Ann. Chem. Pharm.*, **242**, 94.

† If iodine solution is added slowly to a not too-dilute sulfurous acid solution, a distinct separation of sulfur is soon apparent.

‡ The HI acts as a catalyser according to Volhard.

§ *Z. angew. Chem.*, **1904**, 580.

|| *Z. anal. Chem.*, **36**, 19 (1897).

Procedure. — The aqueous solution of formaldehyde, known commercially as "formalin," contains about 40 per cent of formaldehyde. For analysis, dilute 10 ml. of the formaldehyde solution to 400 ml., and of this 1 per cent solution, take 5 ml. (= 0.125 ml. of the original solution) for analysis. Add 40 ml. of 0.1 *N* iodine solution, and immediately afterwards strong sodium hydroxide solution, drop by drop, until the color of the solution is a light yellow; allow to stand for 10 minutes. Then make the solution acid with hydrochloric acid, and titrate the excess iodine with 0.1 *N* sodium thiosulfate solution.

36. Determination of Ferricyanic Acid*

$$1 \text{ liter of } 0.1\ N \text{ iodine solution} = \frac{K_3Fe(CN)_6}{10} = 32.92 \text{ g. } K_3Fe(CN)_6.$$

Principle. — If a neutral solution of potassium ferricyanide is treated with an excess of potassium iodide, the ferricyanide ion is reduced to ferrocyanide ion with separation of free iodine:

$$2\,K_3Fe(CN)_6 + 2\,KI \rightleftarrows 2\,K_4Fe(CN)_6 + I_2.$$

Lenssen titrated the liberated iodine with sodium thiosulfate, but the results are not concordant, because the reaction is a reversible one. The reaction is quantitative, however, as Mohr first showed, if the ferrocyanide is removed from the solution as fast as it is formed. This is accomplished, according to Mohr, by adding an excess of zinc sulfate, free from iron, to the solution. According to the experiments of E. Müller and O. Diefenthäler,† the titration should take place in a solution which is as nearly neutral as possible, but not in one made alkaline by the addition of sodium bicarbonate (see p. 588).

Müller and Diefenthaler's Procedure. — Weigh out 0.7 g. of the ferrocyanide into a glass-stoppered flask, dissolve in about 50 ml. water, and treat with 3 g. of potassium iodide and 1.5 g. of zinc sulfate free from iron. If an acid solution of ferricyanide is to be analyzed, carefully neutralize with caustic soda until barely alkaline and then make acid with a drop of sulfuric acid. Alkaline solutions must always be neutralized with acid.

37. Determination of Ferri- and Ferrocyanide in the Presence of One Another

In one sample determine ferricyanide iodometrically as just described and in another sample determine ferrocyanide by permanganate titration (p. 536).

* Lenssen, *Ann. Chem.*, **91**, 240. Mohr., *Ibid.*, **105**, 60.

† *Z. anorg. Chem.*, **1910**, 418.

38. Determination of Phenol. Method of W. Koppeschaar*

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{C_6H_5OH}{60} = 1.568 \text{ g. } C_6H_5OH.$$

Principle. — If an aqueous solution of phenol is treated with an excess of bromine, the phenol is converted quantitatively into tribromophenol:

$$C_6H_5OH + 3\ Br_2 = 3\ HBr + C_6H_2Br_3(OH).$$

The tribromophenol is a pale yellow, crystalline substance which is quite insoluble in water (43.7 liters of water dissolve 1 g. of tribromophenol). If, after the reaction has taken place, potassium iodide is added to the solution, iodine is liberated corresponding to the excess of bromine, and by titrating this iodine with sodium thiosulfate solution, it is easy to find how much bromine reacted with the phenol.

Requirements. — 0.1 *N* bromine solution and 0.1 *N* sodium thiosulfate solution.

On account of the volatility of free bromine, Koppeschaar uses a solution of potassium bromate and bromide which, upon being acidified, gives a known amount of bromine in accordance with the equation:

$$KBrO_3 + 5\ KBr + 6\ HCl = 6\ KCl + 3\ H_2O + 3\ Br_2.$$

Thus, to obtain 0.1 *N* bromine solution which will keep indefinitely, dissolve *exactly* 2.784 g. of pure potassium bromate (dried at 100°) and about 10 g. of potassium bromide in water and dilute the solution to one liter at 20°. An excess of bromide does no harm.

Procedure. — Weigh out 5 g. of phenol in a weighing beaker, dissolve in a little water, rinse the solution into a liter flask and shake well. Of this solution, pipet off 100 ml., transfer to another liter flask, dilute with water to the mark, mix and transfer 100 ml. of this solution to a stoppered bottle of about 250-ml. capacity, treat with 50 ml. of the bromate solution, shake, make acid with 5 ml. of concentrated hydrochloric acid, shake again, and allow to stand 15 minutes. Then add 2 g. of potassium iodide and titrate the liberated iodine, corresponding to the excess of bromine, with 0.1 *N* thiosulfate solution, using starch as indicator. Then if t ml. of the last solution are used and the weight of phenol was a g.:

$$\frac{(50 - t) \times 0.1568}{a} = \text{per cent phenol.}$$

Remark. — Before making an analysis, a blank experiment should always be made with the bromate solution to make sure that its strength corresponds to the theoretical value.

This method is suitable for the analysis of pure preparations of phenol (carbolic acid) but not for crude phenol, creosote oil, etc.

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* *Z. anal. Chem.*, **15**, 233 (1876).

39. Determination of Thiocyanate. Method of Treadwell-Mayr

$$1 \text{ liter of } 0.1\ N\ KBrO_3 \text{ solution} = \frac{HCNS}{60} = 0.9847 \text{ g. HCNS}$$

In acid and neutral solution thiocyanate does not react with iodine but in alkaline solution the following reaction takes place.

$$KCNS + 4\,H_2O + 4\,I_2 = KHSO_4 + 7\,HI + CNI$$

The reaction takes place very slowly. The oxidation is effected much more rapidly with a bromate-bromide solution.

Procedure.— Treat a measured volume of thiocyanate solution with a measured volume of 0.1 N potassium bromate solution and 2–3 g. of potassium bromide in the liter bottle shown in Fig. 121, p. 585. Evacuate with suction and close the stop-cock. Introduce 30–40 ml. of 6 N hydrochloric acid for each 100 ml. of solution without letting in any air. Shake well. After standing 10 minutes, rinse out the funnel with water and add 2–3 g. of potassium iodide dissolved in a little water. Shake and then titrate the liberated iodine with 0.1 N thiosulfate.

If T is the volume of 0.1 N bromate solution and t the volume of 0.1 N thiosulfate, then

$$(T - t)\frac{KCNS \times 100}{60{,}000 \times a} = \frac{(T - t)\,0.09847}{a} \text{ per cent HCNS.}$$

40. Determination of Sulfur in Steel

Weigh 5 g. of steel into a 250-ml. flask. Stopper the flask with a two-holed rubber stopper carrying a dropping funnel and an exit tube leading to three 150-ml. flasks in series. The stem of the dropping funnel should extend nearly to the bottom of the large flask. Each piece of tubing should start just below the bottom of the stopper in one flask and lead nearly to the bottom of the next one. In the first of the small flasks place 50 ml. of water to collect the hydrochloric acid that distils. In each of the other two small flasks place 40 ml. of ammoniacal cadmium chloride (20 g. $CdCl_2$ dissolved in 400 ml. of water and 600 ml. of 6 N NH_4OH added).

With the apparatus all connected, add 50 ml. of concentrated hydrochloric acid to the steel, about half at one time. If the action is not too vigorous, add the rest of the acid and close the stop-cock of the funnel, while the tube is still full of acid. This is necessary, because if air enters the solution there is danger of some loss of sulfur owing to oxidation. The evolved hydrogen serves to prevent this oxidation, provided air does not enter through the funnel. Again fill the dropping

funnel with 50 ml. of HCl, and add all of this except enough to fill the stem of the funnel.

As soon as the rate of flow of the gas through the Erlenmeyer flasks becomes less than about 3 bubbles per second, place a low flame beneath the flask and maintain a steady flow of gas at this rate. The burner should be furnished with a flame protector, as otherwise a sudden draft will cause trouble with the small flame. The steel sample should dissolve in about 30 minutes, but it is not advisable to heat too quickly as this will result in too much acid being carried over into the first flask. At first the flame beneath the evolution flask should be only about 0.7 cm. high and it should not be much over 4 cm. high until all the iron has dissolved. When this has taken place, boil the solution gently for 10 minutes. When the solution begins to boil, the stop-cock in the separatory dropping funnel may be opened. This boiling serves to expel all the hydrogen sulfide from the evolution flask and from the first Erlenmeyer flask. It is unnecessary to pass hydrogen or carbon dioxide through the apparatus, as has been advocated by some chemists. Finally, making sure that the stop-cock in the dropping funnel is open, remove the flame and promptly disconnect the apparatus.

Filter off the precipitated sulfide and wash once or twice with water. Place the filter and precipitate in a 250-ml. Erlenmeyer flask containing 20 ml. of 3 per cent potassium iodide solution, 25 ml. of 9 N sulfuric acid and 10 ml. of 0.08 N permanganate solution. When all the cadmium sulfide has dissolved, titrate the excess of iodine with the sodium thiosulfate solution.

Computation. — If 10 ml. of the permanganate solution = a g. of pure sodium oxalate, T_1 ml. of thiosulfate solution were used in titrating 10 ml. of permanganate, and T_2 ml. for titrating the same amount of permanganate used in the analysis of a sample of steel weighing s g., then

$$a \times \frac{\mathrm{S}}{\mathrm{Na_2C_2O_4}} \times \frac{(T_1 - T_2) \times 100}{T_1 \times \mathrm{S}} = \frac{23.93\, a\,(T_1 - T_2)}{T_1 \times \mathrm{S}} = \text{per cent S.}$$

Remark. — (1) Instead of the ammoniacal cadmium solution the following zinc solution may be used as absorbent for the hydrogen sulfide: Dissolve 20 g. zinc sulfate in 1 liter of water and add 900 ml. of concentrated ammonium hydroxide. Use 10 ml. of this solution and dilute with 150 ml. of water.

(2) Very little error is introduced if the precipitate is not filtered off. Simply add 40 ml. of concentrated hydrochloric acid to the solution containing the precipitate.

(3) The solution can be titrated directly with iodine, or as is better, an excess of iodine should be added at once and the excess of iodine titrated with thiosulfate. A mixture containing a known weight of potassium iodate and an excess of potassium iodide can be used instead of iodine.

B. Reduction Methods

1. Determination of Ferric Iron (Fresenius)*

In all methods thus far discussed, it was necessary to reduce the iron to the ferrous condition before it could be determined volumetrically. In the following method, first suggested by Penny and Wallace,† but improved by Fresenius, the iron in the *ferric* condition may be determined with accuracy and rapidity.

The hydrochloric acid solution containing ferric chloride is titrated hot with stannous chloride solution until the former becomes colorless. By this means the ferric salt is reduced to ferrous salt:

$$2\,FeCl_3 + SnCl_2 = SnCl_4 + 2\,FeCl_2.$$

Inasmuch as it is not very easy to determine the end-point with accuracy, because the last part of the iron is reduced very slowly, it is customary to run over the end-point and to titrate the excess of the stannous chloride with iodine solution.

Solutions Required. 1. *A Ferric Chloride Solution Containing a Known Amount of Iron.* — Dissolve exactly 10.03 g. of pure iron wire in 150 ml. of 6 *N* hydrochloric acid in a long-necked flask held in an inclined position; oxidize the iron with potassium chlorate and boil off the excess of chlorine. Transfer the ferric chloride solution to a liter flask and dilute to the mark with water; 50 ml. of this solution contain 0.5 g. of pure iron.‡

2. *A Stannous Chloride Solution.* — Heat 25 g. of tin-foil in a covered porcelain dish for 2 hours on the water-bath with 50 ml. of 8 *N* hydrochloric acid and a few drops of chloroplatinic acid to form a Pt-Sn couple which helps dissolve the tin. Add 150 ml. more of hydrochloric acid and an equal volume of water, filter and dilute to 1 liter. As stannous chloride is oxidized by contact with the air, keep the solution in a flask which on one side is connected with the buret as shown in Fig. 109, p. 481 and on the other side with a Kipp carbon dioxide generator.

3. *An Iodine Solution, Approximately Tenth-normal.*

Procedure. — (*a*) Standardization of the Solutions.

First titrate the stannous chloride and iodine solutions against each other. Measure out 2 ml. of the former with a pipet, dilute to about 60 ml., add a little starch solution, and titrate the mixture with iodine until a blue color is obtained.

Next, titrate 50 ml. of the acid ferric chloride solution against the stannous chloride solution.

(*b*) *Determination of Iron in Hematite.* Roast 5 g. of the finely-divided ore at a dull red heat to destroy any organic matter which may be present,

* *Z. anal. Chem.*, **1**, 26.

† *Dingl. polyt. J.*, **149**, 440.

‡ The assumption being made that the iron wire contained 99.7 per cent pure iron.

place the powder in a long-necked flask and heat with 25 ml. of concentrated hydrochloric acid and a little potassium chlorate until the iron oxide is all dissolved, leaving a white sandy residue. Add 20 ml. more of hydrochloric acid and continue the boiling while passing a current of air through the solution, until all the excess of chlorine is completely removed and the escaping vapors will no longer set free iodine when passed into a potassium iodide solution. Dilute the solution thus obtained to exactly 500 ml. and use 50 ml. for the analysis.

Example

1. *Standardization of the reagents*:

2 ml. of stannous chloride solution require 7.2 ml. of iodine solution. 1 ml. iodine solution ..... = 0.278 ml. $SnCl_2$

50 ml. ferric chloride solution (= 0.5 g. iron) require for decolorization ..... 30.34 ml. $SnCl_2$

and for the titration of the excess 0.51 ml. of iodine solution = 0.51 × 0.28 ..... 0.14 ml. $SnCl_2$

Consequently, 50 ml. ferric chloride solution = 0.5 g. iron ..... = 30.20 ml. $SnCl_2$

and 1 ml. $SnCl_2 = \frac{0.5}{30.20} = 0.01656$ g. Fe.

2. *Titration of the solution to be analyzed*:

50 ml. (= 0.5 g. of iron ore) require ..... 18.96 ml. $SnCl_2$

and for the titration of the excess, 0.64 ml. of iodine = 0.64 × 0.28 ..... = 0.18 ml. $SnCl_2$

so that 0.5 g. of ore corresponds to ..... 18.78 ml. $SnCl_2$

and contain, therefore, 18.78 × 0.01656 = 0.3110 g. Fe ..... = 62.20% Fe.

2. Determination of Tin by Ferric Chloride*

This method is suitable for determining tin in tin-plating baths.

Principle. — When a ferric chloride solution is added to a solution containing stannous chloride it is decolorized, then a pale-greenish ferrous solution is obtained and finally, when an excess of ferric chloride is present, a yellowish tint is easily recognized as the end-point. If when the titration is made in this way, there is so much pale-green ferrous salt formed that the end-point is hard to recognize, this difficulty can be overcome by first oxidizing the greater part of the tin with normal potassium chlorate solution.

$$SnCl_2 + 2\,FeCl_3 = SnCl_4 + 2\,FeCl_2$$

$$3\,SnCl_2 + KClO_3 + 6\,HCl = 3\,H_2O + KCl + 3\,SnCl_4.$$

Requirements. — 1. Normal potassium chlorate solution. Dissolve 20.43 g. of pure potassium chlorate, dried at 120°, in a little water and dilute with water at 20° to 1 liter.

2. Normal ferric chloride solution. Dissolve 56 g. of pure iron in 600 ml. of 6 *N* hydrochloric acid. Heat toward the last and gradually introduce 20 g. of potassium chlorate. Boil till all the excess chlorine is removed, dilute to about 900 ml., filter if necessary and dilute to exactly 1 liter at 20°.

* Method of O. Meister.

Standardization of the Ferric Chloride Solution and Simultaneous Determination of the Tin Content of a Solution. — Transfer 25 ml. of the tin solution, which should contain about 30 g. of tin in 300 ml. of 6 N hydrochloric acid into a 200-ml. flask held in an inclined position. Add 0.3 g. of aluminium powder which will cause the precipitation of metallic tin. After the evolution of hydrogen ceases, add 20 ml. of concentrated hydrochloric acid, place a small funnel in the neck of the flask and heat till the tin is all dissolved again. Rinse out the funnel and the neck of the flask with hot water and run in ferric chloride solution from a buret into the boiling solution until the greenish yellow end-point is obtained. Call the volume of ferric chloride solution T.

Reduce another portion of the tin solution in exactly the same way but instead of adding ferric chloride solution, first oxidize the greater part of the tin with t ml. of N potassium chlorate solution and finish with t_1 ml. of the ferric chloride solution. Evidently $T - t_1$ ml. of the ferric chloride solution are equivalent to t ml. of N potassium chlorate and 1 ml. of $FeCl_3$ solution $= \frac{t}{T - t_1} = f$ ml. of N solution $= f \times$ 0.05935 g. of Sn. The tin content of the original solution is then

$$\frac{T \times f \times 59.35}{25} \text{ g. Sn per liter.}$$

3. Determination of Ferric Iron by Means of Titanous Chloride (Knecht and Hibbert)*

$$1000 \text{ ml. of } 0.1\ N\ TiCl_3 \text{ solution} = \frac{Fe}{10} = 5.585 \text{ g. Fe.}$$

Principle. — If an acid solution of a ferric salt is treated with titanous chloride, the iron is immediately reduced in the cold to the ferrous condition:

$$FeCl_3 + TiCl_3 = TiCl_4 + FeCl_2.$$

Preparation of Titanous Chloride Solution. — A concentrated solution of titanous chloride, prepared by the electrolysis of $TiCl_4$, can now be obtained on the market. To such a solution add an equal volume of concentrated hydrochloric acid, boil to expel any hydrogen sulfide and dilute with ten times as much boiled water.

Preserve the solution in contact with an atmosphere of hydrogen, or carbon dioxide in a bottle such as is shown in Fig. 109, p. 481 which is connected with a buret, and in this case with a Kipp hydrogen, or carbon dioxide, generator instead of the soda-lime tube.

* *Ber.*, **36**, 1551 (1903). $TiCl_3$ is a very efficient reducing agent and has been used for many determinations. Cf. Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*, Longmans, Green & Co.

Standardization of the Titanous Chloride Solution. — Prepare a ferric chloride solution of known strength as described on p. 594, and of this solution measure out 50 ml. into a beaker, and slowly add the titanium trichloride with constant stirring, while a current of carbon dioxide is constantly being passed into the beaker. After the solution is nearly decolorized, introduce a drop of potassium thiocyanate solution, and continue the adding of titanous chloride to the disappearance of the red color.

The analysis proper is carried out in exactly the same manner.

4. Determination of Ferrous and Ferric Iron by the Titanium Method

First titrate the ferrous iron with permanganate in the presence of manganous sulfate (cf. p. 517) and then determine the total iron with titanous chloride.

The method can be carried out very rapidly and the results are accurate.

5. Determination of Titanium

Reduce the quadrivalent titanium to the tervalent condition and titrate with methylene blue solution.*

6. Determination of Hydrogen Peroxide*

If titanous chloride is run into an acid solution of hydrogen peroxide, the latter is colored first yellow, then a deep orange, and as soon as the maximum depth of color is produced, it begins to fade upon the further addition of titanous chloride until finally the solution becomes colorless, which is taken as the end-point.

The reaction takes place in two stages:

$$2\,TiCl_3 + 3\,H_2O_2 + 2\,H_2O = 2\,H_2TiO_4 + 6\,HCl$$
$$H_2TiO_4 + 2\,TiCl_3 + 6\,HCl = 3\,TiCl_4 + 4\,H_2O.$$

or combining the two equations:

$$2\,TiCl_3 + H_2O_2 + 2\,HCl = 2\,TiCl_4 + 2\,H_2O.$$

On account of the fact that the reducing value of the titanous chloride solution is not very permanent, it should be standardized against ferric chloride before each series of experiments.

If t ml. of titanous chloride solution of which 1 ml. = α g. Fe were required for the reduction of 1 ml. of hydrogen peroxide, then

$$\frac{34.02 \times \alpha t}{111.7}\text{ g. } H_2O_2 \text{ are present} = 30\,46\,\alpha t \text{ per cent } H_2O_2.$$

* Neumann and Murphy, *Z. angew. Chem.*, **1913**, 613.

If it is desired to express the per cent in per cent by volume of active oxygen (cf. p. 534) the following equation holds:

$$10020 \cdot \alpha t = \text{per cent oxygen by volume.}$$

According to Knecht and Hibbert,* persulfuric acid may likewise be estimated by titration with titanous chloride. The solution of the persulfate is treated with titanous chloride solution and the excess of the latter is titrated with ferric chloride in an atmosphere of carbon dioxide.

7. Determination of Hypochlorous Acid by Means of Arsenious Acid

1 liter of 0.1 *N* Na_2HAsO_3 solution = 3.546 g. chlorine.

(*a*) *Method of Penot*†

On adding an arsenite to a solution of a hypochlorite, the former is oxidized to arsenic acid, while the latter is reduced to chloride:

$$HAsO_3^{--} + 2\,ClO^- = HAsO_4^{--} + 2\,Cl^-.$$

The end-point is reached when a drop of the solution added to a piece of iodo-starch paper will cause no blue coloration.

Alkali hypochlorites and chloride of lime may be analyzed by this method and the results obtained are more reliable than in the case of those obtained by the iodimetric method described on p. 568, for the presence of chlorate has no effect in this case.

Method of Pontius

1 liter of 0.1 *N* KI solution = 2.767 g. KI = 3.546 g. of chlorine.

This method is useful for the determination of the available chlorine in bleaching powder and depends upon the fact that potassium iodide is immediately oxidized to iodate by contact with bleaching powder in the presence of sodium bicarbonate solution.

$$3\,CaOCl_2 + 6\,NaHCO_3 + KI = KIO_3 + 6\,NaCl + 6\,CO_2 + 6\,H_2O.$$

If potassium iodide solution is added to sodium bicarbonate solution containing bleaching powder and starch paste, a permanent blue color will not be obtained until all of the bleaching powder has been decomposed. Then free iodine is formed and the end-point is reached.

$$KIO_3 + 5\,KI + 6\,H_2CO_3 = 3\,H_2O + 6\,KHCO_3 + 3\,I_2.$$

From these equations it is clear that the normal solution of potassium iodide contains only one-sixth mole of the salt instead of one mole.

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* Knecht and Hibbert, *Ber.*, **38**, 3324 (1905).

† *J. pr. Chem.*, **54**, 59 (1851).

Procedure. – Triturate 7.092 g. of chloride of lime in a porcelain mortar with a little water, rinse into a liter measuring-flask and fill to the mark with water. Mix thoroughly and without allowing any of the precipitate to settle, transfer with a pipet 50 ml. of the liquid to a beaker, add 3 g. of sodium bicarbonate and titrate with potassium iodide until a permanent blue is obtained with starch paste as indicator. In this case the volume of iodide used is the same as the per cent of available chlorine in the sample.

Remark. — Pontius recommends standardizing the potassium iodide solution as follows: — Titrate 50 ml. of the chloride of lime suspension as above and another portion with 0.1 *N* arsenite solution by the preceding method of Penot.

III. PRECIPITATION ANALYSES

1. Determination of Silver. Method of Gay-Lussac

This exceedingly accurate determination, which is extensively used for testing silver alloys, depends upon the precipitation of silver chloride from nitric acid solution. Common salt is used as the precipitant.

Solutions Required. 1. *Sodium Chloride Solution of Known Concentration.* — For convenience, it is customary to make the solution of such a strength that 1000 ml. correspond to exactly 5 g. of silver. To help in getting the end-point, however, 0.1 per cent less than the theoretical quantity is used. Weigh out 2.700 g. of chemically pure salt, dissolve in distilled water and dilute to 1 liter at 20°.

2. *Decimal Solution of Sodium Chloride.* — Dilute 100 ml. of the above solution with distilled water to 1 liter.

In laboratories where silver determinations are frequently made, the above solutions are made up in much larger quantities and kept in bottles similar to the one shown in Fig. 109, p. 481. For the stronger solution use a 100-ml. pipet and connect the decimal solution with a buret.

Standardization of the Sodium Chloride Solution. — Weigh out exactly 0.5 g. of chemically pure silver into a 200-ml. flask provided with a well-ground glass stopper, and dissolve in 10 ml. of 6 *N* nitric acid, free from chlorine. Hasten the dissolving by heating on a sand-bath. When the silver has dissolved, heat the solution to boiling to expel the nitrous acid formed. Remove the brown vapors by blowing air into the flask. As soon as no more of these are formed, remove the flask from the sand-bath and allow to cool. To the silver solution add exactly 100 ml. of the stronger salt solution, stopper the flask, and vigorously shake until the precipitated silver chloride collects together, and the supernatant liquid appears clear.

As the salt solution was made up a little weak, the precipitation of the silver is not quite complete and consequently more sodium chloride must be added. For this purpose add half a milliliter of the decimal salt solution from the buret, so that the solution runs down the sides of the flask upon the surface of the liquid, causing a distinct cloud of silver chloride to be formed. Shake the liquid, allow the precipitate to settle, again treat with half a milliliter of the decimal salt solution, and repeat the process until finally the addition of the salt solution fails to produce any further turbidity; the last half cubic centimeter is not used in the calculation.

Example. — 0.5 g. of chemically pure silver ($\frac{1000}{1000}$ fine) required 100 ml. of the standard salt solution + 1 ml. of the decimal solution, *i.e.*, 100.1 ml. of the salt solution correspond to 1000 silver;* this is the value of the salt solution.

* For convenience in calculation, 0.5 g. of pure silver is designated by 1000, 0.25 g. by 500, and 0.1 g. by 250, etc.

Silver Determination. — To obtain absolutely accurate results it is necessary to employ the same amount of silver for the analysis as was used in the standardization of the solution, consequently the approximate amount of silver present in the alloy must be determined. This can be accomplished by cupellation, or volumetrically by the method of Volhard, described further on.

Example. — It was found by cupellation that an alloy contained about $\frac{800}{1000}$ fine silver; for the titration an amount must be taken which will contain 0.5 g. of silver; we have then, $1 : 0.8 = x : 0.5$, $x = 0.625$ g.

Weigh out, therefore, 0.625 g. (= 1250*) of the alloy and proceed exactly as in the standardization.

1250 of alloy require for the precipitation of the silver 100 ml. of the standard salt solution + 3 ml. of the decimal solution, *i.e.*, 1250 parts of the alloy require 100.3 ml. of the standard salt solution. Since 100.1 ml. of this salt solution correspond to 1000 parts of pure silver, there must be $\frac{1000 \times 100.3}{100.1} = 1002$ parts silver in 1250 parts of alloy; so that in 1000 parts of the alloy there will be $\frac{1002 \times 1000}{1250} = 801.6$ parts fine of silver.

This procedure is designated as the French method in contrast to the German or Dutch method. In the latter case, 0.5 g. of the alloy (= 100) is weighed out and the same amount of silver is added which the alloy lacks in fineness. In this way one more weighing is necessary, but the calculation is somewhat simpler.

Example. — By cupellation an alloy is found to contain $\frac{800}{1000}$ silver. In order to make the silver equal 1000, 200 parts of fine silver must be added. For the analysis, therefore, 0.5 g. of the alloy and 0.1 g. of pure silver (= 200) are taken, dissolved in nitric acid, and titrated with sodium chloride.

For the titration of the alloy, 100.25 ml. of the stronger salt solution were required, or of the decimal solution,	1002.5 ml.
and for the titration of 1000 fine silver (0.5 g.)	1001.0 ml.
Difference	= 1.5 ml.

As 1 ml. of the decimal solution corresponds to $\frac{1}{1000}$ silver, it is evident that 1.5 ml. are equivalent to $\frac{1.5}{1000}$ silver. If this amount is added to the assumed silver contents (in this case 800), the true fineness of the silver alloy will be obtained; *i.e.*, 801.5 parts fine silver.

2. Determination of Silver (Volhard)

1 liter of 0.1 *N* KCNS = $\frac{\text{Ag}}{10}$ = 10.79 g. Ag.

If to a silver solution containing ferric-ammonium alum, free from chloride but containing enough nitric acid to discharge the brown

* If 0.5 g. = 1000, then $0.5 : 1000 = 0.625 : x$; $x = 1250$.

color of the iron salt, a solution of alkali thiocyanate is added, white insoluble silver thiocyanate is precipitated:

$$AgNO_3 + KCNS = KNO_3 + AgCNS.$$

When all the silver is precipitated, the next drop of the thiocyanate solution will cause a permanent red coloration due to the formation of ferric thiocyanate.

Requirements. 1. *Tenth-normal Silver Solution.* — Dissolve 10.79 g. of pure silver in nitric acid free from chloride, boil until the nitrous acid* is all removed, and dilute with distilled water to a volume of 1 liter at 20°.

2. *Tenth-normal Potassium (or Ammonium) Thiocyanate Solution.* — As both of these salts are hygroscopic and cannot be dried without decomposition, an exactly tenth-normal solution cannot be prepared by weighing out the solid salt. Dissolve approximately the right amount (about 10 g. KCNS or 9 g. NH_4CNS) in a liter of water and standardize the solution against the silver solution.

3. *Ferric-ammonium Alum Solution.* — A cold, saturated solution of ferric alum to which enough nitric acid is added to cause the disappearance of the brown color. Of this indicator use the same amount for all titrations, about 2–3 ml. for 100 ml. of the silver solution.

For the standardization of the thiocyanate solution, place 20 ml. of the silver solution in a beaker, dilute with about 50 ml. of water, and add 2 ml. of the indicator. Introduce the thiocyanate solution from a buret with constant stirring, until a permanent red color is obtained.

Determination of Silver in Silver Alloys

Dissolve 0.5 g. of the brightly polished metal in 10 ml. of 6 *N* nitric acid. After the silver has dissolved, dilute with 50 ml. of water and boil to expel nitrous fumes. Cool, add 2–3 ml. of the ferric alum solution and titrate with the thiocyanate solution as in the standardization. The presence of metals whose salts are colorless does not influence the accuracy of this determination, except that mercury must be absent because its thiocyanates are insoluble. Nickel and cobalt must not be present to any extent, because their salts are colored, and not more than 60 per cent of copper in an alloy is permissible. In case more copper is present the following procedure must be used: Precipitate the silver by means of an excess of alkali thiocyanate, wash completely with water, place the funnel over an Erlenmeyer flask, break the apex of the filter, wash its contents into a flask by means of concentrated nitric acid and heat the liquid to gentle boiling for three-quarters of an hour. As the sulfuric acid formed will have some influence upon the subse-

* Nitrous acid reacts with thiocyanic acid, forming a red compound which may easily be mistaken for ferric thiocyanate.

quent titration, dilute the solution with water to about 100 ml., and add a concentrated barium nitrate solution, drop by drop, until the sulfuric acid is all precipitated. Then titrate the silver with thiocyanate solution without filtering off the barium sulfate.

Remark. — From experiments in Treadwell's laboratory, he concluded that the Volhard method is less reliable than that of Gay-Lussac. Apparently the precipitate adsorbs potassium thiocyanate. If, however, the solution is standardized against approximately the same quantity of silver (or the equivalent amount of silver nitrate) as is taken for analysis this error is compensated and the results are very exact.

3. Determination of Chlorine

(*a*) *Volhard's Method*

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{Cl}{10} = 3.546 \text{ g. chlorine.}$$

According to Volhard's original directions, the chloride solution was treated with 0.1 *N* silver nitrate solution and then, without filtering off the precipitate, 5 ml. of the ferric-ammonium alum solution were added and the excess of silver titrated with 0.1 *N* potassium or ammonium thiocyanate (see p. 602).

The results are satisfactory with large quantities of chloride, but in the titration of small quantities of chloride too high results are obtained, as was first shown by G. Drechsel* and later confirmed by M. A. Rosanoff and A. E. Hill.† Drechsel showed that it was impossible to get the true end-point of the reaction, as the red coloration gradually disappeared on stirring, remaining permanent only after a considerable excess of thiocyanate had been added. The reason for this is that silver chloride is more soluble than silver thiocyanate. Thus the precipitate gradually reacts with the red ferric thiocyanate, as follows:

$$3\ AgCl + Fe(CNS)_3 = 3\ AgCNS + FeCl_3.$$

To avoid this error Drechsel proceeds as follows:

To the chloride solution in a 200-ml. measuring-flask, add an excess of 0.1 *N* $AgNO_3$ solution, make the solution acid with nitric acid, and shake the stoppered flask until the precipitate coagulates enough to give a clear supernatant liquid. Dilute the solution to the mark, thoroughly mix and filter through a dry filter, rejecting the first 10 ml. of filtrate. Of the filtrate, take 50 or 100 ml., add the ferric alum indicator, and titrate the excess of silver with 0.1 *N* thiocyanate solution. The results thus obtained are excellent.

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* *Z. anal. Chem.*, **16**, 351 (1877).

† *J. Am. Chem. Soc.*, **29**, 269.

Remark. — V. Rothmund and A. Burgstaller* find that it is possible to obtain correct results without filtering off the silver chloride precipitate. They heat the solution after the addition of the excess of silver nitrate, until the precipitate coagulates thoroughly, in which form it reacts less readily with a soluble thiocyanate. After cooling, the ferric alum indicator is added and the titration finished. Rothmund and Burgstaller also find that the coagulation of the silver chloride precipitate by ether† suffices to make the filtration unnecessary. The chloride solution is placed in a flask with tightly fitting glass stopper, 5 ml. of ether added, and an excess of silver nitrate solution. After shaking a few minutes, the supernatant solution becomes clear and the titration can be finished with accuracy.

(*b*) *Fr. Mohr's Method*

If the neutral solution of an alkali or alkali-earth chloride containing a few drops of potassium chromate solution‡ is treated with silver nitrate solution, added from a buret, a red precipitate of silver chromate is formed which, on stirring, disappears on account of its being decomposed by the alkali chloride to silver chloride and alkali chromate:

$$Ag_2CrO_4 + 2\ NaCl = 2\ AgCl + Na_2CrO_4.$$

When all of the chlorine is changed to insoluble silver chloride, the next drop of the silver solution will impart a permanent reddish color to the liquid. For small amounts of chloride in concentrated solutions this method gives very sharp results. If, however, the volume of the solution is too large, the results are not very accurate. In all cases, a blank experiment must be made to see how much of the silver solution is necessary to produce the red shade used in the titration when no chloride is present, and this amount must be deducted from that used in the analysis.

Remark. — If it is desired to titrate free hydrochloric acid, first neutralize the solution. In the case of colorless chlorides having an acid reaction ($AlCl_3$) treat the solution with an excess of neutral sodium acetate solution and then titrate. With colored metal chlorides, precipitate the metal with caustic potash or sodium carbonate, filter, wash the precipitate, make the filtrate acid with acetic acid, and then titrate.

4. Determination of Bromine

(*a*) *Volhard's Method*

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{Br}{10} = 7.992 \text{ g. bromine.}$$

Treat the solution of the bromide with an excess of 0.1 *N* silver solution and titrate with ammonium thiocyanate, using ferric alum as

* *Z. anorg. Chem.*, **63**, 330 (1909).

† Cf. E. Alefeld, *Z. anal. Chem.*, **48**, 79 (1909).

‡ Lunge uses sodium arsenate as indicator, and this is to be recommended on account of the change from colorless to brown being very easy to detect.

indicator. From the required volume of silver nitrate, compute the quantity of bromine.

Remark. — It is not necessary to filter off the silver bromide, because, unlike the chloride, silver bromide is more insoluble than is silver thiocyanate.

(*b*) *Fr. Mohr's Method*

The procedure is the same as in the case of the chloride determination.

5. Determination of Iodine

Volhard's Method

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{I}{10} = 12.69 \text{ g. iodine.}$$

If silver iodide is produced in a solution of an iodide by the addition of silver nitrate, the precipitate will usually enclose a measurable amount of either the soluble iodide or the silver nitrate, so that the analysis cannot be accomplished in the same way as in the analysis of chlorides and bromides.

Place the solution in a glass-stoppered flask, dilute to 200–300 ml., and add the silver solution with vigorous shaking until the yellow precipitate collects together and the supernatant liquid appears colorless. As long as the solution appears milky the precipitation is not complete. Finally add a little more silver nitrate and again shake to precipitate any iodide in the pores of the silver iodide. Then add ferric alum solution, titrate the excess of silver with potassium thiocyanate, and calculate the iodine from the amount of silver used. In this way Volhard obtained exact results.

The ferric solution must not be added before the iodine is completely precipitated, because in acid solution it oxidizes the hydriodic acid with separation of iodine. Silver iodide, however, is without action on ferric salts.

6. Determination of Cyanogen

(*a*) *Volhard's Method*

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{KCN}{10} = 6.511 \text{ g. KCN.}$$

If an excess of silver nitrate is added to a solution containing potassium cyanide and an attempt is made to titrate the excess of the former by means of potassium thiocyanate, using a ferric salt as an indicator, there will be no distinct end-point, because the silver cyanide reacts with the ferric sulfocyanate:

$$3\,AgCN + Fe(CNS)_3 + 3\,HNO_3 = 3\,AgCNS + 3\,HCN + Fe(NO_3)_3.$$

The red color obtained in the titration will disappear on stirring. If, however, the neutral cyanide solution is treated with an excess of the silver solution, then slightly acidified with nitric acid, diluted up to a definite volume in a measuring-flask and filtered through a dry filter the excess of silver can then be titrated in an aliquot part of the filtrate. As usual the first runnings of the filtrate should be rejected.

(*b*) *Liebig's Method**

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{KCN}{5} = 13.02 \text{ g. KCN.}$$

On adding silver nitrate solution, drop by drop, to a neutral or alkaline solution of an alkali cyanide, a white precipitate is formed when the two liquids first come in contact with one another, but on stirring it redissolves owing to the formation of potassium silver cyanide:

$$AgCN + KCN = KAg(CN)_2.$$

As soon as all of the cyanogen is transformed into potassium silver cyanide, the next drop of the silver solution will produce a permanent turbidity:

$$Ag(CN)_2K + AgNO_3 = KNO_3 + 2\,AgCN.$$

The total reaction is, therefore,

$$2\,KCN + AgNO_3 = KNO_3 + Ag(CN)_2K.$$

1 Ag corresponds to 2 CN and the end-point of the reaction is shown by the formation of a permanent precipitate.

Place the alkali cyanide solution in a beaker, add a little potassium hydroxide, and dilute to a volume of about 100 ml. Place the beaker on a piece of black, glazed paper and titrate with constant stirring until the turbidity is obtained.

For the analysis of free hydrocyanic acid, add an excess of potassium hydroxide solution and treat as above.

The addition of 5 ml. of 2 per cent potassium iodide solution slightly increases the sharpness of the end-point in the above analysis. The precipitate then consists of silver iodide of which one molecule will dissolve in two molecules of potassium cyanide, just as silver nitrate does.

Remark. — For the sharp recognition of the end-point in this and all other reactions where there is a turbidity, W. D. Treadwell recommends the following arrangement.

The apparatus, Fig. 122, consists of a wooden box in which an incandescent lamp with frosted bowl is placed. Directly over this light there are two round holes in

* *Ann. Chem. Pharm.*, **77**, 102.

the top of the box over which beakers can be placed. Water-bath rings can be used to fit different beakers. The glass plate G is used to prevent heating the beakers by the rays from the lamp. To detect a turbidity, place the beaker over the hole, light the lamp and view horizontally in a dark or dimly lighted room.

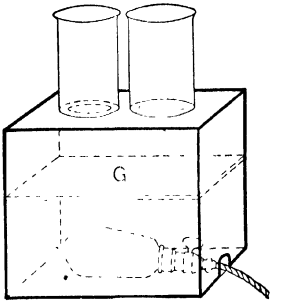


FIG. 122.

7. Determination of Chlorine and Cyanogen in the Presence of One Another

First, determine the cyanide by the method of Liebig, and then add enough silver solution to convert all of the cyanide and chloride into their silver salts. Make the solution acid with nitric acid, dilute with water to a definite volume, filter through a dry filter, and after rejecting the first runnings, use an aliquot part of the filtrate for the titration of the excess of silver by means of potassium thiocyanate, according to Volhard. The calculation of the cyanogen and chlorine is illustrated by the following example:

10 ml. of the solution required for the production of a permanent turbidity t ml. of 0.1 N silver solution. Then an excess of 0.1 N silver solution was added (bringing the total amount used to T ml.). The solution was acidified with nitric acid, diluted to exactly 200 ml., filtered through a dry filter, and after the usual rejection of the first runnings the excess of the silver was titrated in 100 ml. of the filtrate; this required t_1 ml. of 0.1 N potassium thiocyanate solution. Consequently the amount of cyanogen present is $t \times 0.005202$ g., and the chlorine present amounts to $[T - 2\,(t + t_1)]\,0.003546$ g.

8. Determination of Potassium Cyanide in the Presence of Ferrocyanide. Method of W. D. Treadwell*

In this determination the use of potassium iodide is necessary because of the appreciable solubility of silver cyanide in alkali ferrocyanide solution.

Procedure. — To one aliquot part of the solution add 0.1 g. of potassium iodide, 2–3 ml. of 0.1 N caustic alkali solution or ammonium hydroxide, and titrate in a volume of about 100 ml. with 0.1 N silver solution till a turbidity forms. This gives the KCN content.

To determine the ferrocyanide, remove the cyanide by heating another aliquot part of the original solution under a good hood while

* *Z. anorg. Chem.*, **71**, 219 (1911).

introducing a stream of carbon dioxide. This requires about 30 minutes. Then titrate the ferrocyanide according to the directions on p. 590.

9. Determination of Thiocyanic Acid. Volhard's Method

$$1 \text{ liter of } 0.1\ N\ AgNO_3 \text{ solution} = \frac{HCNS}{10} = 5.907 \text{ g. HCNS.}$$

This is the reverse of the silver determination (p. 602). Add an excess of 0.1 N silver solution to the solution containing the thiocyanate, and titrate the excess of silver with potassium thiocyanate solution, using ferric alum as indicator.

10. Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another

Add enough potassium hydroxide to make the solution neutral, dilute to about 100 ml., and titrate the cyanogen by the method of Liebig (p. 606). Then, add an excess of silver solution, make acid with nitric acid, and titrate the excess of silver with potassium thiocyanate in an aliquot part of the filtrate.

11. Determination of Hydrochloric, Hydrocyanic, and Thiocyanic Acids in the Presence of One Another

In one portion determine the cyanogen according to Liebig. To a second portion add an excess of 0.1 N silver solution, make acid with nitric acid, filter, wash the precipitate with water, and titrate the excess of silver in the filtrate according to Volhard. Pierce the filter containing the precipitate and transfer the latter by means of concentrated nitric acid to a flask and boil for three-quarters of an hour. By this means the cyanide and thiocyanate of silver go into solution, while the silver chloride remains undissolved. Dilute the solution to about 100 ml., add enough barium nitrate to precipitate the sulfuric acid formed, and titrate the silver corresponding to the cyanide and thiocyanate with potassium thiocyanate without filtering off the silver chloride or barium sulfate.

Computation. — If t ml. of 0.1 N $AgNO_3$ were used in the first titration, then 2 t ml. would be needed to precipitate all of the cyanide. If T ml. of 0.1 N $AgNO_3$ were required in the second titration to precipitate all of the cyanide, thiocyanate and chloride and t_1 ml. of 0.1 N $AgNO_3$ were used in the last titration, then

$$t \times 0.005202 \text{ g. CN} = t \times 0.01302 \text{ g. KCN}$$
$$(t_1 - 2t) \times 0.005808 \text{ g. CNS} = t \times 0.009718 \text{ g. KCNS}$$
$$(T - t_1) \times 0.003546 \text{ g. Cl} = t \times 0.007456 \text{ g. KCl}$$

12. Determination of Sulfuric Acid by Benzidine Hydrochloride*

$$1 \text{ liter of } 0.1\ N \text{ NaOH} = \frac{H_2SO_4}{20} = 4.904 \text{ g. } H_2SO_4.$$

Benzidine, $C_{12}H_8(NH_2)_2$, is a weak organic base. It forms stable salts with strong mineral acids, of which the sulfate is characterized by its slight solubility, particularly in water containing hydrochloric acid. The base itself is neutral toward phenolphthalein. On account of being such a weak base, therefore, the aqueous solutions of its salts undergo hydrolysis. Thus benzidine hydrochloride is decomposed according to the equation:

$$C_{12}H_8(NH_2)_2 \cdot 2\,HCl + 2\,H_2O \rightleftarrows 2\,HCl + C_{12}H_8(NH_2)_2(HOH)_2$$

into hydrochloric acid and benzidine hydroxide, and the latter breaks down further into benzidine and water:

$$C_{12}H_8(NH_2)_2(HOH)_2 \rightarrow C_{12}H_8(NH_2)_2 + 2\,H_2O.$$

In other words, an aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine, and the amount of acid present may be titrated with alkali, using phenolphthalein as an indicator.

There are two methods which have been used for the volumetric estimation of sulfuric acid by means of benzidine. Müller treated the *neutral* solution of the sulfate with a solution of benzidine hydrochloride of known acidity.

$$C_{12}H_8(NH_2)_2 \cdot 2\,HCl + Na_2SO_4 = 2\,NaCl + \underbrace{C_{12}H_8(NH_2)_2 \cdot H_2SO_4}_{\text{Insoluble}}.$$

The precipitate of benzidine sulfate was filtered off and the filtrate titrated with a standard solution of alkali. The loss in acidity corresponded to the amount of sulfuric acid present. Raschig, on the other hand, recommends treating the neutral or acid solution of the sulfate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulfate, washing it, and then suspending it in water and titrating the sulfuric acid with 0.1 *N* sodium hydroxide at 50°.

Raschig prepares the reagent as follows: Triturate 40 g. of benzidine with 40 ml. of water and rinse the paste into a liter measuring flask with about 750 ml. of water. Add 50 ml. of concentrated hydrochloric acid and dilute to the mark. Shake well. Soon the benzidine will all dissolve forming a brown liquid which may be filtered if necessary. When using as a reagent, dilute with nineteen times as much water.

Procedure. — To the neutral or slightly acid solution of the sulfate, containing not more than 0.1 g. of sulfate anions per 50 ml. of solution, add the diluted benzidine solution in the cold, using 150 ml. for each 0.1 g. of sulfate ions. A crystalline precipitate of benzidine sulfate forms at once, which can be filtered as follows after standing 5 minutes.

Place a Witt perforated porcelain plate in a funnel of 200-ml. capacity. The diameter of the plate should be about 40 mm. on the top. Place 2 pieces of filter-paper on this plate, about 46 mm. in diameter. Insert

* W. Müller, *Ber.*, **35**, 1587 (1902); Müller and Dürkes, *Z. anal. Chem.*, **42**, 477 (1903); F. Raschig, *Z. angew. Chem.*, **1903**, 617 and 818; von Knorre, *Chem. Ind.*, **28**, 2; and Friedheim and Nydegger, *Z. angew. Chem.*, **1907**, 9.

the funnel in a rubber stopper and place in a suction bottle. Moisten the filters with water, apply gentle suction and press the papers to the sides of the funnel so that a tight pad is formed of about 3 mm. depth, which will not allow precipitate to get by. Pour the supernatant liquid through this filter, rinse the precipitate and mother liquor into the funnel and drain. Wash with 15 ml. of water added in small portions. Place the precipitate and filter, without the porcelain plate, in an Erlenmeyer flask, add 50 ml. of water and shake the contents of the stoppered flask until a homogeneous paste is obtained. Remove the rubber stopper from the flask, rinse off with water, add a drop of phenolphthalein solution, heat to about 50° and titrate with 0.1 *N* sodium hydroxide. When the end-point is nearly reached, boil the liquid for 5 minutes, and then finish the titration.

Remark. — This method does not give good results in the presence of ferric salts but this difficulty can be overcome by reducing the ferric ion with hydrazine hydrochloride. There should not be more than 10 moles of HCl, 15 moles HNO_3, 20 moles $HC_2H_3O_2$, 5 moles alkali salt, or 2 moles ferric iron present to 1 mole of H_2SO_4. A satisfactory determination of the sulfur in pyrite may be made by dissolving 0.5 g. of the sample according to the Lunge method (see p. 320), evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 ml. and using 100 ml. for the treatment with benzidine hydrochloride.

13. Determination of Sulfuric Acid: (Hinman)*

$$1 \text{ liter of } 0.1\ N\ Na_2S_2O_3 = \frac{H_2SO_4}{30} = \frac{98.08}{30} = 3.269 \text{ g. } H_2SO_4.$$

This method depends upon the fact that barium chromate is easily dissolved by dilute hydrochloric acid while barium sulfate is not; 1 liter of cold water dissolves about 2 mg. of $BaSO_4$ and 3 mg. of $BaCrO_4$ but the latter salt dissolves easily in acid because $HCrO_4^-$ as an acid is comparable to H_2CO_3. If a solution of barium chromate in dilute hydrochloric acid is added in slight excess to a solution containing SO_4^{--} ions, $BaSO_4$ is precipitated; then upon neutralizing the solution the remainder of the barium is precipitated as $BaCrO_4$, leaving one mole of CrO_4^{--} in solution for each mole of SO_4^{--} originally present. After filtering, the dissolved chromium can be determined iodometrically (p. 572).

The method is rapid and capable of giving theoretical values in the analysis of sulfates containing less than 5 per cent of SO_3. By slightly varying the conditions, however, the results are influenced and the most favorable conditions are not always the same for different sulfates. The method, therefore, is suitable for routine work, but is not theoretically perfect.†

* *Am. J. Sci. and Arts*, **114**, 478 (1877). Cf. Andrews, *Am. Chem. J.*, **2**, 567; Pennock and Morton, *J. Am. Chem. Soc.*, **1903**, 2265; Bruhns, *Z. anal. Chem.*, **45**, 573 (1906); Holliger, *Ibid.*, **19**, 84 (1910), and M. Reuter, *Chem. Ztg.*, **1898**, 357.

† In some cases it is simplest to apply a correction factor. Thus Komarowsky (*Chem. Ztg.*, **31**, 498 (1907) deducts 0.3 ml. from the final buret reading. J. Lurie, at the Mass. Inst. Tech., was able to modify the directions so that correct results could be obtained with several sulfates.

The results are likely to be high, — (1) If the barium chromate contains any water-soluble chromate. Since the solubility of barium chromate in hot water is appreciable there will always be a positive error from this source, if the solution is filtered hot.

The results will be low, — (1) If there is any reduction of chromate other than the desired reduction with iodide; this may be caused by the presence of too much hydrochloric acid during the first precipitation. (2) If any other chromate is precipitated with the barium chromate, such as basic ferric chromate. (3) If the solution is not acid enough during the treatment with iodide the reduction of the chromate is likely to be incomplete. (4) If the solution is hot, or contains an insufficient amount of iodide there is likely to be some loss of the iodine.

Prepare the barium chromate reagent by precipitating barium chloride with potassium chromate at the boiling temperature. Wash the precipitate with hot, dilute acetic acid and then with water till free from chromate. Dissolve 2–4 g. of the dry salt in one liter of normal hydrochloric acid. 1 ml. should precipitate 0.63 mg. to 1.2 mg. of SO_3.

Procedure. — If the solution of the sulfate is acid, nearly neutralize it with caustic alkali solution. Dilute with water until not more than about 5 mg. of SO_3 is present in 100 ml. Heat to boiling and slowly add a slight excess of the barium chromate reagent. Boil for 1 minute or for 5 minutes if any carbonate was present.

To the boiling solution cautiously add pure $CaCO_3$ in small portions until present in slight excess (use ammonia if iron, nickel or zinc is present). Cool to room temperature and bring to a definite volume in a 250-ml. measuring-flask. Filter through a dry filter, reject the first 20 ml. and take 100 ml. of the filtrate for the titration.

Add 2–3 g. of potassium iodide and 10 ml. of concentrated hydrochloric acid. Shake well and allow to stand 15 minutes. Then titrate slowly with 0.02 normal sodium thiosulfate solution.

Remark. — When iron, nickel or zinc salts are contained in the solution, the acid present cannot be neutralized with calcium carbonate, because these salts when boiled with calcium carbonate and a soluble chromate form insoluble basic chromates, so that too little chromic acid will be found in the filtrate corresponding to too little sulfuric acid. In such a case the neutralization is effected with ammonia, an excess being added, the solution boiled until the excess is almost entirely expelled and then filtered.

14. Determination of Phosphoric Acid. Method of Pincus

Principle. — If a neutral solution, or one slightly acid with acetic acid, is treated with uranyl acetate, a greenish-white precipitate of uranyl phosphate is formed:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 = KC_2H_3O_2 + HC_2H_3O_2 + UO_2HPO_4.$$

If at the same time ammonium salts are present, ammonium is contained in the precipitate:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 + NH_4C_2H_3O_2 = KC_2H_3O_2 + 2\,HC_2H_3O_2 + UO_2NH_4PO_4.$$

The end of the precipitation can be determined by testing a drop of the solution on a porcelain tile with potassium ferrocyanide. A brown coloration is formed as soon as an excess of uranyl salt has been added.

To precipitate the phosphoric acid completely, it is necessary to titrate in a boiling hot solution. As, however, a solution of calcium phosphate will become turbid on boiling, owing to the formation of secondary calcium phosphate ($CaHPO_4$), it is best to precipitate the greater part of the phosphoric acid in the cold, then heat to boiling and complete the titration.

Requirements. 1. *Potassium Phosphate Solution.* — Dissolve 19.17 g. (corresponding to 10 g. P_2O_5) of pure, monopotassium phosphate in 1 liter of water.

Confirm the concentration of the solution by evaporating 50 ml. to dryness in a large platinum crucible, igniting the residue over the full flame of a Bunsen burner and weighing as KPO_3; also by precipitating another portion as magnesium ammonium phosphate and weighing as magnesium pyrophosphate.

50 ml. of the solution correspond to 0.5 g. P_2O_5 and should yield 0.8315 g. KPO_3 and 0.7839 g. $Mg_2P_2O_7$.

2. *Calcium Phosphate Solution.* — Dissolve 5.461 g. of $Ca_3(PO_4)_2$, corresponding to 2.5 g. P_2O_5, in a little nitric acid, dilute with water to a volume of 1 liter, and test the concentration of the solution by means of the molybdate method of Woy (p. 381).

3. *Uranyl Acetate Solution.* — Dissolve about 35 g. of uranyl acetate in a liter of water.

4. *Ammonium Acetate Solution.* — Dissolve 100 g. of pure ammonium acetate and 100 ml. of 6 *N* acetic acid, in enough water to make 1 liter of solution.

5. *Potassium Ferrocyanide.* — The salt is used in the powdered form.

Procedure

(*a*) *Standardization of the Uranium Solution*

To 50 ml. of the potassium phosphate, or calcium phosphate, solution add 10 ml. of the ammonium acetate solution, run in the uranyl acetate solution from a buret until a drop of the solution will show a brown coloration when treated with solid potassium ferrocyanide upon a white porcelain tile. Then heat the solution to boiling, when a drop of it will no longer react with the ferrocyanide. To the hot solution add more of the uranium solution, until the brown color is obtained once more.

If for the precipitation of the phosphoric acid contained in 50 ml. of the potassium phosphate solution (0.5 g. P_2O_5), T ml. of the uranium solution were required, its concentration is $\frac{0.5}{T}$ g. P_2O_5 per ml.

For the analysis of alkali phosphates, standardize the solution against the potassium phosphate solution, but for the analysis of an alkaline-earth phosphate use the solution of calcium phosphate.

(b) Determination of Phosphoric Acid in Alkali Phosphate

The solution to be analyzed should be of about the same concentration as that of the potassium phosphate used for the standardization, and titrated in the same way. Phosphate solutions of different concentrations give different results by the titration.

(c) Determination of Phosphoric Acid in Calcium Phosphate

Dissolve 0.25 g. of calcium phosphate in dilute nitric acid, add ammonia until a permanent precipitate is produced, and redissolve this in a little acetic acid. Add 10 ml. of the ammonium acetate solution, and titrate the solution with the standard solution of uranyl acetate.

Remark. — In the presence of iron and aluminium this method will not give accurate results because the phosphates of these metals are insoluble in acetic acid. In such cases, filter the turbid acetic acid solution and determine the phosphoric acid in the filtrate by the above titration. Ignite the precipitate consisting of iron and aluminium phosphates, weigh, and, if it amounts to less than 0.01 g., assume half its weight to be P_2O_5; otherwise determine the phosphoric acid in the precipitate by the molybdate method.

15. Determination of Nickel by Potassium Cyanide*

This method, which permits the volumetric estimation of nickel with speed and accuracy even in the presence of iron, manganese, chromium, zinc, vanadium, molybdenum, and tungsten, depends upon the fact that nickel ions react with potassium cyanide in slightly ammoniacal solution, to form a complex anion, $[Ni(CN)_4]^{--}$,

$$Ni(NH_3)_6Cl_2 + 4\ KCN = K_2[Ni(CN)_4] + 6\ NH_3 + 2\ KCl.$$

If the solution of the nickel salt contains a precipitate of silver iodide, produced by adding a known amount of silver nitrate and a few drops of potassium iodide solution, the turbidity will not disappear until all of the nickel has entered into reaction with the potassium cyanide.

$$AgI + 2\ KCN = K[Ag(CN)_2] + KI.$$

The titration is finished by adding just enough more silver nitrate to cause the precipitate of silver iodide to reappear.

$$K[Ag(CN)_2] + AgNO_3 = 2\ AgCN + KNO_3.$$

* Cf. Campbell and Andrews, *J. Am. Chem. Soc.*, **17**, 126 (1895); Moore, *Chem. News*, **72**, 92 (1895); Goutal, *Z. angew. Chem.*, **1898**, 177; Brearley and Jarvis, *Chem. News*, **78**, 177 and 190 (1898); Johnson, *J. Am. Chem. Soc.*, **29**, 1201 (1907); Campbell and Arthur, *ibid.*, **30**, 1116 (1908); and Grossmann, *Chem. Ztg.*, **32**, 1223 (1908).

Requirements. — **1.** A *nickel solution* of known content. Dissolve 10 g. of pure nickel in 125 ml. of 6 *N* nitric acid, boil off the nitrous fumes and dilute with water to 1 liter at 20°.

2. A *silver nitrate solution.* Dissolve 5 g. of silver nitrate in water and dilute to 1 liter.

3. A *potassium cyanide solution.* Dissolve 15 g. of purest potassium cyanide and dilute to 1 liter.

4. *Potassium iodide solution.* Dissolve 10 g. of potassium iodide in 100 ml. of water.

Standardization of the Potassium Cyanide Solution. — To 10 ml. of the nickel solution, accurately measured with a pipet, add ammonium hydroxide in slight excess, dilute to 100 ml., add 6 drops of potassium iodide solution and about 1 ml. of silver solution from a buret, noting the reading of the buret before adding the silver solution. From another buret, slowly run in potassium cyanide solution, with constant stirring, until the silver iodide precipitate dissolves. Then very carefully add silver nitrate solution until a permanent turbidity is formed and dissolve this by careful addition of more potassium cyanide solution. Since the potassium cyanide solution decomposes slowly, this titration must be made every day that the solution is used.

Next determine the relative strengths of silver solution and potassium cyanide solutions. From a buret, add 30 ml. of the latter, neutralize with ammonia, dilute, add potassium iodide and titrate in exactly the same way as just outlined.

From this last titration in which a ml. of silver nitrate were found equal to b ml. of potassium cyanide, 1 ml. of $AgNO_3$ solution $= \frac{b}{a}$ ml. of KCN solution. If T ml. of potassium cyanide and t ml. of silver nitrate were used in the titration of 10 ml. of nickel solution (= 0.1 g. Ni)

then $$1 \text{ ml. of KCN solution} = \frac{0.1}{T - \frac{b}{a}t} \text{ g. Ni.}$$

Analysis. — To 100 ml. of solution containing approximately 0.1 g. of nickel, add ammonium hydroxide* and continue exactly as in the above standardization with pure nickel solution.

Instead of working with two solutions, F. Sutton† states that equally reliable results can be obtained by using a potassium cyanide solution to which a little silver nitrate has been added. Thus, to the above solution of potassium cyanide there may be added about 0.50 g. of silver

* If the addition of ammonia does not give a clear solution, a few cubic centimeters of ammonium chloride solution should be added.

† *Volumetric Analysis*, 8th edition, p. 252.

nitrate which is first dissolved in water by itself. If this solution is used for titrating a nickel solution to which potassium iodide solution has been added, a precipitate of silver iodide is formed at once which increases with the further addition of the potassium cyanide-silver nitrate solution until all the nickel is converted into potassium nickelocyanide, but the precipitate eventually disappears upon the further addition of the solution.

Remarks. — Instead of titrating the potassium cyanide against a known nickel solution, the standardization may be accomplished with 0.1 *N* silver nitrate solution. In this case it is best to take as end-point the formation of a slight turbidity on adding silver nitrate, rather than the dissolving of the precipitate with potassium cyanide. 1 ml. of 0.1 *N* silver nitrate solution = 0.01302 g. of KCN = 0.002934 g. of Ni.

The method can be carried out in the presence of most of the other elements of the ammonium sulfide group. If a clear solution is not obtained on adding ammonium hydroxide, the addition of ammonium chloride sometimes helps. If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. In case chromium is present, the dark color due to presence of chromic salts may be obviated by adding to the original sulfuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid. Filter the solution, concentrate in a 400-ml. beaker to about 60 ml., then treat with sodium pyrophosphate, as described below. The method is not applicable in the presence of considerable cobalt, the presence of which is betrayed by the solution assuming a dark color upon the addition of potassium cyanide, but when the amount of the latter does not exceed one-tenth the amount of nickel present, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

Zinc causes trouble unless alkali pyrophosphate is added. The titration can be carried out in the presence of aluminium, iron and manganese if citric or tartaric acid or sodium pyrophosphate is added.

The temperature of the solution should not be much above 20°, for in hot solutions the results are not concordant. The quantity of ammonia present should not be too great, because the tendency is for ammonia to impede the reaction if more than a slight excess is present. Potassium cyanide containing sulfide cannot be used; the reagent should be the purest obtainable. The results are accurate. The method has been modified so that it can be used to advantage for the

Determination of Nickel in Nickel Steel

Dissolve 1 g. of steel in a casserole with 10–15 ml. of 6 *N* of nitric acid (*d.* 1.2), adding a little hydrochloric acid if necessary. After the steel has dissolved, add 6–8 ml. of 18 *N* sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved. Cool, add 30–40 ml. of water, and boil the contents of the casserole until the ferric sulfate has all dissolved. Transfer the solution to a 400-ml.

beaker, filtering if necessary, and add 13 g. of sodium pyrophosphate* dissolved in 60 ml. of water at about 60°. The pyrophosphate solution must not be boiled, as this causes the formation of normal phosphate. The addition of the sodium pyrophosphate causes the formation of a heavy white precipitate of ferric pyrophosphate. Cool to room temperature, and add 6 *N* ammonia drop by drop, while stirring constantly, until the greater part of the precipitate has dissolved and the solution has assumed a greenish tinge. At this point, it should react alkaline toward litmus and smell slightly, but not too strongly, of ammonia. Now gently heat the solution, while stirring; the remainder of the pyrophosphate will dissolve, giving a perfectly clear light green solution. If the ammonia is added too fast, or the solution is not carefully stirred, a brownish color is likely to result, but this can usually be overcome by carefully adding a few drops of dilute sulfuric acid. Cool the clear solution to room temperature, add 0.5 ml. of the standard silver nitrate solution and 2 ml. of the potassium iodide. Titrate with potassium cyanide until the precipitate of silver iodide has disappeared, and finish by adding just enough more of the silver nitrate to cause the formation of a slight turbidity again.

16. Determination of Copper by the Potassium Cyanide Method†

Principle. — If an ammoniacal solution of a cupric salt is treated with potassium cyanide, the intense blue color gradually disappears. The reaction is essentially as follows:

$$2\,Cu(NH_3)_4^{++} + 7\,CN^- + H_2O = Cu_2(CN)_6^{----} + CNO^- + 2\,NH_4^+ + 6\,NH_3.$$

The temperature of the solution, the ammonia concentration, and the quantity of ammonium salts present effect the reaction so that a given quantity of copper does not always react with the same quantity of potassium cyanide. The potassium cyanide solution, therefore, must be standardized under exactly the same conditions as under which the analysis is carried out.

Standardization of the Potassium Cyanide Solution. — Dissolve 20 g. of pure potassium cyanide in a liter of water. Weigh out 0.2 g. of pure copper wire, or foil, into a 200-ml. Erlenmeyer flask and dissolve in 10 ml. of 6 *N* nitric acid. After the copper has dissolved add 25 ml. of water and 5 ml. of bromine water. Boil to expel the excess of bromine. Then add 50 ml. of water and 10 ml. of concentrated ammonium hydroxide, cool to room temperature by placing the flask in cold water, and

* Instead of using sodium pyrophosphate to prevent the interference of iron and other metals, many chemists use citric or tartaric acid. In this case the solution is dark colored and the end-point a little harder to detect.

† Cf. Steinbeck, *Z. anal. Chem.*, **8**, 8 (1869). Dulin, *J. Am. Chem. Soc.*, **17**, 346. A. H. Low, *Technical Methods of Ore Analysis.*

add the potassium cyanide solution slowly from a buret, while constantly rotating the contents of the flask. When the solution has become a pale blue, dilute to about 150 ml. and continue adding the potassium cyanide until the solution is just decolorized. The weighed amount of copper divided by the number of milliliters of potassium cyanide required gives the titer of the solution.

Low's Method for Analyzing Copper Ores. — Weigh out 0.5 g. of a rich ore, or from 2–4 times as much of a low-grade ore, into a 200-ml. Erlenmeyer flask and treat with 6–10 ml. of concentrated nitric acid. Boil until nearly all the red fumes are expelled. If necessary, also add 5 ml. of concentrated hydrochloric acid to decompose the ore and continue boiling for a short time. After cooling somewhat, add 14 ml. of 18 *N* sulfuric acid and evaporate until dense fumes of sulfuric acid are evolved. Then, after allowing to cool again, add 25 ml. of cold water and a drop of concentrated hydrochloric acid to precipitate any silver as chloride. Boil to dissolve the copper and ferric sulfates and filter off the precipitated lead sulfate and silicious residue. Wash the residue with hot water and receive the filtrate in a 150-ml. beaker and take care not to let the filtrate exceed 75 ml.

Place a piece of sheet aluminium, about 14 cm. long and 2.5 cm. wide and bent into a triangle, in the beaker. Cover with a watch-glass and boil the contents of the beaker for about 10 minutes, whereby nearly all the copper is deposited as spongy metal. Now remove the flame and wash down the sides of the beaker with cold water. To precipitate the last traces of copper and to prevent the oxidation of the fine deposit, add 15 ml. of strong hydrogen sulfide water and decant the liquid through a 9 cm. filter. Wash off the copper from the aluminium by means of weak hydrogen sulfide water into the flask in which the ore was dissolved and decant the liquid through the filter. Set aside the beaker containing the aluminium foil and some copper. The operation of filtering should take place without interruption and the filter kept well filled with liquid to prevent the oxidation of any precipitate upon it, which would cause it to dissolve and give a turbid filtrate. After washing the deposit 4 times, using in each case 20 ml. of weak hydrogen sulfide water, allow the liquid to drain from the funnel, and then replace the beaker containing the filtrate with the flask containing the deposited copper. Cover the aluminium foil, to which some copper usually adheres, with 10 ml. of 6 *N* nitric acid, heat nearly to boiling, and pour the hot acid through the filter. Replace the flask with the beaker containing the foil, and heat the contents of the flask until all the copper is dissolved and the greater part of the red fumes expelled. Again place the flask under the funnel, cover the aluminium

foil in the beaker with 5 ml. of strong bromine water, and pour this through the filter. Then wash the aluminium foil and the filter with hot water. Boil the solution to expel the excess of bromine, cool to room temperature, treat with 10 ml. of strong ammonia, and titrate with potassium cyanide exactly as in the standardization.

17. Determination of Lead by the Molybdate Method*

Principle. — The lead is precipitated as molybdate from an acid solution and the termination of the reaction is recognized by testing a drop of the solution with a drop of tannin solution, which gives a yellow coloration when an excess of ammonium molybdate is present.

Requirements. — 1. A solution of ammonium molybdate prepared by dissolving about 4.25 g. of ammonium molybdate in water, and diluting to one liter.

2. A freshly-prepared tannin solution containing 0.1 g. of tannin in 20 ml. of water.

Standardization of the Ammonium Molybdate Solution. — Weigh out 0.2 g. of pure lead foil into a 200-ml. Erlenmeyer flask, dissolve in a mixture of 2 ml. concentrated nitric acid and 4 ml. of water and evaporate the solution nearly, if not quite, to dryness. Take up the residue in 30 ml. of water, add 5 ml. of concentrated sulfuric acid, shake, and allow the lead sulfate to settle completely. Filter and wash the precipitate with 3.5 *N* sulfuric acid. Drop the filter, together with precipitate, into an Erlenmeyer flask, add 10 ml. of concentrated hydrochloric acid, and boil the liquid until the filter is completely disintegrated. Then, after adding 15 ml. more of concentrated hydrochloric acid, and 25 ml. of cold water, carefully add 25 ml. of concentrated ammonia, whereby the greater part of the acid is neutralized. Drop a piece of blue litmus paper into the solution, add ammonia to slightly alkaline reaction, and then glacial acetic acid until the litmus paper turns red. Dilute to about 200 ml. with hot water and transfer about two-thirds of the solution to a beaker. Add the ammonium molybdate solution to the latter from a buret until a drop of the solution, brought in contact with a drop of the tannin indicator upon a white porcelain tile, gives a brown or yellow color. Pour in some more of the lead solution to the beaker and repeat the operation until only a few milliliters of the lead solution remain in the flask. Finally add the rest of the solution, and finish the titration by adding the molybdate solution two drops at a time. If t ml. of molybdate are used in titrating a g. of lead the titer of the solution is

$$1 \text{ ml. ammonium molybdate} = \frac{a}{t} \text{ g. lead.}$$

* Alexander, *Chem. Ztg.*, **16**, 181 (1892); Low, *Technical Methods of Ore Analysis.*

Procedure. — Weigh out 0.5 g. of the ore into a 200-ml. Erlenmeyer flask, add 30 ml. of 4 *N* hydrochloric acid and boil until all the hydrogen sulfide is expelled. If the ore should not dissolve completely by this treatment, add a little concentrated nitric acid and continue heating until the ore is completely decomposed. As soon as this has taken place, add 14 ml. of 18 *N* sulfuric acid, and evaporate over a free flame until dense vapors of sulfuric acid are evolved. Allow to cool, add 20 ml. of water and boil the liquid 15 minutes to dissolve all the anhydrous ferric sulfate.

After cooling, filter off the precipitated lead sulfate and silicious residue and wash with cold 3.5 *N* sulfuric acid. The lead sulfate is often contaminated with calcium or barium sulfate, and before the titration it must be purified. To this end, rinse the precipitate by a stream of cold water into the original flask, add 5 g. of pure ammonium chloride, and about 1 ml. of concentrated hydrochloric acid. By boiling all of the lead and calcium sulfates are dissolved but the gangue, which is easily distinguished from either of the above salts, remains behind. Neutralize the solution with ammonia and treat with an excess of ammonium sulfide. Allow the precipitate to settle; filter and wash with hot water until the filtrate no longer gives a test for calcium when tested with ammonium oxalate. As the lead sulfide may be contaminated with some iron sulfide, rinse it again into the original flask, by means of as little hot water as possible, treat with 5 ml. of 2 *N* sulfuric acid, shake until the precipitate is well broken up, add 25 ml. of strong hydrogen sulfide water, filter through the same filter as was last used, and wash with cold water. By this time it is safe to assume that the lead sulfide is free from all calcium and iron. Once more return the filter and precipitate to the original flask, dissolve by boiling with 5 ml. of concentrated hydrochloric acid, boil, and then, when the hydrogen sulfide is practically all expelled, treat with 2–3 drops of concentrated nitric acid to remove the last traces of hydrogen sulfide. Now add 25 ml. of cold water, and treat the solution exactly as in the standardization of the ammonium molybdate.

Remark. — The smelter chemists in the western part of the United States use a much more rapid method, which gives good results in the hands of an experienced operator, provided the lead content of the ore is greater than 15 milligrams.

*Procedure.** — Dissolve the ore in hydrochloric acid or hydrochloric and nitric acids, and filter the solution while hot without diluting any more than to prevent the acid attacking the paper. Wash the residue

* This method was obtained through the courtesy of Mr. Franklin G. Hills of the American Smelting and Refining Co.

rapidly with a hot solution of ammonium chloride until the washings show no blackening when tested with ammonia and a drop of ammonium sulfide. Make the filtrate just alkaline with ammonia and add a slight excess of ammonium sulfide. Heat to boiling, filter off the precipitated sulfides, and wash with hot water. (The alkaline earths may be determined in the filtrate if desired.) Dissolve the sulfides in hot, dilute nitric acid and catch the resulting solution in the same beaker in which the sulfides were precipitated. Add 7 ml. of concentrated sulfuric acid, and evaporate the liquid until dense vapors of sulfuric acid are evolved. After allowing to cool, add 20 ml. of water and boil the liquid to dissolve the anhydrous ferric sulfate. Filter off the precipitated lead sulfate, wash free from acid, dissolve in a slight excess of ammonium acetate solution* and dilute with water. After heating to boiling, titrate the hot solution with ammonium molybdate.

The above procedure serves when alkaline earths are present; but when these are known to be absent, the original solution of the ore can be at once evaporated with sulfuric acid, the resulting lead sulfate dissolved in ammonium acetate solution and titrated without any purification.

18. Determination of Zinc by Potassium Ferrocyanide†

The potassium ferrocyanide method for titrating zinc is very accurate but it requires some experience before an operator becomes skilled in its use. The end-point of the reaction corresponds to the formation of $K_2Zn_3[Fe(CN)_6]_2$.

$$3\,ZnCl_2 + 2\,K_4Fe(CN)_6 = 6\,KCl + K_2Zn_3[Fe(CN)_6]_2.$$

After this point is reached, a slight excess of ferrocyanide will give a brown coloration when tested with uranyl solution (cf. p. 612) or ammonium molybdate on a spot plate. If the solution contains a very small quantity of iron, a little Prussian blue is formed and the color changes to a pea green at the end-point.

Potassium Ferrocyanide Solution. — Dissolve 32.31 g. of pure ferrocyanide in water and dilute to 1 liter. 1 ml. of this solution should react with 7.5 mg. of zinc.

Weigh out into 400-ml. beakers several 0.3 g. portions of pure zinc, weighing to 4 decimal places. Cover with water and dissolve in 20 ml.

* If too much ammonium acetate solution is used, a transitory end-point is obtained in the subsequent titration. It is necessary to use a hot solution, which does not contain too much of the salt. See p. 178.

† The directions here given are based upon the procedures used in the laboratories of the New Jersey Zinc Co. at Palmerton, Pa.

of 6 *N* hydrochloric acid. When the zinc has all dissolved, neutralize with strong ammonia, make slightly acid with hydrochloric acid and add 6 ml. of 6 *N* acid in excess. Add 2 drops of ferrous sulfate solution containing 2.5 g. $FeSO_4 . 7 H_2O$ per liter. This corresponds to about 0.03 mg. of iron. Dilute with water to 200 ml., heat to boiling and titrate as follows: Reserve one-quarter of the solution in a small beaker, to avoid the necessity of titrating to the right end-point at once. To the hot solution add the ferrocyanide with vigorous stirring. The solution assumes a blue color, which should be quite pale and is due to the reaction of ferrocyanide with a very small quantity of ferric iron formed from the ferrous solution added. When an excess of ferrocyanide is present, the blue color changes to a creamy white. Add a little more of the ferrocyanide and pour in all but about 5 ml. of the reserved zinc solution. Again add ferrocyanide till the end-point is reached and about 0.5 ml. more. Add the last of the reserved solution, wash out the beaker with hot water and titrate with ferrocyanide dropwise until the blue color fades sharply to a pea green. This is the end-point.

Repeat the standardization until an agreement within 2 parts in 1000 is obtained.

Analysis of the Ore. — Weigh out into a small beaker enough of the powdered ore to give approximately 0.6 g. of zinc. Moisten with water and add 10 ml. of concentrated hydrochloric acid. If sulfides are present it may be necessary to add 10 ml. of concentrated nitric acid at this point. Digest on the hot plate at a temperature below the boiling point for 1 hour. Remove from the plate and wash down the sides of the beaker and the cover glass. Add 10 ml. of 18 *N* sulfuric acid and evaporate to fumes. In the case of very silicious material it is well to break up the silica with a glass rod before adding the sulfuric acid. Cool and dilute to 50 ml. with water.

If there is any indication of undecomposed mineral in the residue filter it off, wash the residue with hot water. Digest the residue with ammonium acetate solution to remove lead sulfate and continue as directed on p. 416 until the SiO_2 is volatilized as SiF_4. Then after the removal of the excess acid, fuse with potassium pyrosulfate (cf. p. 110) dissolve the melt in dilute sulfuric acid and add the solution to that previously obtained.

The next step is to reduce the ferric salt and precipitate copper, bismuth, etc., by treatment with 1 g. of 20-mesh aluminium powder at a volume of about 50 ml. If it was not necessary to test the residue for zinc, the treatment should precede the filtering of the lead sulfate and silica precipitate. Add 10 drops of saturated sodium thiosulfate solu-

tion, cover the beaker with a watch-glass and heat 20 minutes. This serves to reduce the iron and precipitate all of the copper group metals except about 0.05 per cent of cadmium, which does no harm. Transfer the solution to a 200-ml. measuring-flask. Make up to the mark, mix and filter through a dry paper. Reject the first 10 ml. of runnings and take 100 ml. for the titration. Transfer the solution to a tall, 400 ml.-beaker and neutralize with sodium hydroxide solution till a jelly is formed and the acidity corresponds to about 2 drops of 20 per cent sulfuric acid. Use methyl orange as indicator. Add 3 ml. of 5 per cent sulfuric acid, dilute to 200 ml. and introduce a stream of hydrogen sulfide into the cold solution for 40 minutes, at the rate of at least 8 bubbles per second. Allow the precipitate to settle for 15 minutes, filter and wash with cold water.

Wash back the zinc sulfide precipitate into the beaker and rinse out the hydrogen sulfide tubing with 10 ml. of concentrated hydrochloride in hot water. Run the acid through the filter and wash with hot water. Heat the acid until all of the zinc sulfide has dissolved and the hydrogen sulfide all expelled. Dilute with cold water to 150 ml., add concentrated ammonia until slightly alkaline, neutralize with hydrochloric acid, and continue as in the standardization of the ferrocyanide solution.

19. Determination of Arsenic in Ores. Modified Method of Low-Pearce-Bennett

Of the finely powdered ore, take 0.5 g. if the arsenic content is not over 10 per cent. If the ore is richer, take only enough to furnish 0.05–0.10 g. of arsenic. Mix the ore with 2 g. of anhydrous sodium carbonate and 1.5 g. of potassium nitrate in a No. 8 porcelain crucible and sprinkle about 1 g. of the fusion mixture on top. Cover the crucible and heat very slowly over a small flame, gradually raising the temperature until finally the full heat of a good burner is used for 10 minutes. Cool and extract with 200 ml. of hot water. Filter and wash with hot water until all the soluble alkali salts are removed as shown by the litmus test for sodium carbonate. In this way all of the arsenic is obtained as alkali arsenate.

Make the solution distinctly acid with acetic acid and boil 10 minutes to remove carbonate and nitrite. Cool and add sodium hydroxide until the solution is basic to phenolphthalein. Discharge the color with a few drops of acetic acid and add 20 ml. of 0.1 *N* silver nitrate solution. After the reddish brown precipitate of silver arsenate has coagulated sufficiently, filter and wash with cold water till the washings are free from silver. Dissolve the silver arsenate by pouring small portions of

hot 3 *N* nitric acid through the filter, using about 10 ml. of acid in all. Dilute and titrate the silver by the Volhard method. One ml. of 0.1 *N* KCNS solution = 0.002499 g. of As.

Remark. — This method gives excellent results in the commercial analysis of arsenide ores but chromium and phosphorus interfere as silver chromate and phosphate, etc., behave like the arsenate.

20. Determination of Lead and Arsenic in Commercial Lead Arsenate

Two methods for determining lead and three methods for determining arsenic in this important insecticide will be described. The methods are taken from the Proceedings of the Official Agricultural Chemists of the United States.

If the sample is in the form of a paste dry the whole of it on the water-bath to get the water content. Grind the residue to a fine powder and dry at 110–120° to constant weight. Use this for the following analyses.

(*a*) *Determination of Lead as Sulfate.* Dissolve 2 g. of the dry powder in 80 ml. of 2.5 *N* nitric acid. Heat on the water-bath until all the lead arsenate is dissolved. Transfer to a 250-ml. measuring flask and dilute to the mark at 20°. To 50 ml. of the solution, add 3 ml. of concentrated sulfuric acid and evaporate till dense fumes of sulfuric acid are evolved. This is best accomplished by heating in a 250-ml. Erlenmeyer flask. Allow to cool, cautiously add 50 ml. of water and 100 ml. of 95 per cent alcohol. Allow to stand several hours, then filter and wash 10 times with a mixture of 3 parts concentrated sulfuric acid, 200 of alcohol and 100 of water by volume. Ignite and weigh as lead sulfate (p. 177).

Remark. — If the sample contains any alkaline earth, the lead sulfate will be very impure. It should be purified as directed on p. 178 although this is not specified in the " official " directions

(*b*) *Determination of Lead as Chromate.* Dissolve 0.6906 g. of dry powder in 25 ml. of 3 *N* nitric acid. Filter if necessary. Dilute to 400 ml., heat to boiling and add ammonia water until a slight permanent precipitate is formed. Dissolve this precipitate by a little 1.5 *N* nitric acid and add 2 ml. in excess. To the hot solution, add from a pipet 5 ml. of 10 per cent potassium chromate solution. Allow the precipitate of lead chromate to settle, filter into a Gooch crucible, wash with hot water till free from alkali chromate, dry at 140–150° and weigh as $PbCrO_4$. The weight of the precipitate in grams multiplied by 100 gives the percentage of PbO present.

(*c*) *Determination of Arsenic by Modified Gooch-Browning Method.* Take 100 ml. of the nitric acid solution prepared as described in (*a*), add 6 ml. of concentrated sulfuric acid and evaporate to fumes. Cool, transfer to a 100-ml. measuring flask with cold water and make up to the mark at 20°. Mix thoroughly by pouring back and forth into a dry beaker, allow the precipitate to settle in the stoppered flask and then decant the clear solution through a dry filter. After rejecting the first runnings, take 50 ml. of the filtrate, add 4 ml. of concentrated sulfuric acid and 1 g. of potassium iodide. Dilute to about 100 ml. and boil until the volume is reduced to about 40 ml. In this way the arsenic acid is reduced to the tervalent condition and iodine is liberated. Do not carry the evaporation too far, nor attempt to boil off the last traces of liberated iodine. Arsenic iodide is reddish and colors the concentrated solution very much the same as a little iodine does. It is volatilized if the solution is evaporated too far.

Cool the solution under running water, dilute to about 300 ml. and carefully add sodium thiosulfate solution until all the free iodine is reduced to colorless iodide. At this dilution, the color of arsenic iodide is not apparent. To the acid solution add 15 g. of anhydrous sodium carbonate in small portions and titrate with 0.1 N iodine solution. One ml. 0.1 N I_2 solution = 0.003749 g. of As.

Remark. — Inasmuch as iodine reacts with sodium hydroxide to form hypoiodite and iodide, it is generally recommended to finish the neutralization with sodium bicarbonate solution. This is unnecessary, however, because sodium bicarbonate is formed by the reaction between acid and the normal carbonate and as long as there is free carbon dioxide present in the solution, there is no danger. The quantity of sodium carbonate added should be greater than 1 and less than 2 moles for each mole of sulfuric acid present and 2–3 g. of bicarbonate, formed from the normal carbonate, should remain unneutralized.

(*d*) *Determination of Arsenic by the Distillation Method.* Provide a 250-ml. distilling flask with a long-stem, 50-ml. dropping funnel and connect it to a 60-cm. Liebig condenser. Connect the outlet of the condenser to a 500-ml. Erlenmeyer flask by a short bent tube extending about 10 cm. below the bottom of the 3-hole stopper which closes the flask. Through the middle hole in this stopper insert a 50 cm. piece of straight tubing so that it reaches to within about 1 cm. from the bottom of the flask and acts as a safety tube. Through the third hole introduce a twice-bent glass tube starting from just below the stopper and leading nearly to the bottom of a second 500-ml. Erlenmeyer flask with a 2-hole stopper. Through the second hole insert a twice bent tube leading to a 250-ml. Erlenmeyer flask. Place 50 ml. of water in the first flask, 100 ml. in the second and 50 ml. in the third, and sur-

round the first two flasks with cracked ice. The third flask acts merely as a trap and no arsenic chloride should reach it.

Weigh 0.4–0.6 g. of the dry powder and 5 g. of cuprous chloride directly into the distilling flask, taking care not to let any powder get into the distilling arm. Add 100 ml. of concentrated hydrochloric acid from the dropping funnel and start distilling. When the volume of liquid in the distilling flask has been reduced to 40 ml., add 50 ml. more of acid and again distil to 40 ml. Finally add 25 ml. more of concentrated hydrochloric acid and distil until only 20 ml. are left in the distilling flask. This procedure ensures the complete volatilization of all the arsenic as trichloride from 0.6 g. of such insecticides as Paris Green, London Purple, Lead Arsenate and Zinc Arsenate.

After the distillation is completed, rinse out the connecting tubes and transfer the contents of the first two absorption flasks to a 500 ml.-measuring flask and make up to the mark at 20°.

To 100 ml. of the mixed solution add 15 g. of sodium hydroxide dissolved in a little water and finish the neutralization by adding sodium carbonate until the solution is alkaline to methyl orange. Then add 2 g. of sodium bicarbonate and titrate with iodine in the usual way.

(*e*) Determination of Arsenic by the Potassium Iodate Method of G. S. Jamieson*

In a solution containing tervalent arsenic in the presence of 11–20 per cent of hydrogen chloride, arsenic can be accurately titrated by means of potassium iodate solution (cf. p. 570).

$$2\,AsCl_3 + KIO_3 + 5\,H_2O \rightarrow 2\,H_3AsO_4 + KCl + ICl + 4\,HCl.$$

Transfer 100 ml. of the 500 ml. of solution, obtained after distilling as in the previous method, to a 250-ml. glass-stoppered bottle, add 6 ml. of chloroform and titrate with standard KIO_3 solution containing 3.244 g. KIO_3 per liter. One ml. of this solution reacts with 3 mg. of As_2O_3. If more than 25 ml. of the iodate solution is needed, add 10–15 ml. more of concentrated hydrochloric acid before finishing the titration, in order to maintain the proper acidity. The end-point is explained on p. 571.

To determine arsenic present as *arsenite* in any insecticide, Jamieson recommends the following simple procedure:

Weigh out 0.14–0.4 g. of the powder, depending upon the arsenic content, into a 250-ml. glass stoppered bottle. Add 30 ml. of concentrated hydrochloric acid, 20 ml. of water and 6 ml. of chloroform. Titrate

* *J. Ind. Eng. Chem.*, **10**, 290 (1918).

at once with the iodate solution. Titrate rapidly at first, while shaking the bottle so as to give a gyratory motion to the contents. When the iodine liberated during the first part of the titration has largely disappeared from the solution, insert the stopper, shake well and from this point add the reagent slowly, shaking after each addition. Finally wait 5 minutes after the color is discharged from the chloroform to see if it returns.

PART III

GAS ANALYSIS

The chemical analysis of gas mixtures is accomplished usually by measuring and rarely by weighing the individual constituents, so that it is customary to express the results in per cent by volume. But inasmuch as the volume of a gas is influenced to a marked degree by the temperature and pressure, it is necessary to reduce each measurement to standard conditions of temperature and pressure, and further to take care that these remain constant during the whole of the analysis. A volume of gas V measured over water at $t°$ C. and B mm. barometric pressure,* is reduced to the volume which it would assume at 0° C. and 760 mm pressure in a dry condition by means of the formula

$$V_0 = \frac{V\,(B - w)}{760\,(1 + \alpha t)}.$$

In this formula, V_0 represents the reduced volume,† V the volume of the gas at $t°$ C. and B mm. pressure, w the tension of aqueous vapor, and α the expansion coefficient of the gas (= 0.003665).

As, however, $\alpha = \frac{1}{273}$, the above formula may be written as follows:

$$V_0 = \frac{V\,(B - w)\,273}{760\,(273 + t)}.$$

Instead of reducing the observed volume to the standard conditions by computation, it can be effected mechanically by compression (see p. 342).

* Here is understood the barometer reading reduced to 0° C. The reduction is accomplished by means of the formula: $B_0 = \frac{1 + \beta t}{1 + \alpha t} \cdot B$, in which B_0 represents the reduced reading, B the actual reading at $t°$, α the expansion coefficient of mercury (= 0.000181), β the linear coefficient of expansion of glass (= 0.0000085). For most purposes, however, the reduction to 0° C. can be made with sufficient accuracy by making the following deductions from the actual readings:

5°–12°	1 mm.	21°–28°	3 mm.
13°–20°	2 mm.	29°–35°	4 mm.

† Or volume under *standard conditions*.

The Collection and Confinement of Gas Samples

Since all gases diffuse rapidly into one another even when separated by porous solid bodies or liquids, it is evident that the collection of the sample and its preservation offers certain difficulties. If a gas is confined in a bell jar over water and thus kept out of contact with the air, it will be found that different results will be obtained in the analysis of the gas from day to day. The air gradually penetrates through the water into the bell jar and in the same way the gas within the jar gradually diffuses into the atmosphere. This process will continue until finally the composition of the gas both within and without the jar is the same. The rapidity of the diffusion depends upon the extent to which the gases are absorbed by the liquid which separates them. Those liquids which absorb the gases readily, allow them to pass through it rapidly, and consequently cannot be used for keeping the gases apart. Of all liquids, mercury is best suited for the purpose, because it absorbs only minimum amounts of the different gases.

Gases which combine chemically with mercury, such as chlorine, bromine vapors, hydrogen sulfide, etc., cannot, of course, be collected over mercury; it is best to collect them in dry glass tubes and to seal the latter by fusing together the open ends in case the gas cannot be analyzed immediately. Through glass there is no diffusion, so that gases may be kept unchanged in sealed tubes for years.

If the gas is to be analyzed within a few days after the time of collection, it can be kept in pipet-shaped tubes. The ends are closed by thick pieces of rubber tubing into each of which is inserted a piece of glass stirring-rod with rounded ends; where the rubber tubing comes in contact with the glass it should be fastened tightly with wires. It is not permissible to keep gases in such tubes for a considerable length of time, for rubber, particularly when it has become hard, permits the diffusion of gases to some extent.

For less accurate analyses, the gases can be collected over water which has been previously saturated with the gas to be analyzed, and the analysis must be made immediately afterwards.

From what has been said, it is evident that care must be taken in collecting and keeping the gas to be analyzed. We will now consider briefly a few practical examples.

(*a*) *Collection of Gases in Accessible Places*

1. Draw out the neck of a 200-ml. flask somewhat and insert a glass tube. (Fig. 123.) Draw about 800 ml. of the gas to be analyzed through the flask by means of suction. Then close the neck of the flask by means of a rubber cap and fuse the glass together.

(b) Collection of Gases from Inaccessible Places

Connect the rubber tubing *G*, Fig. 124, on one side with the aspirator *A* of about 30 liters capacity and on the other with the source of the gas, and allow water to flow quickly from the aspirator. After 5 or 6 liters have run out, the air is usually completely expelled from the rubber tubing and replaced by the gas to be analyzed, so that it is now ready for collecting the sample. For this purpose, turn the stop-cock *H* 90° to the right, so that the vessel *R*, which is to receive the gas, is in communication with the outer air, and expel the air from it by raising the mercury reservoir *N*. Then turn back the stop-cock to the position shown in the figure and fill *R* with the gas by lowering *N*. As the tubing between the *T* tube and the stop-cock contained impure

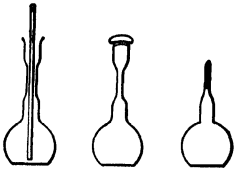


FIG. 123.

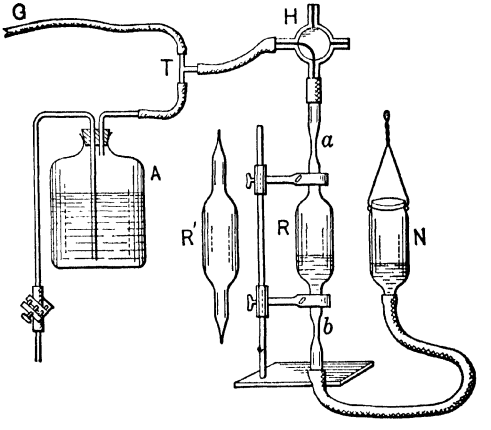


FIG. 124.

gas, again fill *R* with mercury and expel the gas into the air. After the process has been repeated 3 times, fill the receiver for the last time with the gas, close *H*, lower *N* so that the pressure in the tube is less than that of the atmosphere, and fuse together the ends of *R* first at *a* then at *b*. During this sealing of the tube, it should be removed from the ring-stand so that the tube can be revolved a little while being heated in the flame.

In sealing the tube, draw out the ends into a capillary as shown in *R'*, Fig. 124.

If it is necessary to obtain the gas from places at a very high temperature, *e.g.*, from blast-furnaces, producers, etc., glass tubes would melt, and if ordinary iron tubes were not melted they would decompose the gas. In this case it is best to use the water-jacketed iron tube devised by St. Claire Deville and shown in Fig. 125. Cause cold water to run

into the outer condenser at *a* and to run out at *b*, and collect the gas, as described above, through the tube *c*. It is important that the water should run through the tube fast enough to keep the inner tube cold, otherwise the gas will be decomposed. By this means there is no difficulty in collecting gas samples from different heights of the glowing layers of coal in blast-furnaces or producers, or from smoke stacks.

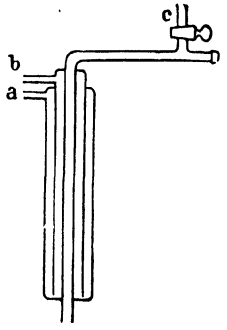


FIG. 125.

Collection of Gases Arising from Mineral Springs

Connect the receiver *R* with the funnel *T* by means of the rubber tubing *q* (Fig. 126). Fill all these parts of the apparatus with spring-water and allow the gas to ascend through the funnel as shown in the illustration. In order that the gas may pass from the funnel into the receiver, raise *R*, so that only the tubing *p* remains in the water, and lower the funnel as deep as possible, causing pressure enough to drive the gas over. Then close the tubing just above *a* by means of a screw-cock, place a beaker filled with spring-water under *p*, remove the apparatus from the spring, fuse together both ends of *R* with the blow-pipe. If the gas is to be analyzed within 2 or 3 days, the receiver may be closed by pieces of short rubber tubing each containing a short piece of glass rod with rounded ends. All of such connections must be fastened by means of wires where the glass comes in contact with the rubber.

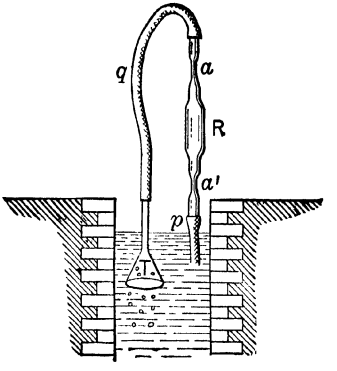


FIG. 126.

Collection of Gases Absorbed in Spring-water

Of the many different methods which have been proposed for the analysis of the absorbed gases in spring-water, the following is probably the most satisfactory.

Fill the flask *A*, Fig. 127, with spring-water up to its upper edge and immediately insert in the neck of the flask and press down the rubber stopper containing the tube *L*, which is fused together at the bottom but has an opening on the side at *l*. Raise the tube *L* so that the opening *l* is within the stopper, thus making an air-tight connection.

Now connect the bulb K with L, which is half full of distilled water and is connected with the capillary tubing C, although the latter is not yet connected with the measuring-tube B, as shown in the illustration. Raise the leveling-tube N until mercury begins to flow out of the right-angled capillary tube, then close the stop-cock H. After this boil the water in the bulb K (which is held in an inclined position) for 3 minutes, meanwhile warming the capillary tubing connected with the measuring-tube. Unless this last precaution is taken, the capillary tubing is likely to break, particularly in winter. After the water in K has boiled vigorously for 3 minutes, remove the flame, quickly connect C with the measuring-tube B and securely fasten the rubber connection with wire. By boiling the water in K, a complete vacuum is produced in the bulb, so that the gas can be at once collected from the spring-water. For this purpose press down the tube L through the rubber stopper until the opening l comes just below its lower edge, lower the leveling-tube N, and open the stop-cock H. At once there is a lively evolution of gas from the water in A and this is subsequently maintained by warming the water. As soon as the eudiometer is full close the stop-cock and read the volume of the gas after bringing the mercury to the same level in N that it is in B. At the same time note the temperature of the water in the condenser M and read the barometer. Drive over the gas into the Orsat tube, O, containing potassium hydroxide solution (1 : 2) and allow it to remain there for the time being. Meanwhile continue boiling the water in A, and measuring the gas in B, etc., until finally no more gas can evolve from the spring-water. Drive over all of the gas into the Orsat tube,

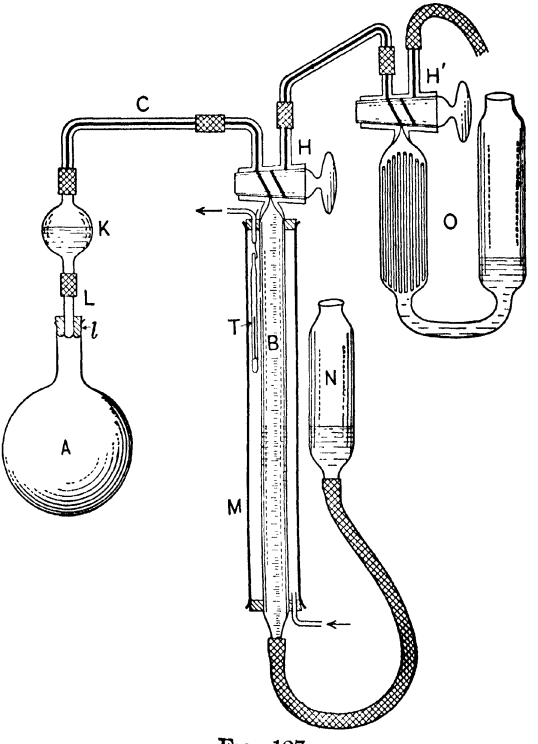


FIG. 127.

after its volume has been noted; by means of the caustic potash, the carbonic acid is quantitatively absorbed. Again drive the unabsorbed gas over into *B* and read its volume. By correctly regulating the velocity of the current of water flowing through the condenser, it is easily possible to maintain a constant temperature throughout the whole of the experiment. The residual gas remaining after the absorption of the carbon dioxide consists usually of nitrogen, oxygen, and in some cases methane. Transfer it to the apparatus of Hempel, and analyze according to methods which will be described further on.

According to this method, the determination of nitrogen, oxygen, and methane gives exact results, but the apparent amount of carbon dioxide is sometimes too much and sometimes too little. If the water contains large amounts of bicarbonate in solution, the carbonic acid found will represent more than was originally present in the free state, for such substances are partly decomposed by boiling their aqueous solution. On the other hand if only a little bicarbonate is present, the result will be too low, for it is not possible to remove all of the free carbonic acid from a solution by boiling it in a vacuum.

Consequently, in all cases the free carbonic acid must be determined by computation. For this purpose determine the total carbonic acid in a fresh sample of the water, according to p. 346, and then if the composition of the solid constituents present is known, the volume of the free carbonic acid can be calculated.

Example. — 1000 g. of Tarasper-Lucius water contain 7.877 g. of total carbonic acid. Of this amount, a part is present in the water as bicarbonate, and the remainder is *free* carbonic acid. If from the total amount of carbonic acid the *combined* acid is deducted, the difference represents the amount of free carbonic acid present.

Calculation of the Carbonic Acid Present as Bicarbonate

This is obtained by multiplying the difference between the cations and anions (expressed in gram equivalents) by the molecular weight of HCO_3, because the sum of the cations in every salt solution is equal to that of the anions present when both are expressed in gram equivalents.

The gram equivalents are obtained by dividing the weight in grams of each element (or radical) by the respective atomic (or molecular) weight and multiplying by the valence.

By boiling 828.3 g. of the water, 1868.9 ml. of CO_2 were obtained at 8.4° and 651 mm. pressure, containing only traces of nitrogen. This corresponds to 1851 ml. per liter, at 0° and 760 mm. pressure, which is more than the calculated amount, because by boiling some of the bicarbonate was decomposed.

CALCULATION OF THE GRAM EQUIVALENTS

1000 *g. of Lucius water contain:*	*Wt. in mg.*	*Milli-equivalents*
Cations		
Potassium (K^+)	166	4.24
Sodium (Na^+)	3906	169.4
Lithium (Li^+)	9	1.30
Ammonium (NH_4^+)	13	0.72
Calcium (Ca^{++})	627	31.34
Strontium (Sr^{++})	9	0.20
Magnesium (Mg^{++})	190	15.60
Iron (Fe^{++})	6	0.20
Manganese (Mn^{++})	0.2	0.008
Aluminium (Al^{+++})	0.6	0.072
	Sum of Cations	223.08 milli-equivalents

Anions	*Wt. in mg.*	*Milli-equivalents*
Chloride (Cl^-)	2400	67.7
Bromide (Br^-)	29	0.36
Iodide (I^-)	0.9	0.007
Sulfate (SO_4^{--})	1727	36.02
Hydrophosphate (HPO_4^{--})	0.08	0.018
Hydrocarbonate (HCO_3)	?	
		104.1 milli-equivalents

Sum of cations 223.1
Sum of anions 104.1
Bicarbonate ions 119.0 = 119 × 0.06101 = 7.262 g. HCO_3 = 5.240 g. CO_2.

CALCULATION OF FREE CARBONIC ACID

Total CO_2 = 7.877 g.; combined CO_2 = 5.240 g.; free CO_2 = 2.637 g. = 1334 ml. at 0° and 760 mm. pressure.

In cases where the amount of bicarbonate present is very small, the total amount of carbonic acid obtained by boiling the water is always too small. Thus in the case of the thermal water of Baden, by boiling there was obtained:

Nitrogen	14.43 ml. per liter
Carbon dioxide	112.12 ml. per liter
	126.55 ml. per liter

while from the analysis, the free carbonic acid was computed to be 180.52 ml. The absorbed gas in the thermal water of Baden is, therefore,

Nitrogen	14.43 ml. per liter
Carbon dioxide	180.52 ml. per liter
	194.95 ml. per liter

Remark. — With the above method of collecting the gas, it is difficult to prevent some water getting into the measuring-tube B, by means of which a small amount of the gas will be reabsorbed. This difficulty is avoided, however, if the flask shown in Fig. 128 is used to contain the water.

This flask is provided with a short tube blown into its neck near the top and connected by means of thick-walled rubber tubing with the mercury reservoir R. In order to determine the contents of the flask, make a scratch on the small tube about 4 cm. from the neck of the flask, drive over the mercury just to this mark, and tightly close the rubber tubing by means of a screw-cock. Then empty the reservoir of mercury, and weigh the flask together with the stopper, glass tube L, rubber tubing, and what mercury remains above Q. Next fill the flask with water, press down the stopper to the mark in the neck of the flask, and raise the tube L until the lower opening l comes within the stopper. After drying the tube L with blotting-paper, weigh the flask and its contents. Etch its capacity upon the bulb of the flask.

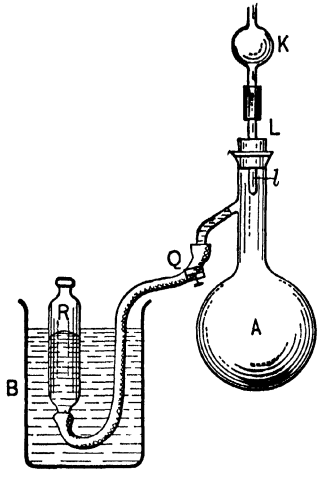


FIG. 128.

For the determination of the gases absorbed in a liquid, fill the flask A in the same way as in the determination of its capacity, connect the bulb-tube K, half filled with distilled water, with L, and connect the latter with a capillary tube as shown in Fig. 127. Remove the air from K and the capillary tubing by boiling the water in the former, as described on p. 631, and then connect the capillary with the measuring-tube B, Fig. 127. Next connect the heavy rubber tubing with the reservoir as shown in Fig. 128, and place the latter in a beaker of hot water. Introduce the tube L into the neck of the flask until the opening l can just be seen, and expel the gas in the same way as described on p. 631, except that in this case the liquid is not allowed to rise so high in K. After three-quarters of an hour the gas will be completely expelled from the liquid. Drive over the last portions of the gas into B by lowering the leveling tube N (Fig. 127), raising the mercury reservoir R (Fig. 106), and carefully opening the screw-cock Q. A warm stream of mercury will then flow into the flask, expelling the gas into the measuring-tube. As soon as the liquid in A has been driven over as far as the stop-cock H, imme-

diately close *H*. Otherwise the procedure is the same as was described on p. 631.

To test the accuracy of this method, the author made a few determinations of the oxygen absorbed in the lake-water at Zurich, and the results were compared with those obtained by E. Martz in this laboratory by means of the method of L. Winkler (see p. 654).

OXYGEN IN 1 LITER OF ZURICH LAKE-WATER

Modified Petersson Method		Method of L. Winkler	
I	II	I	II
7.66 ml.	7.74 ml.	7.67 ml.	7.75 ml.

Collection of Gases Absorbed by Defibrinated Blood

The author has used for this purpose the apparatus shown in Fig. 129. The analysis is carried out as follows:

First fill the rubber tubing, which connects *N'* and *A*, with mercury by raising the leveling tube *N'*, and close the pinch-cock *h''*. Then likewise fill the gas buret *C* with mercury by raising *D* and turning the stop-cock *h* to the position shown in the drawing. By raising the leveling tube *N*, fill the bulb *K* and the vessel *A* with mercury, and allow the mercury to flow into the funnel *M* up to the line *a* and then close the stop-cock *h*. Pour the blood to be examined into *M*, lower *N'*, and, by carefully opening *h*, allow the mercury to fall from *M* until it just reaches the stop-cock *h*, which is then closed. Now fill *M* with blood to the mark *b*, open *h*, and suck down the blood until its upper level is exactly at the line *a*; then close *h* once more. Lower the leveling tube *N* until a good vacuum is produced in *A* and the mercury level falls to near the bottom of *K*. When this is accomplished, the gas escapes from the blood so rapidly that all of *A* is filled with foam; after a few minutes, however, the effervescence subsides and all the blood collects in *K*. Then, raise the leveling tube *N* until the blood reaches the cock *h'* and then close the latter. In this way the greater part of the gas absorbed is separated from the blood. Raise the leveling tube *N'*, open *h''* so that the gas in *A* is under pressure, and by properly opening *h* and the buret stop-cock, drive over the gas into the measuring buret *C*; when this is accomplished, close *h*, lower *N'* until the mercury reaches the cock *h''*, which is then closed and *h'* opened. The blood again effervesces, but not so vigorously as before. Now surround the bulb *K* by water at 55°, which causes further effervescence

from the blood. As soon as the foam subsides, drive over again the gas into C and repeat the process of evacuating until the blood ceases to effervesce. Finally read the volume of the gas in C and note the temperature and pressure. Carry out the rest of the analysis as described on p. 667 or 674.

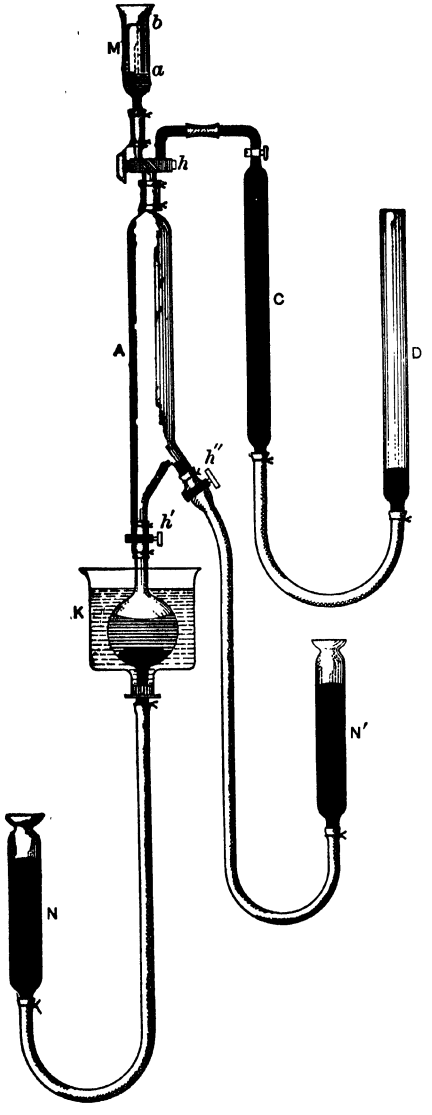


FIG. 129.

The Transference of Gases in Sealed Tubes to the Apparatus Used for the Analysis

Assume the gas to be contained in R, Fig. 130. Place a piece of thick-walled rubber tubing, containing a piece of heavy tubing r, over one of the short tubes connected with the three-way stop-cock H. Turn the stop-cock so that the rubber tubing is above it and fill the latter with mercury. Then turn H 180° toward the left so that the left and upper tubes communicate with one another. As soon as the mercury begins to run out, close the stop-cock. Then introduce one end of R into the rubber tubing containing the mercury so far that its drawn-out point reaches within r, and fasten the rubber tubing securely by wiring, using annealed iron wire because copper or brass wire would be likely to become amalgamated with mercury. In a similar way, connect the other end of R with the rubber tubing filled with mercury of the leveling-tube N, and after this connect the stop-cock H with the measuring apparatus W by means of the capillary tubing E. By raising the leveling bulb K, expel the air from W and the capillary

E, and allow mercury to rise in the funnel *T*. Turn the stop-cock *H* so that communication is established between *R* and *W*, and open the ends of *R* by pressing the capillaries against *r* and *r'*. Then, by raising *N* and lowering *K*, drive over the gas into *W*.

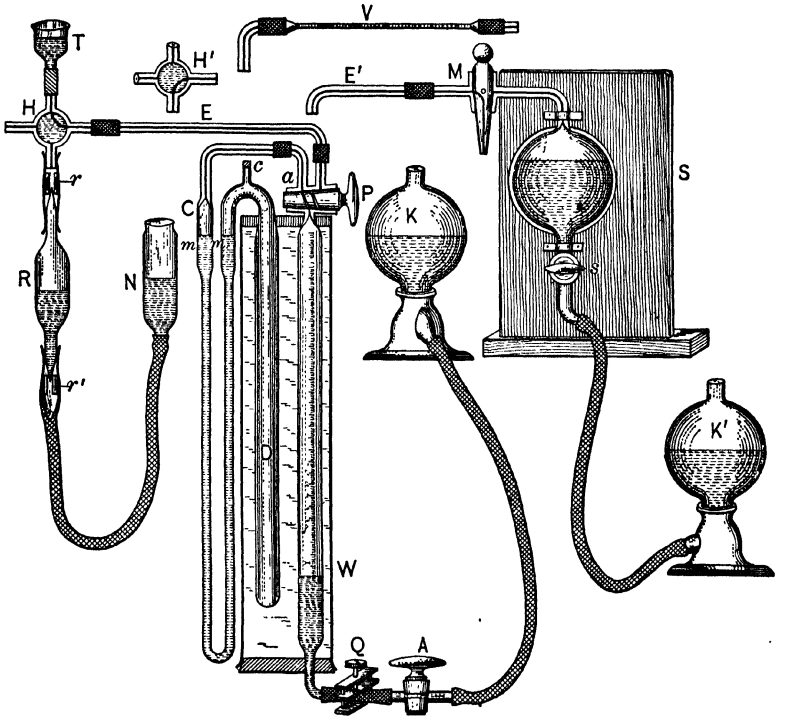


FIG. 130.

Calibrating Gas Measuring Vessels

When vessels are purchased to be used in measuring gases, the correctness of the calibrations should always be tested; the testing can be done with water or with mercury. The calibration with water is carried out in exactly the same way as was described for vessels to be used in measuring liquids (cf. pp. 448–456). The calibration by means of mercury will be illustrated by an example. Assume that it is desired to calibrate the apparatus shown in Fig. 131. The vessel must be thoroughly cleaned (cf. p. 450) and then placed in a vertical position as shown in Fig. 131 II. Connect the lower capillary *a* by means of thick-walled rubber tubing with a leveling vessel containing mercury, and cause the mercury to rise slowly in the vessel to a little above the

upper mark. Then close the stop-cock, remove the leveling tube together with the rubber tubing, and allow the mercury to flow out slowly until the highest point in the meniscus is exactly tangent to the horizontal plane through $\alpha'\alpha'$. To avoid a parallax error, take the reading with a telescope placed 2 or 3 mm. away from the glass. Next allow the entire contents of the vessel, including the space in the stop-cock, to run into a tared flask, and weigh to the nearest centigram. After determining the temperature of the mercury, its volume can be found by means of the table (top of p. 639) prepared by Schlösser.*

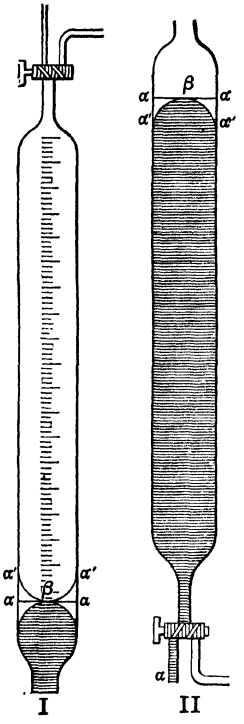


FIG. 131.

If the weight of the mercury at 20.3° amounted to 2025.26 g., then its volume corresponds to $\frac{2025.26}{13.5483} = 149.41$. Since, however, mercury forms a convex meniscus and the volume is desired up to the plane $\alpha\alpha'$, it is evident that the volume of mercury weighed did not include the space $\alpha'\alpha{-}\alpha\alpha'$ and, moreover, since the instrument is to be used in the reversed position, the error is really twice as much, as is evident from the inspection of Fig. 131 I. This is called the *double meniscus correction*. Its value is dependent upon the bore of the tube, as is shown by the table on p. 639.

If the diameter of the vessel in question is 20 mm., then the correction, according to the table, would be 4.016 g. and the true volume will be $\frac{2025.26 + 4.02}{13.5473} = \frac{2029.28}{13.5483} = 149.78$. The volume of this instrument, therefore, is 0.22 cm. less than the intended 150 ml. The volume of the narrower parts of the tube can be found in a similar manner.

The diameter of the tube is best determined by filling with mercury up to a mark, then allowing it to run out until a lower mark is reached, weighing the escaped mercury, and measuring the distance between the two marks with a millimeter rule. If the weight of the mercury is p, the distance between the marks h, the temperature of the mercury 20.3° then the

$$\text{diameter} = 2\sqrt{\frac{p}{h \times \pi \times 13.5483}}.$$

* Schlösser and Grimm, *Z. Chem. App.-Kunde*, **2**, 201 (1907).

WEIGHT OF 1 ML. OF MERCURY IN AIR AT TEMPERATURES BETWEEN 15° AND 30°

Normal temperature 15°

Temperature of Mercury	Weight	Temperature of Mercury	Weight	Temperature of Mercury	Weight
Deg. C.	G.	Deg. C.	G.	Deg. C.	G.
15	13.5593	20	13.5489	25	13.5385
15.5	13.5583	20.5	13.5479	25.5	13.5374
16	13.5573	21	13.5468	26	13.5364
16.5	13.5562	21.5	13.5458	26.5	13.5353
17	13.5552	22	13.5447	27	13.5343
17.5	13.5541	22.5	13.5437	27.5	13.5332
18	13.5531	23	13.5426	28	13.5322
18.5	13.5520	23.5	13.5416	28.5	13.5312
19	13.5510	24	13.5405	29	13.5301
19.5	13.5499	24.5	13.5395	29.5	13.5291
				30	13.5280

TABLE OF MENISCUS CORRECTIONS*

Diameter of Tube in mm.	Double Meniscus, Correction for Hg in mg.	Double Meniscus, Correction for H_2O in mg. = cubic millimeters	Simple Meniscus Correction (H_2O — Hg) in cubic millimeters
3	76	12	3
4	108	20	6
5	174	31	9
6	314	44	10
7	550	61	10
8	790	81	11
9	1038	106	15
10	1288	134	20
11	1540	167	27
12	1796	204	36
13	2058	245	46
14	2326	289	59
15	2596	336	72
16	2872	387	88
17	3152	441	104
18	3436	499	123
19	3726	560	143
20	4016	624	164
21	4314	691	187
22	4614	757	208
23	4920	821	229
24	5230	881	247
25	5544	938	264
26	5864	991	279
27	6185	1042	293
28	6515	1090	308
29	6845	1135	315
30	7182	1179	324

* W. Schlösser. Private Communication.

In many cases it is sufficiently accurate to compute the diameter from the circumference of the tube and then subtract twice the thickness of the glass.

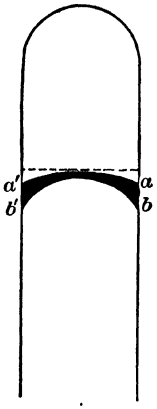


FIG. 132.

If it is desired to determine the total volume of a tube provided with stop-cocks at both ends, the apparatus is weighed empty and then filled with mercury. In this case, it is obvious that no meniscus correction is necessary.

For a measuring vessel calibrated with water, when in a reversed position, the meniscus correction is obtained from the table on p. 639. If an instrument calibrated with water is to be used subsequently with mercury, the water meniscus in calibrating the reversed tube occupies a similar position to that of the mercury meniscus when the instrument is in use (see Fig. 132) but the mercury meniscus is not so deep as that of the water. The volume of the gas is therefore found as much too large as there is difference between the simple meniscus corrections for water and mercury. Thus if the volume of a gas measuring instrument of 10 mm. diameter is found by weighing with water to be 10.167, according to the table on p. 639, then if the instrument is to be used with mercury, the gas volume will be 10.167 − 0.020 = 10.147 ml.

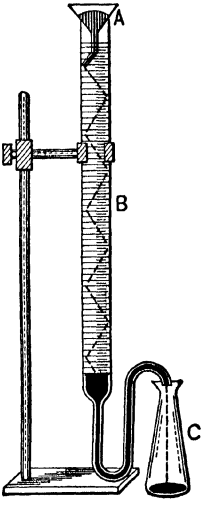


FIG. 133.

Purification of Mercury. Lothar Meyer's Method*

The mercury used for gas-analytical operations must be purified. The principal impurities are copper, cadmium, zinc and sometimes silver and gold. The base metals are removed most readily by allowing the mercury to run in a fine stream through about a meter of 8 per cent nitric acid. This is done in the apparatus shown in Fig. 133. First fill the bottom of the tube *B* with impure mercury and add the nitric acid. Then pour the mercury through the funnel *A*, the stem of which is drawn out to a capillary and bent to an angle of 60°. This causes the mercury to take a zig-zag course as it flows slowly

* *Z. anal. Chem.*, **2**, 241 (1863). C. J. Moore (*Chem. Ztg.*, **1910**, 735) has used a similar apparatus for purifying large quantities of mercury, but filters through buckskin before allowing it to fall through the acid.

through the nitric acid. The dry mercury that first passes over into the flask *C* is impure and must be poured into the funnel and allowed to flow through the acid. In this way a fairly pure mercury is obtained which can be used as it is for most purposes. If the mercury is to be used for calibrating apparatus, it must be distilled.

For this purpose, Hulett's apparatus, shown in Fig. 134, can be used. Place the mercury in the long-necked flask *k* and connect with the receiver *V*. Cover the flask with a hood of asbestos paper and heat on the sand bath. Through the arm *a*, connect the receiver with a suction pump and introduce into the flask, through *b* and the long glass tube that ends in a capillary, a slow current of nitrogen (or carbon dioxide) which has been dried by passing over calcium chloride. Regulate the distillation so that the mercury condenses in the glass arm *c*, where it leaves the hood of asbestos paper. About 150–200 ml. of mercury can be distilled in an hour with this apparatus. Frequently, especially when the nitrogen used contains a little oxygen, the distilled mercury is covered with a thin coating of oxide. This may be removed by filtration. To filter the mercury, perforate the point of a paper filter several times with a needle, place the filter in a funnel and pour the mercury upon the filter. The pure metal runs through the holes in the paper while the impurity remains behind.

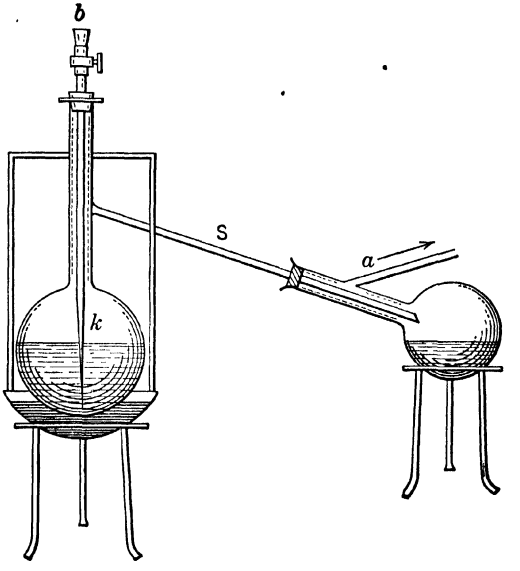


FIG. 134.

For the distillation of large quantities of mercury the apparatus* shown in Fig. 135 is suitable. Place the mercury in the container *R* (an inverted bottle with the bottom cut off). The tubing that rises above *R* is about 5 mm. in diameter and that below is only 2 mm. wide. The flask *K* has a capacity of about 300 ml. and is fastened by a clamp to an iron rod attached to the wall of the room. The lower end of the

* Apparatus of M. Gony.

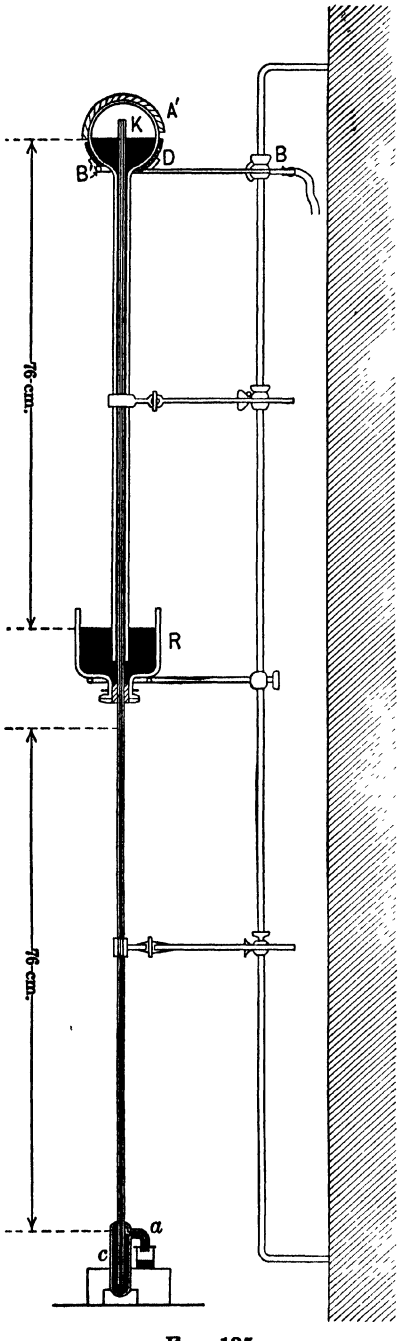


FIG. 135.

long neck of K reaches nearly to the bottom of R. By suction applied at a produce a partial vacuum in K. This causes mercury to rise in the tube from R into K. Light the ring burner at $B - B'$ upon which the flask K rests. Keep the suction working. The mercury soon boils and the vapor escapes into the tube but is condensed by the cooler liquid and falls in drops into the vessel c. As soon as all the air has been expelled from K, the lower half of the tube fills with mercury to a height corresponding to the atmospheric pressure. The vessel c also fills. At this point remove from a the rubber tubing that leads to the source of the suction and collect the dropping mercury in a flask.

To protect the flask K, wrap the lower half with wire gauze D and cover the upper half with a loose asbestos cap.

Subdivisions of Gas Analysis

According to the manner of determining the amount of gas, a distinction is made between:

1. *Absorption Methods.*
2. *Combustion Methods.*
3. *Volumetric Methods.*

In an *absorption method* the mixture of gases is treated with a series of absorbents. The difference in the volumes of the gas before and after it has been acted upon by each absorbent represents the amount of gas absorbed. The absorption of the gas may take place in the

measuring-tube itself, or, what is better, in separate absorption vessels.

In this way, the amount of carbon dioxide, heavy hydrocarbons (ethylene, benzene, acetylene, etc.), oxygen, and carbon monoxide may be determined in illuminating-gas, producer gas, water-gas, or Dowson gas.

After the constituents capable of absorption have been removed, a gas residue is left consisting of hydrogen, methane, and nitrogen; the two former constituents are determined by combustion, while the latter is always determined by subtracting the total amount of other gases found from 100 per cent.

For a *combustion analysis* the unabsorbed constituents of the gas mixture are mixed with air, or oxygen, in more than sufficient amount to ensure complete combustion, and burnt in a suitable apparatus; the amount of combustible gas is determined by measuring the contraction, the amount of carbon dioxide formed, and the excess of oxygen.

Finally, if the gas evolved by means of a chemical reaction is measured and from the volume of the latter the weight of the body producing it is calculated, we have made use of what is called a *gas-volumetric* method. (Cf. Determination of Carbonic and Nitric Acids, pp. 338 and 393.)

DETERMINATION OF GASES

1. Carbon Dioxide, CO_2. Mol. Wt. 44

Density = 1.5290* (Air = 1). Weight of 1 liter = 1.976 g.

Molar volume = 22.26 l. Critical temperature = +31.5° C.

Carbon dioxide is absorbed to a considerable extent by water; 1 vol. water absorbs: At 0°, 1.7967 ml. CO_2, At 15°, 1.0003 ml. CO_2. At 25°, 0.8843 ml. CO_2, or in general

$$\beta\dagger = 1.7967 - 0.07761 \times t + 0.0016424 \times t^2,$$

Absorbent. — *Potassium Hydroxide Solution* 1 : 2.

One ml. of caustic potash of the above strength will absorb at least 40 ml. of CO_2. Sodium hydroxide solution is not used on account of the difficult solubility of sodium bicarbonate.

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* This number is the mean from the observations of Lord Rayleigh (1897) = 1.52909, Leduc (1898) = 1.52874, and Christie (1905) = 1.52930.

† β is called the absorption coefficient of the gas. This signifies the volume of gas, measured at 0° and 760 mm. pressure, which 1 ml. of a liquid at $t°$ will absorb when the pressure upon the surface of the liquid is 760 mm. If h ml. of liquid, at $t°$ and B mm. pressure, absorb V_t ml. of the gas, then the absorption coefficient can be computed by the equation: $\beta = \frac{V_t}{h\,(1 + \alpha t)}$.

Small amounts of CO_2 may be absorbed by means of a definite volume of standard $Ba(OH)_2$ solution, and the excess of the latter titrated with 0.1 *N* HCl, using phenolphthalein as indicator. (See p. 508.)

2. Carbonyl Sulfide, COS

Density = 2.0999 (Air = 1). Weight of 1 liter = 2.7147 g. Molar volume = 22.13 l. Boiling Point, −47.5°. Density of Liquid COS, 1.0604. Critical temperature, between 94° and 102°.

Vapor pressure of liquid COS in atmospheres: 0° = 14.5, 5° = 17.4, 22.8° = 20.3, 41° = 28.1, 67° = 36.7, 74° = 48.4, 94° = 62.9, 102° = ∞.

Formation. —

1. Hydrolysis of thiocyanic acid: $HCNS + H_2O = NH_3 + COS$.
2. Passing CO and CO_2 over boiling S: $CO + S = COS$.

$$6\,CO_2 + 9\,S = 3\,SO_2 + 6\,COS.$$

3. Action of phosgene on metal sulfides: $CdS + COCl_2 = CdCl_2 + COS$.
4. Decomposition of thiocarbamate with 10 per cent hydrochloric acid: $C(=O)(S \cdot NH_4)(NH_2) + 2\,HCl = 2\,NH_4Cl + COS$.
5. Heating pyrite with potassium oxalate.

Carbonyl sulfide is colorless, odorless and tasteless. It shows the following behavior toward reagents:

1. *Water* absorbs an equal volume of gas at ordinary temperatures. The solution is odorless and tasteless at first but soon hydrolyses slightly: $COS + H_2O = CO_2 + H_2S$.

2. *Dilute caustic potash* solution does not absorb COS much better than water does. *Concentrated caustic potash* solution absorbs it forming potassium carbonate and sulfide: $COS + 4\,KOH = K_2CO_3 + K_2S + 2\,H_2O$. The absorption is so slow that COS can be freed from CO_2 and H_2S by washing with potassium hydroxide solution. Alcoholic caustic potash absorbs COS quickly and completely.

3. *Ammonia.* Concentrated ammonium hydroxide solution absorbs COS slowly but completely, forming ammonium thiocarbamate: $COS + 2\,NH_3 = NH_2COSNH_4$ and in the presence of hydrogen peroxide, sulfate and carbonate are formed:

$$COS + 4\,H_2O_2 + 4\,NH_3 = (NH_4)_2SO_4 + (NH_4)_2CO_3 + 2\,H_2O.$$

4. *Barium hydroxide* solution does not give a precipitate at once as with CO_2 but after about 1 minute a turbidity results.

5. Neutral or acid solutions of *silver nitrate* or *lead acetate* do not give precipitates of sulfide for about 8 minutes. In an ammoniacal solution of silver or zinc, or in a caustic alkali solution of lead salt, a precipitate of sulfide is formed immediately.

6. *Copper sulfate* in acid solution absorbs almost no COS.

7. *Iodine* in neutral or alkaline solution has very little oxidizing effect. Chlorine and bromine act only slightly at ordinary temperatures.

8. *Bromine* in alkaline solutions oxidizes COS readily: $COS + 4\,Br_2 + 12\,KOH = K_2CO_3 + K_2SO_4 + 8\,KBr + 6\,H_2O$.

9. *Fuming sulfuric acid* absorbs COS at room temperature without much oxidation; on being heated, sulfuric acid and CO_2 are formed.

10. *Triethyl phosphine* does not absorb COS (Difference from CS_2).

11. *Palladous chloride* absorbs COS quickly and quantitatively at 40–50°: $PdCl_2 + COS + H_2O = 2\,HCl + CO_2 + PdS$.

12. Mixed with 1.5 volumes of oxygen, COS burns with explosive violence and blinding light. In contact with glowing platinum COS decomposes smoothly into CO and S without change in volume.

Preparation of Pure Carbonyl Sulfide. Method of Klason*

The method is based upon the hydrolysis of potassium thiocyanate with dilute sulfuric acid:

$$KCNS + 2\,H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS.$$

The reaction is not quite so simple as the above equation would indicate for besides the products shown some CO_2, SO_2, CO, H_2S, HCN, CS_2, C_2H_5SH and HCO_2H are formed.

Dissolve 195 g. of potassium thiocyanate in 100 ml. of water and pour the solution in a cooled mixture of 2460 g. concentrated sulfuric acid and 1900 ml. of water in a 2.5 liter flask. The solution is pink at first, then violet and finally yellow. The evolution of gas starts at 18° but soon becomes so violent that it is necessary to cool with ice. After the evolution of gas slackens, warm gently on the water-bath but do not let the temperature rise above 30°. To purify the gas, pass it first through a saturated, aqueous solution of copper sulfate mixed with an equal volume of concentrated sulfuric acid, then through 33 per cent caustic potash solution; in this way H_2S, CO_2, HCN and HCO_2H are removed completely. To remove CS_2, which is always present, pass the gas through a mixture of 1 part triethyl phosphine, 9 parts pyridine and 10 parts nitrobenzene. Dry the COS by passing it through 2 worm tubes cooled with salt-ice mixture, then through a

* *J. pr. Chem.*, **1887**, 64.

calcium chloride tube and finally through 2 phosphorus pentoxide tubes. Liquefy the gas by cooling with ether and carbon dioxide snow and seal it into glass tubes.

To make use of the gas, transfer it to a small, perfectly dry gasometer and keep it over mercury. To fill the gasometer, first chill the contents of a sealed tube with ether and carbon dioxide snow, break off the point of the tube and connect with the gasometer using dry rubber tubing. Take the tube out of the freezing mixture and hold it loosely in cotton containing a little carbon dioxide snow. Reject the first quarter of the gas through the stop-cock of the gasometer, letting it escape under a good hood.

Quantitative Determination of Carbonyl Sulfide

(*A*) *Determination of* COS *and* CO_2 *in the Presence of Each Other*

Absorb the 2 gases in an ammoniacal solution of calcium chloride; calcium carbonate and ammonium thiocarbamate are formed. Add neutral hydrogen peroxide, boil, filter off the calcium carbonate, carefully avoiding contamination from the carbon dioxide in the air, wash with hot water, dissolve in T ml. of 0.1 N hydrochloric acid and titrate back with 0.1 N sodium hydroxide solution (p. 487). The difference $T - t$ multiplied by 1.113 gives the volume of the original CO_2 (at 0° and 760 mm.) together with that formed from the COS. Evaporate the filtrate to small volume, make acid with hydrochloric acid and determine the sulfuric acid as barium sulfate (p. 404). If the weight of $BaSO_4$ is p g. then 94.8 p ml. of COS were present, measured under standard conditions. It may be assumed, without serious error, that an equal volume of CO_2 was formed from it.

Remark. — This method of analysis is suitable for the determination of large quantities of COS and CO_2. If but little COS is present mixed with considerable CO_2, Dede* recommends passing 25 liters of the gas through palladous chloride solution heated to 50°. The COS is decomposed quantitatively into an equivalent quantity of PdS. Filter off the precipitate, dissolve it in hydrochloric acid and potassium chlorate and determine the sulfur as barium sulfate.

(*B*) *Determination of* COS, H_2S *and* CO_2 *in a Mixture*

First determine the hydrogen sulfide content by bubbling the gas through a measured volume of 0.1 N iodine solution until it is nearly decolorized. Determine the excess of iodine by titration with sodium

* *Chem. Ztg.*, **1914**, 1075.

thiosulfate solution. If t ml. of 0.1 N iodine were used in reaction with H_2S, then 1.108 t ml. of H_2S were present, measured under standard conditions.

In a second equally large volume of the gas absorb the 3 gases in an ammoniacal solution of calcium chloride. Afterwards boil with hydrogen peroxide and continue the analysis as in Method *A*. Assume that t_1 ml. of 0.1 N acid were neutralized by the calcium carbonate and that p g. of $BaSO_4$ was formed. Then

$$COS = (p - t \times 0.01167)\ 94.8 \text{ ml. at } 0° \text{ and } 760 \text{ mm.}$$
$$CO_2 = t_1 \times 1.113 - (p - t \times 0.01167)\ 94.8 \text{ ml. at } 0° \text{ and } 760 \text{ mm.}$$

The Heavy Hydrocarbons

Ethylene (Ethene), C_2H_4; Benzene, C_6H_6; Acetylene (Ethine), C_2H_2.

3. Ethylene, C_2H_4.* Mol. Wt. 28.03

Density = 0.97378 (Air = 1). Weight of 1 liter = 1.2561 g.†
Molar volume = 22.27. Critical temperature = +9° C.

Preparation of Ethylene. — One of the most satisfactory methods consists in treating an alcoholic solution of ethylene bromide with zinc dust:‡

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

In the neck of a round-bottomed, short-necked, 200-ml. flask insert a rubber stopper with 3 holes, carrying respectively a safety tube provided with mercury seal, a gas delivery tube, and a dropping funnel. In the flask place a sufficient amount of zinc dust, moistened with alcohol, and gently heat at the start by placing the flask in a bath of water at about 50°. From the dropping funnel slowly introduce a mixture of 1 part ethylene bromide and 20 parts absolute alcohol. Pass the escaping gas first through olive oil, to remove a little ethylene bromide which is carried over mechanically, then through caustic potash solution, and finally through water; collect over mercury, for example, in the Drehschmidt pipet (Fig. 130, p. 637). The gas thus obtained is nearly pure, particularly if the mixture of ethylene bromide and alcohol has stood for some time over anhydrous sodium carbonate to remove traces of hydrobromic acid.

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* And its homologues.

† T. Batuecas, *Helv. Chem. Acta*, **1**, 136 (1918).

‡ Gladstone and Tribe, *Ber.*, **7**, 364 (1874).

Absorption Coefficient for Water

1 volume of water absorbs at 0° 0.256 ml. C_2H_4; at 15° 0.161 ml. C_2H_4; at 20° 0.149 ml. C_2H_4, or in general, $\beta = 0.25629 - 0.00913631\,t + 0.000188108\,t^2$.

Alcohol absorbs more ethylene; the general formula is $\beta = 3.594984 - 0.077162 \cdot t + 0.0006812 \cdot t^2$.

Absorbents. — 1. Fuming sulfuric acid* (with 20–25 per cent free SO_3), 1 ml. absorbs 8 ml. of C_2H_4. According to Bone†, oxygen is also absorbed appreciably but hydrogen and nitrogen are not.

2. Bromine water.‡

Ammoniacal cuprous chloride solution will also absorb ethylene.

With bromine, ethylene bromide, $C_2H_4Br_2$ is formed. If a titrated bromine water is used for the absorption, the amount absorbed can be determined by titrating the excess of bromine. This excellent method, proposed by Haber,§ is at present the best known for the determination of ethylene in the presence of benzene. (See p. 651.)

4. Benzene, C_6H_6. Mol. Wt. 78.05

78.05 g. of benzene vapor occupy a volume of 22.391 liters under standard conditions.

Benzene is readily soluble in alcohol, ether, carbon bisulfide, caoutchouc, ethylene bromide, bromine, and fuming sulfuric acid.

Absorbents. — Fuming sulfuric acid|| and bromine water containing an excess of bromine. After the solution has been used once, the absorption is incomplete.

Inasmuch as benzene is neither brominated nor oxidized by bromine at ordinary temperatures, it was difficult to understand why bromine water should absorb it quantitatively. In fact, Berthelot¶ and Cl. Winkler** disputed it, but the results of Treadwell and Stokes†† have been confirmed by Haber. Haber suggested that the absorption of benzene by bromine was of a purely physical nature, and M. Korbuly‡‡ has shown that such is the case. Just as bromine can be removed from

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* Ethionic acid, $C_2H_6S_2O_7$, and carbyl sulfate, $C_2H_6S_2O_7$ are formed.

† *J. Chem. Soc.*, **61**, 879 (1892).

‡ Treadwell and Stokes, *Ber.*, **21**, 3131 (1888).

§ Haber and Oechelhäuser, *Ber.*, **29**, 2700 (1896).

|| Benzene sulfonic acid is formed, $C_6H_6SO_3$.

¶ *Compt. rend.*, **83**, 1255.

** *Zeitschr. f. anal. Chem.*, **1889**, p. 281.

†† Treadwell and Stokes, *loc. cit.*

‡‡ *Inaug. Dissertation*, Zurich, 1902.

aqueous solution by shaking with benzene, so benzene can be removed by shaking with bromine, or even ethylene bromide and other like solvents.

By means of highly concentrated nitric acid (*d* 1.52) benzene is also absorbed; this solvent cannot be used in the analysis of gases containing carbon monoxide, for the latter is quantitatively oxidized to carbon dioxide by nitric acid of this strength, and is therefore removed with the benzene * when the acid vapors are neutralized by caustic potash solution.

Behavior of Benzene to Water

Benzene vapors are absorbed to a considerable extent by water and all aqueous salt solutions, a circumstance which must be considered when an exact gas analysis is to be made. To determine how much benzene is absorbed by water, M. Korbuly performed the following experiments:

Different amounts of air containing 3.16 per cent of benzene vapor were shaken in a Drehschmidt's pipet with the same amount of water (5 ml.) until no more benzene was absorbed. He obtained the following results:

Experiment	Gas Taken in ml.	Per Cent Benzene Present by Volume	Amount of Benzene Absorbed at the End of Three Minutes
1	58.92	3.16	1.28 ml. = 2.17%
2	61.14	3.16	0.80 ml. = 1.31%
3	58.32	3.16	0.52 ml. = 0.89%
4	59.86	3.16	0.44 ml. = 0.73%
5	60.78	3.16	0.28 ml. = 0.46%
6	59.88	3.16	0.08 ml. = 0.01%
7	60.20	3.16	0.02 ml. = 0.00%

Potassium hydroxide behaves similarly.

In the analysis of a mixture of carbon dioxide and benzene, it is customary to first remove the carbon dioxide by means of potassium hydroxide solution and then the benzene with fuming sulfuric acid or bromine. It is evident, then, that both of the results obtained will be inaccurate if a fresh solution of potassium hydroxide is used for the absorption of the carbon dioxide, for this will absorb not only the whole of the carbon dioxide, but in many cases nearly all of the benzene. Accurate results may be obtained by using a solution of potassium hydroxide which has been saturated with benzene vapors.

* Treadwell and Stokes, *loc. cit.*

5. Acetylene, C_2H_2. Mol. Wt. 26.02

Density = 0.9087 (Air = 1).* Weight of 1 liter = 1.1750 g.
Molar volume = 22.03 l. Critical temperature = +37° C.
Boiling Point = −80.6° C.

Acetylene is quite soluble in water; 1 volume of water at the ordinary temperature absorbs an equal volume of this gas. In amyl alcohol, chloroform, benzene, glacial acetic acid, and acetone it is much more soluble; thus 1 volume of acetone absorbs 31 volumes of acetylene.†

Preparation of Pure Acetylene

(a) Method of M. Bretschger‡

Pass the crude acetylene, prepared from calcium carbide and water, through an acid solution of copper sulfate, then through aqueous chromic acid, caustic potash, and finally over slaked lime; then subject to a fractional distillation. Pass the gas through a small bulb cooled by liquid air which causes the acetylene to solidify. Afterwards, by gently heating, evaporate off the acetylene and dry the gas by passing it through calcium chloride tubes.

(b) Method of M. Stahrfoss and P. A. Guye§

Pass the impure acetylene, prepared from calcium carbide and water, through a solution of potassium permanganate, then through caustic potash solution and finally over phosphorus pentoxide. Freeze by means of liquid air and then fractionate.

The method of preparing acetylene by decomposing copper acetylide cannot be recommended, because the gas is then strongly contaminated with ethylene (C_2H_4) and vinyl chloride (C_2H_3Cl).

Absorbents: Fuming sulfuric acid.|| By saturated bromine water, acetylene is absorbed rapidly in the cold but 0.1 *N* bromine water containing hydrochloric acid absorbs acetylene so slowly that it permits the titration of ethylene in the presence of acetylene (see p. 698).

By means of ammoniacal cuprous chloride, acetylene is absorbed and forms red copper acetylide ($Cu_2C_2H_2)O$. This reaction is so characteristic that it is used for the

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* M. Bretschger (*Inaug. Dissert.*, Zurich, 1911), M. Stahrfoss and P. A. Guye (*Arch. sci. phys. et nat.*, **28**, 1909). The mean of their two values is used.

† Hempel, *Gasanalytische Methoden.*

‡ *Loc. cit.*

§ Private Communication from Professor Guye.

|| $C_2H_4SO_4$ is formed.

Qualitative Detection of Acetylene

in gas mixtures. This test is best performed by the method of L. Ilosvay von Nagy Ilosva.*

Preparation of the Reagent. — Place 1 g. of copper nitrate (chloride or sulfate) in a 50-ml. measuring-flask and dissolve in a little water. To the solution, add 4 ml. of concentrated ammonia (20–21 per cent NH_3) and 3 g. of hydroxylamine hydrochloride. Shake the liquid until it becomes colorless, and immediately dilute with water up to the mark.

The Qualitative Test. — Place a little of the reagent in a 500-ml. glass-stoppered cylinder and pass the gas to be tested for acetylene (illuminating-gas) over it until the color of the reagent becomes pink. Stopper the cylinder and shake. If acetylene is present, a beautiful red precipitate is immediately formed. Another method of making the test is to pass the gas through a small bulb-tube containing glass-wool moistened with the reagent.

Remark. — If the reagent is placed under kerosene it can be kept for about one week, but if copper wire is added to the solution, it can be kept much longer. The solution is much less permanent when it is prepared from the chloride or sulfate, even when copper is added to it.

Separation of the Heavy Hydrocarbons from One Another

It has been attempted repeatedly to separate ethylene from benzene, but usually in vain. The separation as proposed by Berthelot, of absorbing the ethylene with bromine water and afterwards removing the benzene by means of concentrated nitric acid, is erroneous in every respect.† The method of Harbeck and Lunge‡ is correct in principle but very tedious, and the original modification of Pfeiffer§ always gives too high results.

Recently Pfeiffer|| has improved his method so that it gives the same results as that of Harbeck and Lunge.

Haber and Oechelhäuser,¶ on the other hand, have devised a method which is accurate and to be recommended.

Principle. — In one portion of the gas, the sum of the ethylene and benzene is determined by absorption with bromine water or fuming sulfuric acid, while in a second portion the gases are absorbed in titrated bromine water, and the excess of

* *Berichte*, **32** (1899), p. 2698.

† Treadwell and Stokes, *loc. cit.*

‡ *Zeit. f. anal. Chem.*, **16**, 26 (1898).

§ *J. f. Gasbeleuchtung und Wasserversorgung*, **1899**, 697, and *Ber.*, **29**, 2700.

|| See *Chem. Ztg.*, 1904 (884).

¶ *J. Gasbeleuchtung und Wasserversorgung*, **1896**, 804, and *Ber.*, **29**, 2700.

the latter is determined iodimetrically. From the amount of bromine required the ethylene is calculated:

1 ml. 0.1 N I = 1.113 ml. C_2H_4 at 0° C. and 760 mm. pressure.

As this analysis is performed in the Bunte buret, it will not be described in detail until this has been described. (See p. 698.)

6. Oxygen, O = 16. Mol. Wt. 32

Density = 1.1053 (Air = 1). Weight of 1 liter = 1.4289 g.
Molar volume = 22.39 l. Critical temperature = −119° C.

Oxygen is only slightly soluble in water; according to the experiments of L. W. Winkler,* one liter of water will absorb the following quantities of oxygen, nitrogen and air at 760 mm. pressure:

ABSORPTION COEFFICIENTS OF ATMOSPHERIC AIR

Temperature	Oxygen	Nitrogen	Air
	ml.	ml.	ml.
0°	10.24	18.57	28.81
5°	8.98	16.45	25.43
10°	7.97	14.67	22.64
15°	7.16	13.29	20.45
20°	6.50	12.19	18.69
25°	5.93	11.31	17.24
30°	5.47	10.59	16.06
35°	5.11	9.92	15.03
40°	4.83	9.35	14.18
45°	4.58	8.93	13.51
50°	4.38	8.59	12.97
55°	4.22	8.31	12.53

From these data, the absorption coefficient of pure oxygen for water at 0–55° can be computed.

ABSORPTION COEFFICIENTS OF OXYGEN FOR WATER

Temperature	β	Temperature	β
0°	0.04890	30°	0.02608
5°	0.04286	35°	0.02440
10°	0.03802	40°	0.02306
15°	0.03415	45°	0.02187
20°	0.03102	50°	0.02090
25°	0.02831	55°	0.02012

Oxygen can be determined by combustion or by absorption.

* *Ber.*, **34**, 1410 (1901).

The Determination of Oxygen by Combustion

The determination of oxygen by combustion may be effected by exploding it with hydrogen (Bunsen) or by conducting a mixture of the two gases through a glowing platinum capillary (Drehschmidt), exactly as in the determination of carbon monoxide (cf. p. 658). In both cases the combustion takes place in accordance with the equation:

$$\underset{1\text{ vol.}}{O_2} + \underset{2\text{ vols.}}{2\,H_2} = \underset{0\text{ vol.}}{H_2O}$$

Three volumes of gas, therefore, disappear for each volume of oxygen present. If the contraction resulting from the combustion of a mixture of oxygen and an excess of hydrogen is designated by V_C, then the amount of oxygen present $= \frac{1}{3} V_C$.

The Determination of Oxygen by Absorption

The absorbents of oxygen are:

1. *Alkaline Pyrogallol Solution* (*Liebig*)

Mix 1 vol. of 22 per cent aqueous pyrogallol solution with 5–6 times as much 60 per cent potassium hydroxide solution. 1 ml. of this solution absorbs 12 ml. of oxygen.

At a temperature of 15°, or higher, the absorption takes place quickly; the oxygen in 100 ml. of air will be absorbed in 3 minutes or less. At lower temperatures the absorption takes place less readily and at 0° the above quantity of oxygen cannot be absorbed completely in half an hour.

A pyrogallol solution of the above concentration will not evolve carbon monoxide during the absorption.

2. *Phosphorus* (*Lindemann*)

The absorption of oxygen by means of phosphorus takes place by simply allowing the gas containing the oxygen to remain over moist phosphorus. The formation of white clouds indicates the presence of oxygen, and their disappearance shows that the absorption is complete. A temperature of 15–20° is best suited for the absorption.

The oxygen is completely absorbed at the end of three minutes from 100 ml. of air at this temperature. At lower temperatures the absorption requires more time and at 0° more than an hour is necessary.

If the gas contains more than 60 per cent of oxygen, moist phosphorus will absorb none of it at the ordinary atmospheric pressures. In this case the gas must be diluted with nitrogen or hydrogen until a mixture

is obtained containing less than 60 per cent oxygen, or the gas must be allowed to act upon the moist phosphorus under diminished pressure. In the latter case, however, the phosphorus easily becomes heated enough to melt it and the reaction becomes too violent.

Oxygen is not absorbed by moist phosphorus if the gas contains traces of heavy hydrocarbons, ethereal oils, alcohol, or ammonia. According to Hempel* 0.04 per cent of ethylene, and according to Haber† 0.17 per cent, suffices to prevent completely the absorption of oxygen.

3. *Chromous Chloride*

Consult the paper by Otto von der Pfordten, *Annal. Chem. Phys.* **228**, 112.

4. *Copper*

Conduct the gas over glowing copper, or introduce it into a Hempel pipet containing rolls of copper gauze and an ammoniacal solution of ammonium carbonate.

5. *Sodium Hyposulfite*,‡ $Na_2S_2O_4$ (Franzen§)

An alkaline solution of sodium hyposulfite is an excellent absorbent for oxygen. The reagent may be prepared for use in the Hempel pipet by dissolving 50 g. of the salt in 250 ml. water and 40 ml. of 60 per cent caustic potash solution. For absorption in the Bunte buret, the above solution is too concentrated; in this case 10 g. hyposulfite in 50 ml. water and 50 ml. of 10 per cent caustic soda, may be used.

The absorption takes place in accordance with the equation:

$$2\,Na_2S_2O_4 + 2\,H_2O + O_2 = 4\,NaHSO_3.$$

Sodium hyposulfite has the advantage over other absorbents that the absorption is always complete at the end of 5 minutes.

Determination of Absorbed Oxygen in Water. Method of L. W. Winkler||

1000 ml. 0.1 *N* $Na_2S_2O_3$ solution $= \frac{O}{20} = 0.8$ g. $= 559.8$ ml. oxygen at 0° and 760 mm. pressure.

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* *Gasanalytische Methoden.*

† *Experimental-Untersuchung über Zersetzungen und Verbrennungen von Kohlenwasserstoffen*, Habilitationschrift, Munich, 1896.

‡ Not to be confused with sodium thiosulfate which is often called "hyposulfite" especially in the trade.

§ *Berichte*, **39**, 2069 (1896).

|| *Ibid.*, **21**, 2843 (1888).

Principle. — If water containing dissolved oxygen is heated in a closed vessel with manganese hydroxide, the latter is oxidized to manganous acid according to the following equation:

$$Mn(OH)_2 + O = H_2MnO_3.$$

The amount of oxygen taken up is determined iodimetrically by adding hydrochloric acid and potassium iodide to the manganous acid and titrating the liberated iodine,

$$H_2MnO_3 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2 \quad \text{and} \quad 2\,KI + Cl_2 = 2\,KCl + I_2.$$

Reagents Required. — 1. *An approximately 4 N $MnCl_2$ solution* obtained by dissolving 400 g. of $MnCl_2 \cdot 4\,H_2O$ in water and diluting to 1000 ml. The manganese chloride must be free from iron.

2. *Sodium Hydroxide Solution Containing Potassium Iodide.* — On account of the nitrite usually present in commercial sodium hydroxide, prepare the solution from sodium carbonate and calcium hydroxide. Siphon off the clear liquid and concentrate in a silver dish until its density is 1.35. In 100 ml. of this solution, dissolve 10 g. of potassium iodide.

A portion of the alkaline potassium iodide solution on being acidified with hydrochloric acid should not immediately turn starch paste blue, and, furthermore, large amounts of carbonate must not be present.

3. 0.1 *N Sodium Thiosulfate Solution.*

Procedure. — Take a glass-stoppered flask of about 250-ml. capacity and determine its exact capacity by weighing it first empty and then filled with water at 20°. If the water to be analyzed is saturated with air, simply pour it into the flask; otherwise conduct the water through it for 10 minutes. By means of a pipet reaching to the bottom of the flask, introduce 1 ml. of the alkaline potassium iodide solution and immediately afterwards 1 ml. of the manganese chloride solution. Stopper the flask, shake, and allow to stand until the precipitate has settled. Then, by means of the long-stemmed pipet, add about 3 ml. of concentrated hydrochloric acid and once more shake the contents of the flask. The precipitate dissolves readily with liberation of iodide; titrate the latter with sodium thiosulfate in the usual way.

Remark. — The results obtained by this method agree closely with those obtained by boiling the water as described on p. 634.

7. Carbon Monoxide, CO. Mol. Wt. 28.00

Density = 0.96702 (Air = 1). Weight of 1 liter = 1.2502 g.
Molar volume = 22.397 l. Critical temperature = −136° C.

Preparation. — Heat concentrated sulfuric acid in a fractionating flask to a temperature of 140°–160° upon an oil bath, and allow formic acid (*d.* 1.2) to drop into it:

$$HCOOH = H_2O + CO.$$

To free the escaping gas from water and acid vapors, pass it first through a Liebig condenser, which leads to an empty flask to receive the condensed water, and from thence into a concentrated caustic potash solution.

This method* yields about 60 liters of carbon monoxide in half an hour, using about 500 ml. of concentrated sulfuric acid. The method of Wade and Panting,† according to which very pure carbon monoxide can be prepared by allowing concentrated sulfuric acid to drop upon potassium cyanide, is not, according to Allner, a suitable process for preparing large quantities of the gas; because considerable potassium cyanide becomes coated with pyrosulfuric acid during the reaction, so that there is considerable danger involved in working with the residues.

By the action of hot concentrated sulfuric acid upon oxalic acid, it is very easy to prepare a mixture of equal volumes carbon monoxide and carbon dioxide; on account of the large amount of the latter, however, this method is less satisfactory than that of Allner.

The gas is only very slightly soluble in water;

ABSORPTION COEFFICIENTS OF CARBON MONOXIDE FOR WATER‡

Temperature	β	Temperature	β
0°	0.03537	30°	0.01998
5°	0.03149	35°	0.01877
10°	0.02816	40°	0.01775
15°	0.02543	45°	0.01690
20°	0.02319	50°	0.01615
25°	0.02142	55°	0.01548

‡ L. W. Winkler, *Ber.*, **34**, 1414 (1901).

In alcohol the gas is about 10 times more soluble than it is in water.

Its determination is effected either by absorption or by combustion.

Absorbents. — Ammoniacal Cuprous Chloride. Shake 200 g. of commercial cuprous chloride in a closed flask with a 25 per cent solution of ammonium chloride, and to every 3 volumes of this mixture add 1 volume of ammonia, *d* 0.91. In order that the solution may remain active, place a spiral of copper wire into the flask, long enough to reach from the bottom up to the stopper.

1 ml. of this solution will absorb 16 ml. of carbon monoxide.

Formerly it was the almost universal custom to absorb carbon monoxide by means of a *hydrochloric acid* solution of cuprous chloride, but today this is not done on account of the following reasons. The ab-

* W. Allner, *Inorg. Dissert.*, Karlsruhe, 1905.

† *J. Chem. Soc.*, **73**, 255.

sorption of carbon monoxide by means of cuprous chloride takes place according to the equation:

$$Cu_2Cl_2 + 2\ CO \rightleftarrows Cu_2Cl_2 \cdot 2\ CO.*$$

The compound $Cu_2Cl_2 \cdot 2\ CO$ is extremely unstable and can only be formed when there is a certain pressure exerted by the carbon monoxide, so that when the acid solution is used the absorption will never be quantitative. Further, if a gas free from carbon monoxide (nitrogen or hydrogen) is shaken with such a solution after it has been used several times, a part of the $Cu_2Cl_2 \cdot 2\ CO$ in solution will be decomposed according to the above equation in the direction of right to left, until the partial pressure of the carbon monoxide set free is sufficient to restore equilibrium. Consequently the volume of the gas will appear greater after it has been treated with the cuprous chloride solution than it was originally.

When an *ammoniacal* cuprous chloride solution is employed, the absorption of the carbon monoxide is almost quantitative, but after such a solution has been used repeatedly it will readily give up some of the gas, although not so readily as is the case of the solution of cuprous chloride in hydrochloric acid or calcium chloride.† It is advisable, therefore, to adopt the suggestion of Drehschmidt, and first absorb the greater part of the gas by means of an old solution of cuprous chloride, afterwards removing the last traces by means of a freshly-prepared solution, or one which has been used but a few times.

Besides carbon monoxide, the ammoniacal cuprous chloride solution will absorb acetylene, ethylene, etc., so that these gases must be removed previously by means of fuming sulfuric acid or bromine water.

By long shaking with concentrated nitric acid (*d.* 1.5), carbon monoxide is completely oxidized to carbon dioxide, and the latter can be removed by treatment with potassium hydroxide solution.‡

Determination of Carbon Monoxide by Combustion with Air or Oxygen

The following reaction shows how carbon monoxide may be determined by combustion: $\underset{\text{2 vols.}}{2\ CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2\ CO_2}$.

From the reaction it follows:

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* The compound has been isolated in the solid state, according to W. A. Jones (*Am. Chem. J.*, 22, 287) its formula is $CuCl_2 \cdot 2\ CO \cdot 4\ H_2O$, but according to the experiments of C. v. Girsewald in the author's laboratory, the formula is $Cu_2Cl_2 \cdot 2\ CO \cdot 2\ H_2O$.

† Cuprous chloride is soluble in a concentrated solution of calcium chloride. 1 ml. of this solution absorbs 12–15 ml. of CO.

‡ Treadwell and Stokes, *Ber.*, **21**, 3131 (1888).

1. The difference in the volume of the gas mixture before and after the combustion is for 2 vols. CO; 3 − 2 = 1 and for 1 vol. CO = ½. This difference is designated as the contraction, V_C. *The contraction caused by the combustion of carbon monoxide is, therefore, equal to half the original volume of* CO.

2. *The volume of the carbon dioxide formed is equal to the volume of the carbon monoxide originally present.* If, then, the carbon dioxide is determined by absorption with caustic potash, the volume of the carbon monoxide is at once obtained, provided no other combustible gas containing carbon is present at the same time.

3. For the combustion of 2 vols. of CO, 1 vol. of oxygen is necessary, and consequently *the amount of oxygen consumed is equal to half the volume of the carbon monoxide.*

Methods of Effecting the Combustion

The combustion of the carbon monoxide can be carried out in several different ways: (1) By explosion. (2) By conducting the gas over glowing palladium or platinum. (3) By conducting the gas over copper oxide.

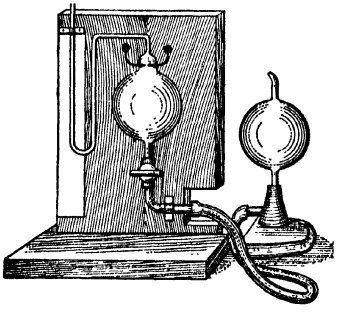


FIG 136.

1. *Combustion by Explosion.* — Mix the gas with a sufficient amount of air in a measuring buret, such as is shown in Fig. 130, and connect the latter by means of the capillary *E* with the Hempel's explosion pipet shown in Fig. 136. Drive over the gas into the latter so that the capillary is entirely filled with mercury, close the stop-cocks of the capillary and of the explosion pipet, and cause an electric spark to pass between the two platinum points which are fused into the glass walls of the pipet; this immediately causes an explosion to take place. Afterwards once more drive the gas back into the measuring buret, and again determine its volume. The difference in volume before and after the explosion represents the contraction.

This most excellent method can in some cases lead to erroneous results. In practice, it is usually desired to determine the amount of combustible gas in a mixture containing nitrogen obtained after treatment with the different absorbents. If the amount of combustible gas present is too small in proportion to the amount of non-combustible gas, there will be no combustion whatsoever; while on the other hand, if this relation is too large, a part of the nitrogen will be burnt to nitric acid (hydrogen is usually present). According to Bunsen, the com-

bustion is complete when 30 parts of combustible gas are present for each 100 parts of non-combustible gas. Consequently, if the explosion method is to be used for the analysis, the approximate composition of the gas must be known.

2. *Combustion by Conducting the Gas over Glowing Palladium or Platinum.* — This is the most certain of all methods for effecting the combustion, because it is entirely independent of the proportion of combustible gas present,* and there is no danger of any of the nitrogen being oxidized. The combustion is best effected, as proposed by Drehschmidt, by passing the gas through a thick-walled platinum capillary tube containing 3 palladium wires. Place the platinum capillary (Fig. 130, *V*) between the gas buret and the Drehschmidt pipet *S* (Fig. 130), and heat it by means of the non-luminous flame of a Teclu burner. Repeatedly pass the gas through the glowing capillary until there is no further diminution in volume, showing the combustion to be complete. There is no danger to be feared from explosions even when pure detonating gas is passed through the platinum tube, and by this method CO, H, and CH_4 are completely oxidized. In the analysis of gases containing only small amounts of the above gases (*e.g.*, exhaust gases from gas-motors) the so-called fractional combustion is employed. By this means either hydrogen and carbon monoxide are oxidized while methane is not, or carbon monoxide is alone burned.

Fractional Combustion. — If, according to Haber, an absolutely dry gas mixture, consisting of considerable nitrogen and oxygen with little carbon monoxide, hydrogen, and methane, is slowly conducted (at the rate of about 700–800 ml. per hour) through a glass U-tube 3 mm. in diameter which contains a palladium wire 55 cm. long, folded into 3 lengths of about 18 cm., then if the temperature of boiling sulfur is maintained, the hydrogen and carbon monoxide will be completely burned, while methane will escape from the tube in an unchanged condition. By connecting the U-tube with a weighed calcium chloride tube and then with 2 weighed soda-lime tubes (see p. 357) the increase in the weight of the former will show the amount of water formed from the hydrogen, and the gain in weight shown by the soda-lime tubes corresponds to the amount of carbon dioxide formed from the carbon monoxide. If, after passing through the soda-lime tubes, the gas is passed through a combustion-tube filled with platinized asbestos, or copper oxide, which is heated to a dark-red heat, the methane is quantitatively burned to water and carbon dioxide; the former can be

* It is only necessary to make sure that a large excess of oxygen is present. Cf. Hempel, *Z. anorg. Chem.*, **31**, 447 (1902).

absorbed in a calcium chloride tube and the latter in 2 soda-lime tubes, all three tubes being weighed before the gas is passed through them. In this way a check is obtained upon the accuracy of the determination, for the proportion of carbon to hydrogen found should be 1 : 4.

The combustion of carbon monoxide alone from a mixture of this gas with hydrogen, methane, and air can be effected satisfactorily as follows:

After the gas has been freed from CO_2, unsaturated hydrocarbons, and aqueous vapor, conduct it through a U-tube* containing 60–70 g. of pure iodine pentoxide† heated to 160°; by this means the carbon monoxide is alone oxidized with liberation of iodine according to the equation $I_2O_5 + 5\ CO = 5\ CO_2 + I_2$.‡ If the gas is now conducted through 2 Péligot tubes containing potassium iodide solution, the iodine will be absorbed and can be titrated at the end of the experiment with 0.1 *N* sodium thiosulfate solution.

1 ml. 0.5 *N* $Na_2S_2O_3$ solution corresponds to 5.6 ml. CO, measured under standard conditions.

If, after the carbon dioxide and water have once more been removed from the gas, it is passed through a combustion-tube half filled with copper oxide and half with platinized asbestos, both heated to dark redness, the hydrogen and methane will be completely burned to water and carbon dioxide, which can be absorbed and weighed as before. From the amounts of each, the hydrogen and methane present in the gas can be calculated.

Qualitative Detection of Traces of Carbon Monoxide in the Air

If blood is diluted with water until the solution shows only a slight red color, it will give a characteristic absorption spectrum; 2 dark absorption bands appear between the *D* and *E* lines. If to this dilute blood solution a few drops of a concentrated, freshly-prepared ammonium sulfide are added, the dark bands disappear, and instead a single broad band will appear at a place between the positions of the previous bands. Blood containing carbon monoxide behaves quite differently. When the latter gas is present, the blood takes on a rose color and the solution gives almost the same absorption spectrum as pure blood (the bands

* The U-tube is heated in a small paraffin bath.

† Iodine pentoxide is prepared by heating iodic acid in a current of dry air at 180° until the water is completely removed.

‡ Nicloux, *Compt. rend.*, **126**, 746; Kinnicutt, *J. Am. Chem. Soc.*, **23**, 14; Marcelet, *Z. anal. Chem.*, **50**, 315 (1911); Morgan, *J. Am. Chem. Soc.*, **29**, 1589; V. Froeboese, *Z. anal. Chem.*, **54** (1915); Sinatt and Cramer, *Z. angew. Chem.*, **1915**, Ref. 9; A. Seidell and P. W. Meserve, *Hyg. Lab. Bull.* **92**, Washington, 1914; Moser and Schmidt, *Z. anal. Chem.*, **1914**, 217.

shift slightly toward the violet) but in this case *the two bands do not disappear on the addition of ammonium sulfide.*

To detect traces of carbon monoxide in the air, Vogel directs that a 100-ml. bottle, filled with water, be emptied in the room containing the gas, and that 2–3 ml. of blood, highly diluted with water, and showing only a very faint red color (although still giving the blood spectrum in a column as thick as a test-tube) be poured into the bottle and shaken for some minutes. To the solution a few drops of ammonium sulfide solution are added and the liquid is examined by means of the spectroscope. If the two bands are now visible, carbon monoxide is present. According to Vogel as little as 0.25 per cent of CO can be detected in this way.

Hempel has improved this method to a marked degree. He found that it was not possible to completely remove small amounts of carbon monoxide by shaking with the dilute solution of blood, and furthermore concentrated blood solutions could not be used because they foam so much. By using a living animal, its lungs furnish a better means of absorption, for the gas then comes in contact with undiluted blood. A mouse is placed between two funnels which are joined together by means of a broad band of thin rubber and the gas to be tested is passed through the funnels at a speed of 10 liters per hour. At the end of 2 or 3 hours the mouse is killed by immersing the funnels in water and a few drops of its blood are taken from the region near the heart. In this way Hempel was able to detect with certainty as little as 0.032 per cent CO. With such small amounts of CO the live mouse showed no symptoms of poisoning; this was first apparent when 0.06 per cent of the gas was present. In the latter case after half an hour the mouse breathed with difficulty and lay exhausted on its side.

Potain and Drouin detect small amounts of carbon monoxide by passing the gas through a dilute solution of palladous chloride, whereby metallic palladium is precipitated:

$$PdCl_2 + CO + H_2O = 2\,HCl + CO_2 + Pd.$$

The solution is decolorized, or turns a pale gray, when large amounts of CO are present, but appears a light yellow in color when only traces are present.

In order to estimate better the decrease in color, Potain and Drouin filter off the deposited palladium and compare the color of the filtrate.

For the detection of small amounts of carbon monoxide, C. Winkler recommends a method which, as the author has found, will often lead to error. According to Winkler, the gas to be tested is conducted through a solution of cuprous chloride in a saturated solution of sodium chloride, afterwards diluting with 4–5 times as much water, causing

the precipitation of snow-white cuprous chloride. If this turbid solution is treated with a drop of sodium palladous chloride, a black precipitate of metallic palladium is obtained. Unfortunately, however, the palladium is often precipitated even in the absence of a trace of carbon monoxide; for cuprous chloride itself will readily reduce salts of palladium.

It is true, on the other hand, that at a definite concentration the reduction of the palladous chloride is only effected by means of carbon monoxide, but it is difficult to always obtain the right conditions, and herein lies the inaccuracy of the method. If the solution be too concentrated with respect to sodium chloride, even large amounts of carbon monoxide will fail to precipitate a trace of palladium, because in that case the solution contains not only copper but also palladium in the form of complex sodium salts: $Na_2[Cu_2Cl_4]$ and $Na_2[PdCl_4]$.

The sodium palladous chloride is not reduced by carbon monoxide and there is even less likelihood of the two sodium salts acting upon one another. If the solution be diluted with water, both salts break down according to the equations

$$Na_2[Cu_2Cl_4] \rightleftarrows 2\,NaCl + Cu_2Cl_2, \qquad Na_2[PdCl_4] \rightleftarrows 2\,NaCl + PdCl_2,$$

and only when the palladium is in the ionic condition is it capable of entering into the reaction. The fact that the reduction of the palladous chloride is effected by means of CO at a concentration at which Cu_2Cl_2 is incapable of causing any reduction is easy to understand, for the gas, CO, comes in contact more readily with a sufficient number of palladium ions than does the difficultly soluble cuprous chloride.

8. Hydrogen, H. Mol. Wt. 2.016

Density = 0.06960* (Air = 1). Weight of 1 liter = 0.089979 g.

Molar volume = 22.405 l. Critical temperature = −238°.

Hydrogen is practically insoluble in water.

ABSORPTION COEFFICIENTS OF HYDROGEN FOR WATER†

Temperature	β	Temperature	β
0°	0.02148	30°	0.01699
5°	0.02044	35°	0.01666
10°	0.01955	40°	0.01644
15°	0.01883	45°	0.01624
20°	0.01819	50°	0.01608
25°	0.01754	55°	0.01604

* Lord Rayleigh, *Proc. Roy. Soc.*, **53**, 1134 (1893).

† L. W. Winkler, *Ber.*, **24**, 99 (1891).

A. Determination by Absorption. Method of Paal and Hartmann*

Colloidal palladium, in the presence of a protective colloid, sodium protalbinate, is capable of absorbing an enormous quantity of hydrogen. The absorption takes place slowly but quantitatively. The absorbent can be regenerated, after each experiment, by treatment with oxygen or by adding an easily-reducible organic substance. Paal and Hartmann made use of sodium picrate for this purpose· the picric acid is oxidized to triaminophenol:

$$C_6H_2(OH)\,(NO_2)_3 + 9\,H_2 = C_6H_2(OH)\,(NH_2)_3 + 6\,H_2O.$$

According to the experiments of Brunck† a solution of 2 g. colloidal palladium and 5 g. of picric acid dissolved in 22 ml. of *N* sodium hydroxide diluted to 100–110 ml. with water is a suitable absorbent. Such a solution can be purchased. The above quantity of reagent should absorb about 4 liters of hydrogen; about 20–30 minutes, with repeated shaking, is required for the absorption. The reagent is useful for determining hydrogen in the presence of saturated hydrocarbons.

As soon as the efficiency of the absorbent is lost, rinse out the contents of the absorption pipet with water and add dilute sulfuric acid as long as any precipitate forms but avoid too much excess which tends to cause the palladium *sol* to go into solution as palladous sulfate, as a result of atmospheric oxidation. The precipitate of solid palladium and protalbinic acid also contains picric acid. Wash with water, which removes some of the acids but no palladium. Then suspend the mass in water and add sodium hydroxide solution, dropwise, until a colloidal solution is obtained. Then add the proper quantity of sodium picrate and the absorbent is ready for use again.

B. Determination by Combustion

Mix a measured volume of the gas with more than half as much oxygen and burn the hydrogen by one of the following methods. The hydrogen can be determined by measuring the contraction in total volume.

$$\underset{2\text{ vols.}}{2\,H_2} + \underset{1\text{ vol.}}{O_2} = \underset{0\text{ vol.}}{2\,H_2O}.$$

It is evident that by the combustion of two volumes of hydrogen, three volumes of gas will disappear (the water formed occupies a negligible volume). The contraction, therefore, is equal to $\frac{3}{2}$ the volume

* *Ber.*, **43**, 243 (1910).

† *Chem. Ztg.*, **1910**, 1313 and 1331.

of the hydrogen consumed. If the contraction is denoted by V_C and the volume of the hydrogen by V_H, then $V_C = \frac{2}{3} V_H$, and consequently $V_H = \frac{2}{3} V_C$.

In many cases the weight of the water formed is determined by absorption in weighed calcium chloride tubes; from the gain in weight, p, the volume of hydrogen is computed as follows: $\frac{22{,}405}{18.016} \times p = 1243.6 \times p$ ml. hydrogen under standard conditions.

Combustion of Hydrogen, according to Cl. Winkler

The following method is employed frequently in *technical* analyses for the separation of hydrogen from methane.

Conduct a mixture of hydrogen and air over gently-ignited palladium asbestos, by which means the hydrogen is quantitatively burned to water and the methane is not affected. Fig. 137 represents the apparatus required. *A* is the eudiometer and is connected by means of the capillary *E*, in which is found a short fiber of palladium-asbestos, with a Hempel pipet filled with water.

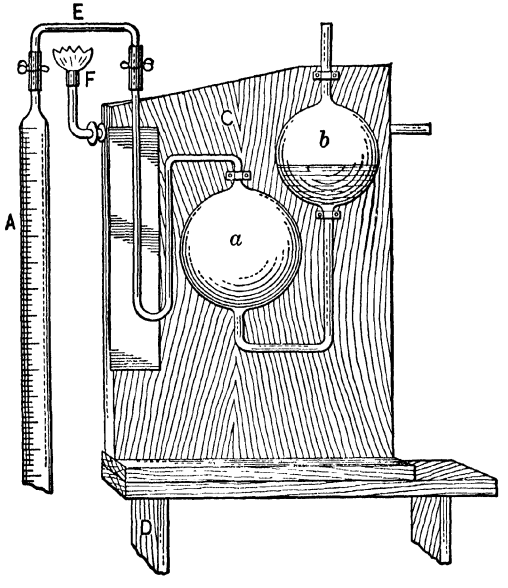


Fig. 137.

Heat the capillary, *E*, by a small flame *F*, at the place where the palladium-asbestos rests, to a temperature of about 300–400°, but not hot enough to soften the glass. After the gas, which is mixed with air,* has been passed back and forth through the capillary 3 times,† the combustion is complete. If the above-specified temperature is not exceeded, no trace of methane will be burned and the hydrogen determination will be accurate. It is, however, difficult to regulate this temperature

* If oxygen is used instead of air, some of the methane is sure to be oxidized. Cf. O. Brunck, *Zeit. f. angew. Chem.*, 1903, p. 195.

† Pass the gas over the catalyzer so slowly that the palladium at the end toward the gas stream does not glow at all or only very slightly.

closely enough to prevent the combustion of some methane unless, as recommended by Haber, the tube is heated by means of sulfur vapor; the results are usually from 0.5–1 per cent too high.

Preparation of Palladium-asbestos. — Dissolve 3 g. of sodium palladous chloride in as little water as possible, add 3 ml. of a cold, saturated solution of sodium formate and enough sodium carbonate solution to make the solution alkaline. Then add about 1 g. of soft, long-fibered asbestos which sucks up the whole of the liquid. Dry the mixture on the water bath; by this means finely-divided palladium is deposited uniformly through the asbestos:

$$Na_2PdCl_4 + HCOONa = 3\,NaCl + HCl + CO_2 + Pd.$$

The hydrochloric acid formed by the above reaction is neutralized by the sodium carbonate. In acid solutions formic acid hardly reduces palladous chloride at all.

After the asbestos has thoroughly dried, soften the mass with hot water, place in a funnel and wash with hot water until the soluble salt is completely removed. Dry once more and preserve in a well-stoppered bottle.

Insert the palladium-asbestos fiber into the capillary tube as follows: Roll the fiber between the fingers to a little round wad, place it in the opening of the unbent capillary tubing and by gentle tapping upon the table force it along to the center of the tube. Then bend the tubing as shown in the figure.

Remark. — Inasmuch as the palladium-asbestos is likely to become shoved into the capillary, it is perhaps more satisfactory to use a palladium wire wound into a spiral as catalyzer.*

9. METHANE, CH_4. Mol. Wt. 16.03

Density = 0.5545. (Air = 1). Weight of 1 liter = 0.7168 g.
Molar volume = 22.36 l. Critical temperature = −82° C.

Preparation. — Methane is conveniently prepared by a process analogous to that used in making ethylene† (cf. p. 647). Allow a mixture of equal parts methyl iodide and alcohol (*d.* 0.805) to act upon a zinc-copper couple which has been washed with alcohol.

$$2\,CH_3I + 2\,Zn + 2\,HOH = ZnI_2 + Zn(OH)_2 + 2\,CH_4.$$

* Private communication from Dr. Leutold of Hamburg.

† Gladstone and Tribe, *J. Chem. Soc.*, **45**, 154.

Prepare the zinc-copper couple by pouring a 2 per cent copper sulfate solution 4 times over granulated zinc, then washing with water, and finally with alcohol.

By allowing the mixture of methyl iodide and alcohol to drop upon the copper-coated zinc, a steady stream of methane is obtained at the ordinary temperature. Purify the gas by shaking it with fuming sulfuric acid, and then with caustic potash solution. It then contains about 98.4 per cent of CH_4 and about 1.6 per cent of nitrogen.

Methane can be prepared easily by the hydrolysis of aluminium carbide (Moissan).

$$Al_4C_3 + 12\,H_2O = 4\,Al(OH)_3 + 3\,CH_4.$$

Wash the gas with water, then with fuming sulfuric acid and finally with a mixture of colloidal palladium and ammonium picrate (see p. 663). Thus prepared, the gas is about 99.8 per cent pure.

Methane, also called marsh-gas or fire damp, is only slightly soluble in water.

ABSORPTION COEFFICIENTS OF METHANE FOR WATER*

Temperature	β	Temperature	β
0°	0.05563	30°	0.02762
5°	0.04805	35°	0.02546
10°	0.04177	40°	0.02369
15°	0.03690	45°	0.02238
20°	0.03308	50°	0.02134
25°	0.03006	55°	0.02038

In alcohol, the gas is about ten times as soluble as it is in water.

Inasmuch as no satisfactory absorbent for methane is known, it is always determined by combustion. From the equation representing the combustion, $\underset{1\text{ vol.}}{CH_4} + \underset{+2\text{ vols.}}{2\,O_2} = \underset{1\text{ vol.}}{CO_2} + \underset{0\text{ vol.}}{2\,H_2O}$, the following deductions can be made:

1. *Contraction.* — The contraction caused by the combustion of methane is equal to twice its original volume.

2. *Carbon Dioxide.* — By the combustion of methane an equal volume of carbon dioxide is produced.

3. *Oxygen Consumed.* — For the combustion of one volume of methane two volumes of oxygen are necessary.

* L. W. Winkler, *Ber.*, **34**, 1419 (1901).

Analysis of Illuminating and Producer Gases

The analysis of all such gases is best performed either by the method of Hempel* or that of Drehschmidt.†

Hempel's Method

Hempel's apparatus is shown in Fig. 130, p. 637. It consists of a eudiometer, W, with 0.2 ml. graduations and connected by means of rubber tubing with the leveling-bulb K. The eudiometer is also connected with the compensation-tube D and the latter is connected with a manometer C; both the tubes W and D are surrounded by a cylinder containing water.

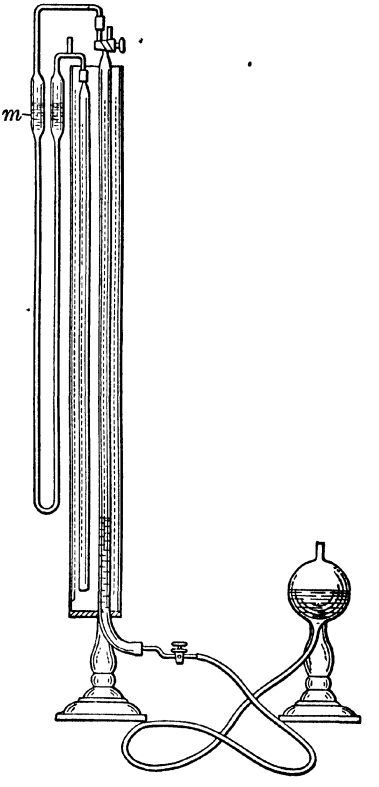


Fig. 138.

Calibration of the Apparatus. — First fill the manometer-tube with mercury by raising the leveling-bulb K with the stop-cock p in the position shown in Fig. 130, so that there is an open connection between W and c. Allow the mercury to pass over into C until the mark mm is reached. Then determine the volume of the manometer-tube from the mark m to the point a (Fig. 130) as follows:

By carefully lowering the bulb K draw the mercury over into C exactly to the point a when the stop-cock p is closed. Allow a little air to enter into the eudiometer through the right-hand capillary tube above p (the tube E should be withdrawn as in Fig. 138). Place the leveling-bulb K upon a solid support so that the mercury level in it is at the same height as in W, and with the stop-cock p still open, read the position of the mercury in W. Close the stop-cock, raise K a little and turn p to the position shown in Fig. 130. By raising K still higher, drive the air over into the manometer-tube C until the mercury has exactly reached the mark m, then close the

* *Gasanalytische Methoden* (1900).

† *Ber.*, **21**, 3242 (1888).

stop-cock *A* (Fig. 130). Then adjust the position of the mercury by turning the stop-cock *p* one way or the other, and once more read the position of the mercury in *W*. The difference between the two readings represents the volume of the tube between the marks *m* and *a*, an amount which must be added to all subsequent readings.

Introduce a drop of water at *c*, by means of a fine pipet, into the compensation-tube *D* and either fuse together the end of the tube, or close with a cork stopper and make air-tight with sealing wax.

Procedure for the Analysis. — If the analysis is to be carried out on the spot, collect a large sample of the gas in a Drehschmidt pipet (Fig. 130 *S*). To accomplish this, connect the capillary tube *E'* by means of rubber tubing with the source of the gas, and turn the stop-cock *M* so that the tube *E'* is in connection with the bulb of the pipet with the leveling-bulb and the stop-cock *s* open. Fill the pipet with the gas, then turn the stop-cock *M* so that it communicates with the outer air, and completely expel the gas from the pipet. In this way draw the gas in and out of the pipet at least 3 times to make sure that all foreign gas (air) is removed from the rubber tubing. Then collect the sample of gas and close the two stop-cocks *M* and *s*.

In order to bring the gas to be tested from the Drehschmidt pipet into the eudiometer, connect the two instruments by means of the capillary *E'* (imagine the capillary *E* in Fig. 130 to be replaced by *E'*) and firmly wire the rubber connections to the glass. Turn the stop-cock *M* to the position shown in Fig. 130, raise the leveling-bulb *K* (after previously causing the mercury in the manometer-tube to reach to the point *a*) and fill the buret with mercury until the latter begins to flow from out of the tip of the key at *M*; then close the cocks *A* and *p*. Turn the cock *M* so that the pipet *S* and the buret *W* are in connection, raise *K'*, open *s*, lower *K*, and open both *p* and *A*.

After about 40 ml. of the gas have passed over into the eudiometer, close the cocks *A* and *M*, dip the key of the stop-cock *M* (which must be entirely filled with mercury) into a beaker containing mercury, and suck the gas in the capillary into *W* by lowering *K* and opening *A* and *p*. As soon as the capillary *E* is entirely filled with mercury, close *A*, *p* and finally *M*.

Now determine the volume of the gas in *W* as follows: Open *A* and raise *K* so that the mercury in the bulb is a little higher than it is in *W*. After this open *p* and drive the gas over towards *C* until the mercury in both arms of the manometer-tube is at about the same height; then close *A* immediately. Make the last fine adjustment of the mercury levels within the tubes by closing or opening the screw-cock *Q*. Read

the volume of the gas,* and to the reading add the correction corresponding to the volume between the marks M and a.

From this point the analysis begins.

1. Determination of Carbon Dioxide

With the stop-cock p closed, turn the cock M as shown in Fig. 130, remove the Drehschmidt pipet, and replace by a second, clean pipet completely filled with mercury. On connecting the stop-cock M with the rubber connector of the capillary E', it should be in the position shown in the drawing. By this means the mercury in the rubber tubing can flow out through the key. After wiring the rubber tightly to the glass, introduce 3–5 ml. of caustic potash solution (1 : 2) through the key into the pipet M and wash out the alkali in the capillary with about 2 ml. of distilled water and then with a little mercury; after this drive over the gas itself into the pipet. When the mercury has filled the whole capillary, both to the right and left of M, close A, p, and M. Raise the bulb K' so that extra pressure is placed upon the gas in the pipet and close s. Gently shake the pipet for 3 minutes without disconnecting it from the eudiometer, after which return the gas to W as follows: Open M, p, and A, lower K, raise K', and open s. When almost all of the gas has been driven out of the pipet, close M, p, A, and Q, place the leveling-bulb on the table below, and K' upon the support (missing from Fig. 130, but shown in Fig. 138) upon which the pipet itself rests. Now open M, p, A, and s, and screw up Q a little so that the gas is very slowly sucked into the buret. As soon as the caustic potash solution has reached M, close it. Now remove the gas remaining in the capillary to the left of M by sucking mercury through the key of M into W. Finally read the volume of the unabsorbed gas in the same way as before. The difference between the two readings represents the amount of CO_2.

2. Determination of the Heavy Hydrocarbons or Illuminants

Remove the pipet containing the caustic potash solution and replace it with another containing fuming sulfuric acid.† Drive the gas over into the latter, and allow to stand with occasional passes to and fro,

* The reading is best made with the help of a small telescope, the ocular of which is provided with cross-hairs. For this purpose the telescope connected with a Bunsen spectroscope is suitable.

† In this pipet the bulb-tube K' is fused on to the absorption-bulb, so that it is a little higher than the latter, in the same way as in the Hempel pipet (Fig. 141). Mercury is acted upon by fuming sulfuric acid.

for 45 minutes, then empty the pipet in precisely the same way as before. Return the gas to the pipet containing the caustic potash solution in order to remove the acid vapors, and finally transfer to the buret *W* and read its volume. The difference before and after the treatment with fuming sulfuric acid represents the sum of the heavy hydrocarbons or illuminants (C_2H_4, C_6H_6, C_2H_2, etc.). It is not usually customary to attempt to separate the benzene from the ethylene.

3. Determination of Oxygen

Carry out this part of the analysis in exactly the same way as the determination of the CO_2, but using an alkaline solution of pyrogallol in the absorption pipet (cf. p. 653).

4. Determination of Carbon Monoxide

The determination of carbon monoxide may be effected either by absorption with ammoniacal cuprous chloride or by simultaneous combustion with hydrogen and methane.

For the absorption method, the procedure is the same as in the case of the determination of the heavy hydrocarbons, *i.e.*, the absorption is effected in a pipet containing only ammoniacal cuprous chloride (no mercury). Shake the gas for 3 minutes with a solution of cuprous chloride which has already been used and then the same length of time with a fresh, or little used, solution (cf. p. 657). Before reading the volume of the unabsorbed gas, free it from ammonia vapors, by shaking with 4 *N* hydrochloric acid in a Drehschmidt pipet.

5. Determination of Hydrogen and Methane

After the removal of the carbon monoxide, the gas may consist of hydrogen, methane, and nitrogen. Add an excess of oxygen to this mixture (with illuminating-gas twice its volume, while with Dowson, water, and producer gas only a little more than half as much oxygen is necessary). Connect the eudiometer *W* with a Drehschmidt pipet entirely filled with pure mercury* using a Drehschmidt platinum capillary (Fig. 130, *V*), heat to bright redness with the non-luminous flame of a Teclu burner, taking care that the inner flame mantle does not come in contact with the platinum. Pass the gas mixture C times in a slow stream through the hot platinum tube, but take care that no mercury

* There must be no trace of caustic potash in the pipet because in that case CO_2 would be absorbed and an inaccurate result would be obtained. To make sure that all the alkali is removed, wash the pipet first with water, then with hydrochloric acid, and finally with water once more.

enters the latter. Then measure the volume of the burned gas without removing the platinum capillary, and determine the carbon dioxide by introducing some caustic potash into the pipet and shaking the gas with it; after 3 minutes' shaking, return the unabsorbed gas to the eudiometer, closing the stop-cock M as soon as the caustic potash solution reaches it.

Calculation of Hydrogen and Methane

Assume V ml. of gas to be taken for the analysis. The residue remaining after the absorption of the CO_2, C_nH_{2n}, O_2, and CO is mixed with oxygen and burned. The contraction produced is V_C and the CO_2 formed amounted to V_K.

It was shown on p. 666 that the volume of the methane is equal to the volume of the CO_2 formed, V_K, and in per cent: $\frac{V_K}{V} \times 100 =$ per cent CH_4.

Since by the combustion of one volume of CH_4 two volumes of gas disappear, it is evident that by the combustion of V_K ml. of CH_4 the contraction will amount to $2\ V_K$.

If the latter value be subtracted from the total contraction V_C, the difference represents the contraction caused by the combustion of the hydrogen present $(V_C - 2\ V_K)$ and two-thirds of the latter represents the amount of hydrogen. Therefore $200\ \frac{(V_C - 2\ V_K)}{3\ V} =$ per cent H.

Determination of Carbon Monoxide, Methane, and Hydrogen by Combustion

After the absorption of the CO_2, C_nH_{2n}, and O_2, the residual gas consists of CO, CH_4, H_2, and N_2. Add a measured volume of oxygen* explode the mixture, and determine both the contraction, V_C, and the carbon dioxide formed, V_K. After this determine the unused oxygen by absorption with alkaline pyrogallol solution. If the excess of oxygen is subtracted from the amount originally added, the difference will give the amount of oxygen necessary for the combustion, V_O.

* The purity of the oxygen must be tested before the analysis, because the commercial product almost always contains nitrogen. To a measured volume of nitrogen add a definite amount of oxygen, as otherwise the amount of the residual gas might be too small to fill the manometer-tube between the marks a and m (Fig. 130). Prepare the nitrogen by allowing air to stand over phosphorus in a Hempel pipet. (Cf. p. 653.)

If the volume of CO is denoted by x, the CH_4 by y, and finally the H_2 by z, the following three independent equations hold true.

$$1.\ V_C = \tfrac{1}{2}x + 2y + \tfrac{3}{2}z,$$
$$2.\ V_K = x + y,$$
$$3.\ V_O = \tfrac{1}{2}x + 2y + \tfrac{1}{2}z;$$

and from these equations

$$x = \tfrac{4}{3}V_K + \tfrac{1}{3}V_C - V_O = CO,*$$
$$y = V_O - \tfrac{1}{3}(V_K + V_C) = CH_4,$$
$$z = V_C - V_O = H_2.$$

Analysis according to H. Drehschmidt†

The apparatus of Drehschmidt, like that of Hempel, consists of the gas-buret B and the compensation-tube C, both of which are contained in a cylinder filled with water (Fig. 139).

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* According to A. Wohl (*Ber.*, **1904**, 433) the results are not quite accurate when obtained in this way because the molecular volume does not always equal the theoretical value of 22.41 liters. Nernst, in his book on Theoretical Chemistry, gives the following molecular volumes:

For 1 g.-mol. of the gas,	or referred to oxygen
H_2 = 22.43 l.	H_2 = 1.0017
O_2 = 22.39 l.	O_2 = 1.0000
CO = 22.39 l.	CO = 1.0000
CH_4 = 22.44 l.	CH_4 = 1.0020
CO_2 = 22.26 l.	CO_2 = 0.9939

Taking these values into consideration, A. Wohl obtains for x CO, y CH_4, and z H_2, the following formulas:

$$x = 0.3329\ V_c - V_o + 1.3394\ V_k,$$
$$y = -0.3336\ V_c + 1.0020\ V_o - 0.3340\ V_k;$$
$$z = 1.0005\ V_c - 1.0017\ V_o - 0.0060\ V_k.$$

F. Haber (*Thermodynamik techn. Gasreaktionen*) sees no reason for modifying the Bunsen formulas in this way, for when a combustion analysis is carried out by explosion, the volume of gas after the explosion is so poor in carbon dioxide that the partial pressure of the latter does not vary much from that of an ideal gas, and, therefore, follows Avogadro's Rule.

It is quite another matter in the case of mixtures rich in carbon dioxide, as often occur in gas-volumetric analyses. In that case the weight of carbon dioxide (or of carbonate) is computed from the volume of the gas and accurate values are obtained by using the observed molecular volume of 22.26 for this gas (see p. 340).

The necessity of using the observed molecular volume instead of the theoretical value has been shown by Treadwell and Christie (*Z. angew. Chem.*, **1905**, 1930) for chlorine. With other vapors (NH_3, HCl, SO_2, N_2O) also, the observed molecular volume should be used.

† *Ber.*, **21** (1888), 3242.

Through the stop-cocks *a* and *b*, connect *B* and *C*, by means of capillary glass tubing containing a drop of a colored solution (indigo and sulfuric acid); in order to determine the position of the latter, the capillary is provided with a millimeter graduation. The three-way cock *a* can be turned so that *C* connects with the outer air or with the capillary,

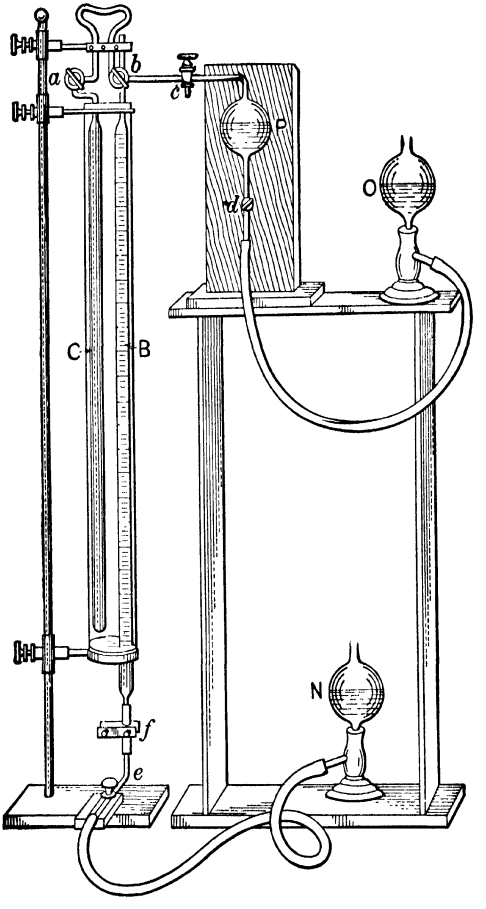


FIG. 139.

or so that the capillary is in connection with the air; it has an opening through the top of the key. The cock *b* has a right-angled boring like *H*, Fig. 130. The buret is divided into millimeters and must be calibrated with mercury before using. The apparatus is used in the same way as described under the Hempel method, p. 667.

TECHNICAL GAS ANALYSIS

Method of Hempel

The apparatus necessary is shown in Fig. 140. It consists of a long measuring-tube ending at the top in a thick-walled capillary tube and connected at the bottom by means of rubber tubing about a meter long with the leveling tube.

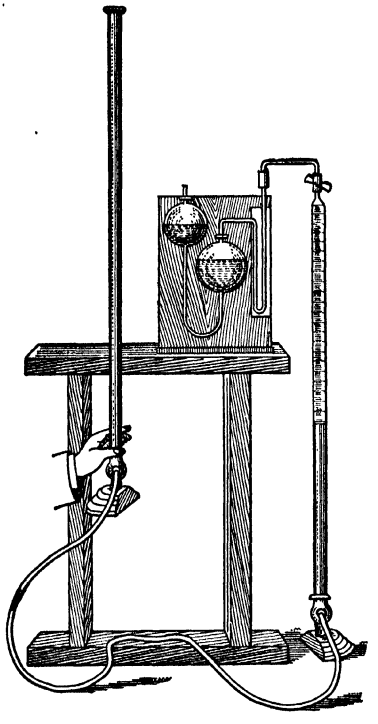


FIG. 140.

The gas is confined over water which has been saturated with the gas to be examined, and the absorption is effected in Hempel's absorption pipets such as are shown in Figs. 141, 142, 143, and 144. Fig. 141 represents a *simple* pipet for liquid absorbents, and Fig. 142 shows a *compound* absorption pipet. The latter is used for solutions which undergo change on exposure to the air, *e.g.*, an alkaline solution of pyrogallol, or an ammoniacal cuprous chloride solution. The liquid in the two right-hand bulbs serves to protect the solutions on the left. Fig. 143 shows the pipet used for fuming sulfuric acid. The small bulb is filled by the glass-blower with glass beads, which serve to give to the sulfuric acid the largest possible surface, so that the absorption is effected much more readily. Fig. 144 is a pipet used for solid absorbents, such as phosphorus, etc. In order to fill it with phosphorus, hold the pipet upside down, fill the cylindrical part with distilled water, and introduce small sticks of colorless phosphorus. After filling the pipet, insert the rubber stopper, place the apparatus right side up, pour water into the bulb, and remove any air-bubbles in the cylindrical part of the pipet by blowing through the bulb until the water flows out from the top of the left-hand capillary; then close by means of rubber tubing and a pinch-cock.

Analysis of Illuminating-gas

First, prepare the confining liquid by conducting the gas through distilled water in a wash-bottle for several minutes with constant shaking.

Completely fill the gas-buret with this liquid and then close the upper rubber tubing with a pinch-cock. To fill the buret with gas, connect the receiver with the buret by a piece of rubber tubing through which

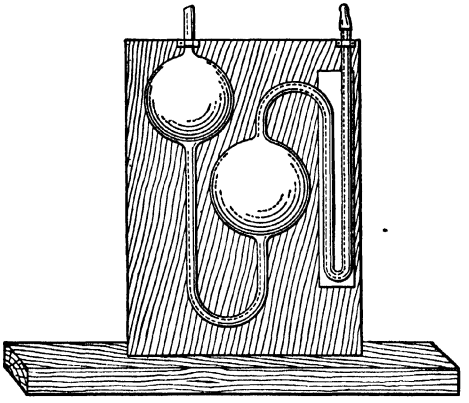


FIG. 141.

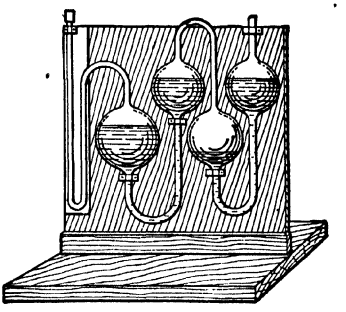


FIG. 142.

the gas has been flowing for 2 or 3 minutes, lower the leveling-tube, open the pinch-cock, and allow a little more than 100 ml. of the gas to flow into the buret. Now close the upper cock, raise the leveling-tube, until the lower meniscus of the confining liquid is exactly at the

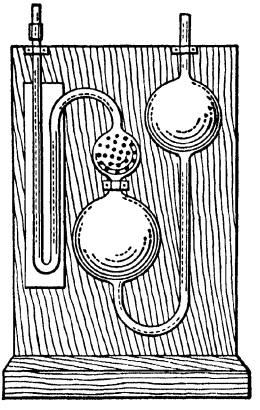


FIG. 143.

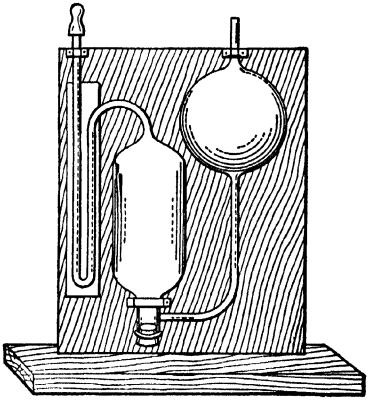


FIG. 144.

100-ml. mark, and then close the rubber between the leveling-tube and the buret with a pinch-cock placed near the buret, allow the apparatus to stand until the water no longer rises in the buret; this requires 2–3 minutes. When the water is stationary, carefully open the lower pinch-cock (for there is excess pressure in the buret) which causes the

water-level to sink. When the 100-ml. mark is again reached, close this cock, and open the upper pinch-cock an instant to allow the excess of gas to escape and then immediately close. To make sure that the buret contains exactly 100 ml. of the gas, open the lower pinch-cock and after bringing the water in the leveling-tube to the same height as in the buret, take the reading; the lowest point of the meniscus should coincide exactly with the 100-ml. mark of the buret. Finally close the lower pinch-cock.

1. Determination of Carbon Dioxide

Connect the buret with a pipet containing caustic potash solution by means of a capillary filled with water, as shown in Fig. 140, raise the leveling-tube, open first the lower pinch-cock and then the upper one,* and drive the gas over into the pipet. The confining liquid should now fill the entire capillary. Close the upper pinch-cock and shake the pipet and its contents for 3 minutes.† Return the gas to the buret taking care that none of the alkali enters with it.

Bring the liquid in the leveling-tube to the same level as that in the buret; close the lower pinch-cock and after the water has completely drained from the sides of the tube, read the volume of the unabsorbed gas.

2. Determination of the Heavy Hydrocarbons, or Illuminants, C_nH_{2n}

Connect the buret by a dry, empty capillary with sulfuric acid pipet (Fig. 143) and pass the gas back and forth 4 times, taking care that no water enters the pipet and that the sulfuric acid does not reach the rubber connection.

Before the experiment mark the position of the sulfuric acid upon the milk-glass plate back of the pipet and at the end of the experiment the acid must come to the same mark. The gas in the buret is now contaminated with acid vapors which are removed by passing it into the potash pipet, afterwards returning it to the buret.

3. Determination of Oxygen

This can be effected by shaking the gas in the compound pipet with alkaline pyrogallol solution, but far preferably by means of phosphorus.

* In the figure this pinch-cock is lacking.

† The absorption takes place more rapidly with one of Hempel's new pipets, which is similar to the one shown in Fig. 143, except that the right-hand bulb is replaced by a movable leveling-bulb, as in Fig. 130. The latter is filled with mercury, upon which the liquid absorbent floats. For the absorption of CO_2, it is only necessary to pass the gas back and forth once.

In the latter case, drive the gas over into the phosphorus pipet and allow it to remain there until the white vapors disappear; this usually requires but 3–4 minutes (cf. p. 653). If no white vapors can be detected, this shows conclusively that the absorption of the heavy hydrocarbons was incomplete (cf. p. 653). In such a case, the gas must be again treated with sulfuric acid and afterwards with phosphorus. If no white fumes are then formed, no oxygen is present, a case which practically never occurs, for in the determination of the hydrocarbons a little air containing oxygen always reaches the gas from the small capillary.

4. Determination of Carbon Monoxide

Shake the gas 3 minutes with an old solution of ammoniacal cuprous chloride and then the same length of time with a fresh solution. (See pp. 657, 670.)

5. Determination of Hydrogen and Methane

After the absorption of the carbon monoxide place the residual gas in the hydrochloric acid pipet and wash the buret with hydrochloric acid to remove traces of alkali, and then fill with distilled water.

Transfer 15–16 ml. of the gas in the hydrochloric acid pipet to the buret, and, after reading its volume, drive it over into an explosion pipet containing mercury (Fig. 136). Accurately measure 100 ml. of air (containing 20.9 ml. of oxygen) in the buret and add to the contents of the explosion pipet. Then close the latter by a pinch-cock, mix the contents of the pipet by shaking, lower the leveling-tube so that the gas is placed under reduced pressure, and close the glass stop-cock of the pipet. Connect the platinum wires, which are fused in the upper part of the bulb, with the poles of a small induction coil so that sparks pass between the platinum points within the pipet. The explosion at once occurs with a flash without breaking the pipet. Return the gas to the buret. Objection has been raised to reading the volume of the gas and then determining the amount of carbon dioxide formed, as a measure of the amount of methane burned, because the gas in the buret is confined over water which absorbs appreciable quantities of carbon dioxide. It has been found, however, that the error caused by absorption of CO_2 by the water is so slight, during the short time of waiting, that it is best to determine the CO_2 with caustic potash after the explosion, as Hempel also recommended. (See p. 678.) Finally, determine the amount of unused oxygen by means of absorption with phosphorus. If the excess of oxygen is subtracted from the total amount

added (20.9 ml.), the amount of oxygen required for the combustion is known (V_o), so that we have two equations from which the amount of hydrogen and methane can be computed.

If x is the volume of the hydrogen, and y the volume of the methane we have

$$(1) \quad V_c = \tfrac{3}{2}\, x + 3\, y, \qquad (2) \quad V_o = \tfrac{1}{2}\, x + 2\, y,$$

and

$$x = \tfrac{4}{3}\, V_c - 2\, V_o, \qquad y = V_o - \tfrac{1}{3}\, V_c.$$

The values thus obtained are referred to the total gas residue and in this way the amount of hydrogen and methane present in the illuminating gas can be determined.

Great accuracy is naturally not to be expected by such an analysis, but the procedure is very satisfactory for an approximate estimation. Better results are obtained by the

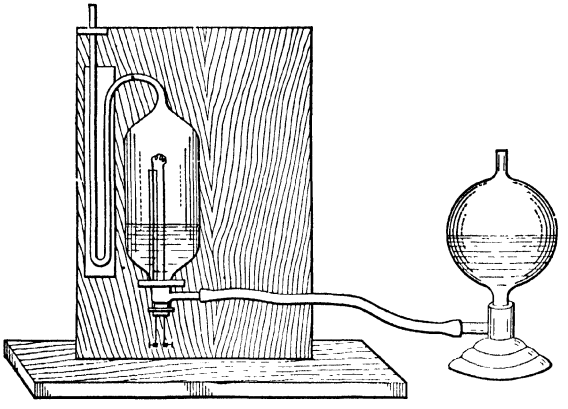


Fig 145.

(*b*) *Method of Winkler-Dennis*

In this method, the entire gas residue is transferred to a Hempel pipet containing mercury and connected with a leveling bulb (Fig. 145). Through the rubber stopper at the bottom two steel needles are inserted (knitting needles), the longer of which is enveloped throughout its whole length by a glass tube, and the upper end is connected, at about three-quarters the height of the cylindrical part of the pipet, with a thin platinum spiral.

Connect the pipet with a Hempel buret containing 100 ml. of oxygen*

* The oxygen used for experiments in gas analysis should preferably be prepared in the laboratory by heating potassium chlorate in a small retort, which is prepared by blowing a bulb (of about 20 ml. capacity) at the end of a narrow piece of glass tubing; after introducing about 5 g. of potassium chlorate, the tubing is bent to a right angle close to the bulb. Connect the end of the tube with a short piece of rubber tubing and heat the bulb over a free flame. As soon as oxygen begins to come off freely (lighting a glowing splinter) connect the rubber tubing from the retort with a Drehschmidt absorption pipet which contains a little caustic potash solution and is filled with mercury (cf. Fig. 130, p. 637). Do not at once fill the

over water, produce a lower pressure in the oxygen buret by lowering the leveling tube and then closing the rubber tubing with a screw-cock; after this place the leveling tube in a high position. Now connect the bottom ends of the two needles of the pipet with the wires of a small storage battery of such a strength that the platinum spiral is heated to dull redness. By lowering the leveling bulb, reduce the pressure in the pipet slightly and by opening the two upper screw-cocks between the pipet and the oxygen buret and gradually opening the lower screw-cock on the buret, conduct a very slow stream of oxygen into the pipet. Since a large excess of the gas residue is present at the start, the combustion takes place quietly; explosions never occur. During the combustion the platinum spiral begins to glow more brightly; to prevent its melting, place a variable resistance* in the circuit to regulate the strength of current, and the glowing of the platinum.

As soon as all the oxygen is in the pipet, allow the spiral to glow 2–3 minutes longer, then stop the electric current and allow the gas to remain in the pipet for 15 minutes so that it will assume the room temperature. Then transfer to a Hempel buret and measure its volume. Determine the carbon dioxide in the usual manner.

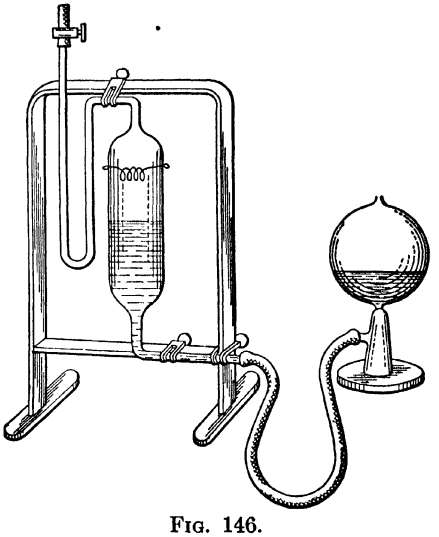


FIG. 146.

Remark. — By this method it is possible to burn pure acetylene without any explosion. The oxygen, however, must not be conducted, as above, into the acetylene because in that case the combustion of the acetylene will be incomplete and considerable carbon will deposit. First introduce oxygen into the combustion pipet, bring the platinum wire to glowing, and then introduce the acetylene; the combustion takes place smoothly without deposition of any carbon.

The Winkler-Dennis pipet is open to the objection that the rubber stopper eventu-

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pipet but allow the gas to pass through the cock *M* into the air. After about a minute, one can assume that the air from the retort and rubber tubing has been entirely replaced by oxygen. Lower the leveling bulb *K* of the pipet, open the cock, *s* and turn the cock *M* 90° so that the pipet fills with oxygen. When the filling is accomplished, close *M* and remove the retort. By shaking the pipet any carbon dioxide formed by the burning of dust, etc., is absorbed.

* The resistance mentioned on p. 180 is suitable to use here.

ally leaks; for this reason the author prefers the form of apparatus devised by his assistant, M. Bretschger, as shown in Fig. 146.

Instead of burning the gas residue according to the Winkler-Dennis method, it may be conducted over glowing cupric oxide.*

Orsat's Apparatus

For the analysis of flue gases, Orsat has constructed the apparatus shown in Fig. 147. It consists of the 100-ml. measuring-tube *B* surrounded by a cylinder containing water, and connected on the one hand with 3 Orsat tubes by means of the cocks *I*, *II*, *III*, and on the other hand with the outer air through the stop-cock *h*. The Orsat tube *III* contains caustic potash solution, *II* alkaline pyrogallol solution, and *I* ammoniacal cuprous chloride solution.

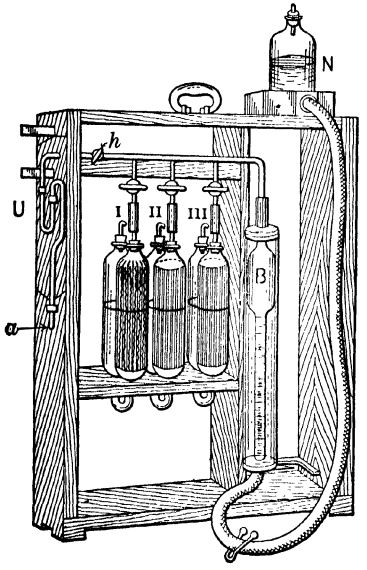


Fig. 147.

Manipulation. — By raising the leveling-bottle *N* and opening the stop-cock *h*, fill the measuring-tube *B* with water. As soon as the water is above the mark in the widened part of the measuring-tube, close the rubber tubing between the leveling-bottle and the measuring-tube by a pinch-cock. Connect *a* with the source of the gas, draw it into the measuring-tube by lowering the leveling-bottle and opening the pinch-cock. The U tube on the outside of the apparatus is filled with glass-wool and serves as a filter; any smoke being removed from the gas to be examined. The sample thus collected is naturally contaminated with the air from the rubber tubing, the U tube, and the capillary, which must be removed. The cock *h* serves for this purpose and is provided with a T boring. Turn the cock so that the buret communicates with the outer air through a small tube (not shown in the illustration) and expel the gas by raising the bottle *N*. Repeat this process of filling and emptying 3 times, and use the fourth filling of the tube *B* for the analysis. Bring the gas in the buret to the 0 mark, and place it under atmospheric pressure by quickly opening and then closing *h*. After this drive over the gas into the potash-bulb and

* Jäger, *J. Gasbeleuchtung*, **1898**, 764. G. v. Knorre, *Chem. Ztg.*, **1909**, 717.

back again to the measuring-tube several times, until there is no further absorption; after this again read the volume of the gas. In the same way pass the gas successively into the pyrogallol and the cuprous chloride tubes, thus obtaining the volumes of CO_2, O_2, and CO in the gas.

Bunte's Apparatus

This apparatus, shown in Fig. 148, differs from those previously described, inasmuch as the absorption takes place in the measuring vessel itself, whereas in the other cases the absorption takes place in the pipets.

The Bunte buret has a capacity of 110–115 ml. between *a* and *b*; *a* is a three-way cock, while *b* is bored only once.

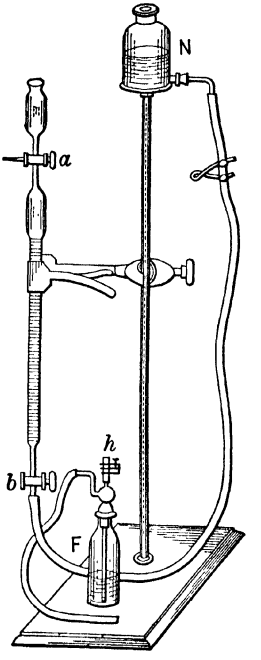


FIG. 148.

Manipulation. — Connect the buret with the leveling-bottle *N*, as shown in the illustration, open *a* and *b*, and allow the water to run up to the mark in the funnel above *a*. Connect the key of the stop-cock *a* with the source of the gas, lower *N*, turn *a* to the proper position, and draw the gas into the buret. After 101–103 ml. of the gas have entered the buret, close *a* and *b*, raise *N*, and by opening *b* compress the gas in the buret until the confining liquid has exactly reached the zero mark. Now cautiously open the cock *a*, when some of the gas in the buret will escape through the water in the funnel. The gas in the buret is now under a pressure equal to that of the atmosphere plus the pressure from the column of water in the funnel, and all subsequent measurements are taken under the same conditions.

Absorptions. — In order to introduce the different absorbents into the buret connect its lower end by means of the rubber tubing *h* with the bottle *F* containing a little water and with the water blown up into the rubber tubing. Open the cock *b* and the screw-cock *h*. Allow the water in the buret to run out until it exactly reaches the cock *b*, which is then closed. Place the absorbent in a small dish, introduce the lower tip of the buret into the liquid, and open the cock *b*. Inasmuch as the gas in the buret is under less than atmospheric pressure, the absorbent is sucked up into the buret. Now close the cock *b*, grasp the buret above *a* and below *b* (in order not to warm the gas), and shake its con-

tents well; again dip the tip of the buret into the absorbent in the dish and draw up a little more of the latter into the buret. Repeat this process until no more of the absorbent is sucked up into the buret. It would now be incorrect to read the volume of the unabsorbed gas, for it is under quite a different pressure than at the beginning of the analysis; namely, the atmospheric pressure less the pressure of the column of liquid remaining in the buret with the cock *b* open. Furthermore the vapor tension of the liquid in the buret is different from that of the water originally present. In order to obtain the original conditions, connect the buret with the bottle *F*, which now only contains enough water to fill the rubber tubing and the glass tube, and drain off the absorbent from the buret into the bottle until the upper level of the liquid reaches the cock *b*.* Then dip the end of the buret into a dish containing water, which rises into the buret on opening *b*. Close the latter and allow water to run into the buret from the funnel until the original pressure is established, when the volume of the gas is once more read. The difference gives at once the per cent of absorbed gas.

By means of this excellent method the carbon dioxide can be removed by caustic potash, heavy hydrocarbons by bromine water, oxygen by alkaline pyrogallol solution, and carbon monoxide by cuprous chloride.

Analysis of Gases which are Absorbed Considerably by Water

Under this heading belong N_2O, SO_2, H_2S, Cl_2, SiF_4, HF, NH_3, etc.

1. Nitrous Oxide, N_2O. Mol. Wt. 44.02

Density = 1.5297† (Air = 1). Weight of 1 liter = 1.9766 g.
Molar volume = 22.26 l. Critical temperature = + 36° C.

This gas is best prepared according to the method of Victor Meyer,‡ by allowing sodium nitrite to act upon a concentrated solution of a salt of hydroxylamine:

$$NH_2OH \cdot HCl + NaNO_2 = NaCl + 2\,H_2O + N_2O.$$

Procedure. — Add a concentrated, aqueous solution of sodium nitrite drop by drop from a separatory funnel, with constant cooling, to a concentrated solution of hydroxylamine hydrochloride in a small evolution flask; in this way the gas evolved is pure and escapes in a regular

* The absorbent is now by no means exhausted, so that it can be returned to the proper bottle, and used for several other determinations.

† Lord Rayleigh, *Proc. Roy. Soc.*, **74**, 181 (1904).

‡ *Ann. Chem. Pharm.*, **157**, 141.

stream. It is not advisable to proceed in the opposite way, namely, to add the hydroxylamine solution to a concentrated nitrite solution, for in the latter case the decomposition is likely to take place with explosive violence; it is still less advisable to add one of the reagents in the solid form. In a very dilute condition the solutions scarcely act upon one another.

Nitrous oxide is never pure when it is prepared by heating ammonium nitrate; it is always contaminated with nitrogen and nitric oxide, but the latter may be removed by washing the gas with a solution of ferrous sulfate.

According to L. Pollak the solubility of nitrous oxide between 0° and 22° C. is expressed by the formula $\beta = 1.18719 - 0.042265 \cdot t + 0.000610 \cdot t^2$, but according to Bunsen its solubility is greater, being expressed by the formula $\beta = 1.3052 - 0.045362 \cdot t + 0.0006843 \cdot t^2$.

The gas is absorbed to a much greater extent by alcohol than by water. According to Pollak, the absorption coefficient for alcohol is, $\beta = 3.22804 - 0.04915 \cdot t + 0.00023 \cdot t^2$, but according to Bunsen it is somewhat greater: $\beta = 4.17805 - 0.069816 \cdot t + 0.000609 \cdot t^2$.

The determination of nitrous oxide can be effected with accuracy by combustion, and this may be carried out in two different ways:

1. According to Bunsen, by exploding with hydrogen, or according to v. Knorre, by means of the Drehschmidt capillary. The contraction produced is equal to the original volume of the nitrous oxide:

$$\underset{1\text{ vol.}}{N_2O} + \underset{1\text{ vol.}}{H_2} = \underset{0\text{ vol.}}{H_2O} + \underset{1\text{ vol.}}{N_2}.$$

2. According to Pollak, by combustion with pure carbon monoxide, either by explosion or with the help of the Drehschmidt capillary; the volume of the CO_2 formed, which is measured, is equal to the volume of the nitrous oxide:

$$\underset{1\text{ vol.}}{N_2O} + \underset{1\text{ vol.}}{CO} = \underset{1\text{ vol.}}{CO_2} + \underset{1\text{ vol.}}{N_2}.$$

There is no contraction in this case.

2. Nitric Oxide, NO. Mol. Wt. 30.01

Density = 1.0366* (Air = 1). Weight of 1 liter = 1.3402 g.
Molar volume = 22.39 l. Critical temperature = −94°.

Preparation of Nitric Oxide

Pure nitric oxide can be prepared (*a*) according to L. Winkler,† by adding 50 per cent sulfuric acid from a dropping funnel to a dilute

* Computed from observations of Gray (1905), Guye and Davila (1906).
† *Ber.*, **34**, 1408 (1901).

solution of one part potassium iodide and two parts potassium nitrite in a fractionating flask. At the laboratory temperature, the following reaction takes place, $2\,HNO_2 + 2\,HI = 2\,H_2O + I_2 + 2\,NO$, and by washing the gas with potassium hydroxide solution, a pure gas is obtained.

(*b*) According to Emich,* by shaking a nitrate solution with concentrated sulfuric acid and mercury in a nitrometer. $2\,KNO_3 + 6\,Hg + 5\,H_2SO_4 = 2\,KHSO_4 + 3\,Hg_2SO_4 + 4\,H_2O + 2\,NO$. This method is suitable for preparing small quantities of nitric oxide. A somewhat less pure gas, but one suitable for many purposes can be prepared by

(*c*) the method of Deventer.† Place a concentrated solution of potassium ferrocyanide and somewhat less than an equivalent weight of sodium nitrite in a flask and introduce 80 per cent acetic acid from a dropping funnel. A steady stream of gas is produced

$$2\,K_4Fe(CN)_6 + 2\,KNO_2 + 4\,HC_2H_3O_2 = 4\,KC_2H_3O_2 + 2\,K_3Fe(CN)_6 + 2\,H_2O + 2\,NO$$

which L. Moser‡ found to contain 90–97 per cent of NO and 3–10 per cent N_2.

ABSORPTION COEFFICIENTS OF NITRIC OXIDE FOR WATER§

Temperature	β	Temperature	β
0°	0.07381	30°	0.04004
5°	0.06461	35°	0.03734
10°	0 05709	40°	0.03507
15°	0.05147	45°	0.03311
20°	0.04706	50°	0.03152
25°	0.04323	55°	0.03040

Although nitric oxide is only slightly soluble in water, its determination will be discussed at this place because this gas frequently occurs with nitrous oxide, and must therefore be determined at the same time.

Nitric oxide may be determined by absorption with a concentrated solution of ferrous sulfate or an acid solution of potassium permanganate, likewise, according to E. Divers,|| by an alkaline solution of sodium sulfite (40 g. Na_2SO_3 + 4 g. KOH in 200 ml. H_2O) with the

* *Monatshefte*, **13**, 73 (1892).
† *Ber.*, 26, 589 (1893).
‡ *Z. anal. Chem.*, **1911**, 406.
§ L. W. Winkler, *Ber.*, **34**, 1414 (**1901**).
|| *J. Science Coll. Imp. University;* Tokio, **11**, 11 (1893).

formation of $Na_2N_2O_2SO_3$.* It can be determined accurately according to Baudisch,† as follows: Introduce a measured volume of the gas into an absorption pipet filled with mercury and containing a moist stick of solid potassium hydroxide and add, from a buret, a measured volume of air. The NO gas is immediately oxidized to N_2O_3 which is absorbed by the potassium hydroxide, $4\ NO + O_2 + 4\ KOH = 2\ H_2O + 4\ KNO_2$. Since 5 volumes of gas disappear for each volume of NO originally present, it is evident that the contraction, V_C, is $\frac{5}{4}$ as large as the original volume of NO and $NO = 0.8\ V_C$.

According to v. Knorre and Arndt,‡ NO can also be determined by combustion. Mix the gas with hydrogen and pass the mixture very slowly through a Drehschmidt capillary (p. 637) heated to bright redness. Under these conditions the nitric oxide is reduced to nitrogen.

$$2\ NO + 2\ H_2 = 2\ H_2O + N_2, \text{ and the volume of } NO = \tfrac{2}{3}\ V_C.$$

If the mixture is passed too rapidly through the capillary tube containing the glowing platinum or if the catalyst is not hot enough, appreciable quantities of ammonia are formed and the results are inaccurate.

It is not possible to carry out the reaction in an explosion pipet: with pure NO and H_2 there is no explosion and if considerable NO_2 is present the reaction is not quantitative although a very violent explosion may occur.

Combustion of Nitric Oxide and Carbon Monoxide in a Drehschmidt Capillary

According to Henry a mixture of carbon monoxide and nitric oxide is not explosive. On the other hand, according to Pollak, by conducting a mixture of these gases through a Drehschmidt platinum capillary heated to bright redness, the combustion is quantitative if at the same time the carbon dioxide formed is removed by means of caustic potash;§ otherwise the oxidation is not quantitative. According to the equation

$$\underset{2\text{ vols.}}{2\ NO} + \underset{2\text{ vols.}}{2\ CO} = \underset{0\text{ vol.}}{2\ CO_2} + \underset{1\text{ vol.}}{N_2}$$

the contraction produced is equal to $\frac{3}{2}$ the volume of the nitric oxide.

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* Nitric oxide is only partially absorbed by an alkaline solution of pyrogallol, forming alkali nitrite, N_2O, and N_2. C. Oppenheim, *Ber.*, **36**, 1744 (1903).

† *Ber.*, **46**, 3232 (1913).

‡ *Ber.*, **21**, 2136 (1889).

§ Cover the mercury in the Drehschmidt tube with a concentrated caustic potash solution, by which means the CO_2 is absorbed immediately after its formation.

Remark. — If considerable nitrous oxide is present at the same time, the combustion in the Drehschmidt capillary takes place quantitatively without the removal of the carbon dioxide. In this case the contraction is $\frac{1}{2}$ the volume of the nitric oxide.

Analysis of a Mixture of Nitrous and Nitric Oxides

I. *Combustion with Hydrogen*

Mix the gas with an excess of hydrogen and pass it through the Drehschmidt platinum capillary heated to bright redness as described above. If the volume of the $N_2O = x$ and that of the $NO = y$, we have: (1) $x + y = V$. (2) $x + \frac{3}{2} y = V_C$ (contraction), from which can be calculated: $x = 3\ V - 2\ V_C$, $y = 2\ (V_C - V)$.

II. *Combustion with Carbon Monoxide*

To the gas mixture add an excess of carbon monoxide, pass through the red-hot platinum capillary, and determine first the contraction, V_C, and then the carbon dioxide, V_K. If x is the volume of N_2O, y the volume of NO, then $x + y = V_K$ and $\frac{1}{2} y = V_C$ from which it follows: $x = V_K - 2\ V_C$ and $y = 2\ V_C$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of One Another

I. *By Combustion with Hydrogen in a Drehschmidt Capillary*

After noting the contraction formed by the combustion with hydrogen, add an excess of oxygen to the gas residue and burn the mixture in the Drehschmidt capillary; two-thirds of the contraction which now takes place is equal to the amount of unused hydrogen in the first oxidation. If this quantity is deducted from the amount of hydrogen originally added, the difference, V_H, represents the amount of hydrogen necessary.

We have now:

	N_2O		NO		N_2	
1.	x	+	y	+	z	$= V$
2.	x	+	$\frac{3}{2} y$			$= V_C$
3.	x	+	y			$= V_H$

from which we can compute

$$x = 3\ V_H - 2\ V_C$$
$$y = 2\ (V_C - V_H)$$
$$z = V - V_H.$$

II. *By Combustion with Carbon Monoxide in the Drehschmidt Capillary*

In this case, using the same notation $x + y + z = V$, $0.5\,y = V_C$, and $x + y = V_K$ (volume of carbon dioxide). From this it follows: $x = V_K - 2\,V_C$, $y = 2\,V_C$ and $z = V - V_K$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of Carbon Dioxide

The accurate determination of nitrous oxide in the presence of carbon dioxide offers great difficulties. It is not possible to determine the former by combustion with hydrogen in the Drehschmidt capillary, because when the carbon dioxide is present it takes part to some extent in the combustion, $CO_2 + H_2 = H_2O + CO$, and the previous absorption of the carbon dioxide by means of a large quantity of caustic potash is equally unsatisfactory, because considerable nitrous oxide will be absorbed by the reagent. The best way to effect this determination consists in absorbing the carbon dioxide by solid, moist potassium hydroxide contained in an absorption pipet filled with mercury. The difference in volume before and after the absorption gives the volume of CO_2. Transfer the residual gas to the mercury pipet, add a measured volume of air and absorb the NO as described on p. 685. In the residue determine N_2O according to p. 683, and the N_2 by difference.

3. Nitrogen, Mol. Wt. 28.02

Density = 0.96727 (Air = 1). Weight of 1 liter = 1.2505 g.
Molar volume = 22.41 l. Critical temperature = −149°.

Pure nitrogen is best prepared by heating a concentrated solution of potassium nitrate and ammonium chloride, present in amounts proportional to their molecular weights, and then conducting the escaping gas over glowing copper to reduce traces of nitric oxide.

Nitrogen is but slightly soluble in water.

ABSORPTION COEFFICIENTS OF NITROGEN FOR WATER*

Temperature	β	Temperature	β
0°	0.02348	30°	0.01340
5°	0.02081	35°	0.01254
10°	0.01857	40°	0.01183
15°	0.01682	45°	0.01129
20°	0.01542	50°	0.01087
25°	0.01432	55°	0.01051

* L. Winkler, *Ber.*, **24**, 3606 (1891).

Nitrogen cannot be determined by any of the ordinary methods of gas analysis. It is always estimated by determining all the other constituents present in a mixture and subtracting the sum of the percentages found from 100.

Technical preparations of nitrogen, prepared from the air, always consist of nitrogen and small amounts of rarer elements. According to Cavendish these latter may be obtained by adding oxygen and allowing a strong electric spark to pass through the mixture. In this way the nitrogen is completely oxidized to nitric acid, which can be removed by means of caustic potash solution. Then, by absorbing out the oxygen, the rarer gases are obtained. A still better process is that of Hempel, in which the nitrogen is absorbed by passing the gas over a glowing mixture of 1 g. magnesium, 5 g. freshly burnt lime, and 0.25 g. sodium. The rare gases are not absorbed by this treatment.

According to Bunsen, there is no combustion of nitrogen when detonating gas explodes in the presence of air, provided not more than 30 volumes of combustible gas are present for each 100 volumes of non-combustible gas. There is no oxidation of nitrogen during a combustion of a gas mixture which is passed through a Drehschmidt platinum capillary.

At this place, some data concerning the ordinary atmosphere will be given. According to Hann, 1 liter of dry air contains

Oxygen	209.9 ml.	= 0.2999 g.
Nitrogen	780.3 ml.	= 0.9757 g.
Argon	9.4 ml.	= 0.0167 g.
Carbon Dioxide	0.3 ml.	= 0.0006 g.
Hydrogen	0.1 ml.	= 0.00001 g.

1 liter of dry air at 0° and 760 mm., weighs 1.293 g.

Analysis of Gases by Titration of the Absorbed Constituents

If a mixture of gases contains several constituents, of which two are removed by the same absorbent, and one of these can be determined by titration, it is a matter of no difficulty to determine the amount of each. The diminution in volume after treatment with the absorbent represents the amount of the two constituents, the titration value represents the amount of one of them, and the difference shows the amount of the other. Such problems can be solved in a variety of ways, and only a few examples will be mentioned.

1. Chlorine, Cl. Mol. Wt. = 70.92

Density = 2.488 (Air = 1).* Weight of 1 liter = 3.2164 g.
Molar volume = 22.04 l. Critical temperature = +146°.

Determination of Carbon Dioxide in Electrolytic Chlorine†

The apparatus shown in Fig. 149 is suitable for this purpose.

Fill the absolutely dry eudiometer, *B* (the capacity of which between the two stop-cocks is accurately known, and for convenience may be 100 ml.), through the lower cock, after drying the gas by passing it through a long calcium chloride tube.‡ After 5–10 minutes it is safe to assume that the air has been completely replaced by the gas. Now close the lower three-way cock and then the upper one. Note the temperature and barometric pressure.

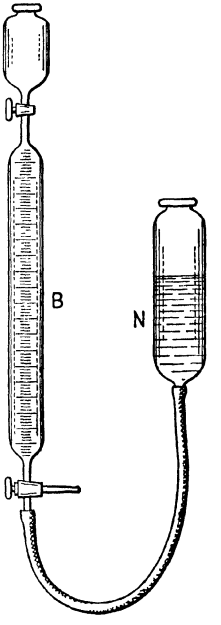


FIG. 149.

Connect the tip of the buret with the reservoir *N* by rubber tubing. Turn the three-way cock so that the reservoir communicates with the outer air, and then thoroughly wash the lower tip of the buret and the stop-cock, and close the latter. Prepare a solution of potassium arsenite by dissolving 4.95 g. As_2O_3 in dilute potassium hydroxide, adding dilute sulfuric acid until the solution is neutral to phenolphthalein and then diluting to 1 liter.§ Place 100 ml. of this solution in *N* and expel any air in the rubber tubing by pinching it with the thumb and finger. By raising *N* and opening the stop-cock, cause a little of the arsenite solution to flow into the buret which is inclined from side to side in such a way that the walls are thoroughly wet with the arsenite solution. The chlorine is slowly absorbed, as is evident from the fact that the solution slowly rises in the buret. As soon as there is no further absorption, close the lower stop-cock and make the solution in the buret flow back and forth several times, by inverting the buret and then turning it

* Leduc, *Compt. rend.*, **116**, 968 (1893); Treadwell and Christie, *Z. angew. Chem.*, **47**, 446 (1905).

† Treadwell and Christie, *Z. angew. Chem.*, **47**, 1930 (1905).

‡ If the buret and gas are not perfectly dry, some chlorine will be absorbed by the water. This will not affect the gas reading, but will be harmful in the subsequent titration.

§ An ordinary solution of arsenite prepared with sodium bicarbonate cannot be used here.

back again. After 1–2 minutes all of the chlorine will have been absorbed. Then in order to absorb all the carbon dioxide present, lower the tube N, pour 10 ml. of potassium hydroxide solution (1 : 1) in the funnel, and carefully introduce it into the buret. Again close the stop-cock and run the alkali solution back and forth in the buret.

After bringing the liquid in the buret and in the leveling tube to the same height, take the reading. By deducting this from the original volume of the gas, the volume of the chlorine plus that of the carbon dioxide is obtained. To determine the chlorine, empty the contents of the buret and of the leveling-tube into a large Erlenmeyer flask and turn the stop-cock to the position shown in the drawing so that the liquid in the rubber tubing can flow out. Remove the tubing from the buret and rinse it out with distilled water which is also allowed to run into N. Now add the contents of the buret and rinse the buret itself with distilled water.

To the contents of the Erlenmeyer flask add 2 drops of phenolphthalein solution, hydrochloric acid until the red color just disappears, 60 ml. of 3.5 per cent sodium bicarbonate solution, and a little starch solution. Titrate the excess of the arsenious acid with 0.1 N iodine solution.

Determine the ratio of the arsenite solution to the iodine in the same way as in the above titration. Place 100 ml. of arsenite solution in an Erlenmeyer flask, add 10 ml. of caustic-potash solution, 2 drops of phenolphthaleïn, hydrochloric acid to decolorization, and then 60 ml. of sodium bicarbonate solution. Dilute to the same volume as that of the original experiment and titrate with iodine. If n ml. were used in the analysis and n_1 ml. are required in the direct titration of the sodium arsenite solution then $n' - n$ multiplied by 1.102* gives the number of milliliters of chlorine gas at 0° C. and 760 mm. pressure. In other words,

$$V'_0 = (n' - n) \times 1.102.$$

As, however, the original gas was measured at the temperature $t°$ C. and under the pressure B mm., it follows according to p. 627, that

$$V'_0 = \frac{V' \cdot B \cdot 273}{760 \cdot (273 + t)},$$

from which can be computed

$$V' = \frac{V'_0 \cdot 760\,(273 + t)}{B \cdot 273}.$$

---

* This value is derived from the fact that the density of chlorine is 2.488 at 20°,

$$\frac{70.92}{0.001293 \times 2.488} = 22{,}040.$$

Therefore, 35.46 g. of chlorine at 0° and 760 mm. occupy a volume of 11,020 ml.

If V is the original volume of the gas used and R that of the residual gas in the buret, then

$$\begin{aligned} Cl_2 + CO_2 + \text{Residue} &= V \\ \text{Residue} &= R \\ \hline Cl_2 + CO_2 &= V - R \\ - Cl_2 &= V' \\ \hline CO_2 &= V - (R + V') \end{aligned}$$

and in per cent

$$x = \frac{[V - (R + V')] \cdot 100}{V} = \text{per cent } CO_2.$$

Remark. — In the first edition of this book the mixture of chlorine and carbon dioxide was absorbed by means of 5 per cent caustic soda solution and the solution titrated with arsenious acid. This method is not entirely correct, however, because it is based upon the assumption that the chlorine is absorbed by the alkali in accordance with the equation,

$$2\,NaOH + Cl_2 = NaCl + NaClO + H_2O,$$

whereas in reality there is always some chlorate formed and escapes the titration.* Offerhaus, † therefore, uses two burets for the determination, absorbing the chlorine and carbon dioxide in one by means of caustic potash solution, and absorbing the chlorine in another sample of gas by means of potassium iodide and then titrating with 0.1 N thiosulfate solution.

This is, however, an unnecessary complication, for besides requiring an additional buret it involves the use of more of the expensive potassium iodide. It is possible, however, to carry out the analysis in one buret by absorbing first the chlorine with 10 per cent potassium iodide solution, and then introducing caustic potash solution from the top of the buret. Hereby the carbon dioxide is absorbed and the iodine is transformed into iodide and iodate (the solution becomes nearly colorless):

$$Cl_2 + 2\,KI = 2\,KCl + I_2,$$
$$3\,I_2 + 6\,KOH = 5\,KI + KIO_3 + 3\,H_2O.$$

To determine the amount of iodine originally set free, allow the contents of the buret to flow into a potassium iodide solution which is acid with hydrochloric acid:

$$5\,KI + KIO_3 + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2,$$

* The error here is practically constant and amounts to 0.77 per cent chlorine. The work can be carried out according to the original method, adding, for the sake of accuracy, 0.7 per cent to the value of chlorine found. Cf. O. Steiner, *loc. cit.*, and Treadwell and Christie, *loc. cit.*

If the weight of chlorine found by titration is used in connection with the theoretical molecular volume, a considerable error will be introduced for, in spite of the formation of chlorate, about 0.9 per cent too much chlorine will be found in electrolytic chlorine.

† Cl. Winkler (Industriegase II, 318) and Offerhaus (*Z. angew. Chem.*, **1903**, 1033), also Lunge-Berl, *Chem. techn. Untersuchungsmethoden*, 6th edition, Vol. I, p. 582, and O. Steiner, *Z. Elektrochemie*, **1904**, 327.

and titrate the liberated iodine with 0.1 N sodium thiosulfate solution.

The method has no advantage over that described above but is just as accurate.

Schloetter* has described another method for the examination of electrolytic chlorine gas. The chlorine is absorbed by means of hydrazine sulfate, whereby 2 volumes of chlorine set free 1 volume of nitrogen. The carbon dioxide is then absorbed by means of caustic soda solution.

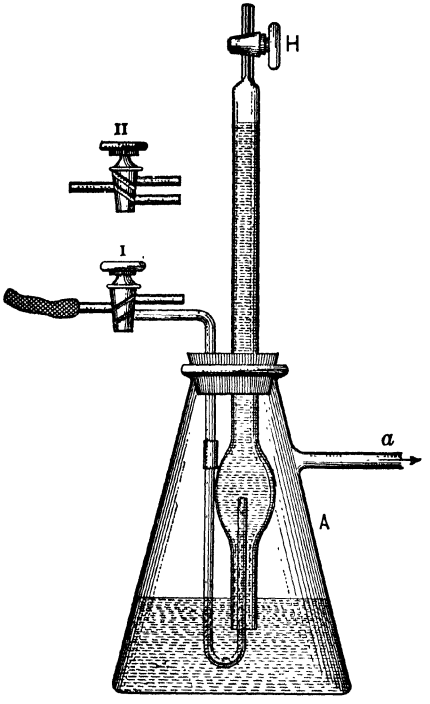


FIG. 150.

P. Ferchland† determines the chlorine by absorption with mercury in the residual gas after the CO_2 has been absorbed with caustic potash. This last method, according to the experiments of Busvold,‡ gives good results; it is to be recommended especially for the analysis of chlorine gas from the Deacon process.

Examination of the Unabsorbed Gas Residue. — Usually the residual gas is too small in amount (as in the above case) to examine quantitatively, so that for this part of the analysis a larger sample of the gas should be taken. The apparatus shown in Fig. 150§ has been used for this purpose with good results. The thick-walled filter-bottle A has a capacity of about 1.5 liters. It contains about 500 ml. of strong caustic potash solution and the absorption-tube with stop-cock H is fastened air-tight within it.

Manipulation. — First fill the absorption-tube with the caustic potash solution by suction through H finally closing the latter. Then turn

* *Z. angew. Chem.*, **1904**, 301.

† *Z. Elektrochem.*, **13**, 114.

‡ *Inaug. Dissert.*, Zurich, 1909, also P. Philosophoff. *Chem. Ztg.*, **1907**, 959.

§ This apparatus has been used often by the author in the study of electrolytic chlorine gas and was described first in this text-book. Since then a similar apparatus has been recommended by Thiele and Deckert, *Z. angew. Chem.*, **20**, 437 (1907).

the patent cock to the position *II*, and by suction through the left side-arm, fill the glass tube with the caustic alkali solution up to the cock. Turn the latter to the position *I*, connect the left side-arm, by means of a short piece of rubber tubing and a long piece of glass tubing, with the source of the gas and aspirate several liters of gas through this tube. As soon as it is safe to assume that all of the air has been driven out from the tubing turn the cock to the position *II*, connect the aspirator at *a* with the flask *A* in which a slight vacuum is produced, whereby the gas begins to collect in the absorption-tube. Chlorine and carbon dioxide are completely absorbed, while the residual gas collects in the upper part of the absorption-tube. Allow the gas to enter the tube until from 50–70 ml. of the gas residue are obtained; Then close the cock *I*, remove the aspirator, drive the gas over into a Hempel's gas-buret and analyze according to the methods already described.

60.9 ml. of the gas residue from electrolytic chlorine containing 99.0 per cent Cl_2 and 0.6 per cent CO_2, gave:

Oxygen	= 40.7			O_2	= 66.9
Carbon monoxide	= 2.6	and in per cent		CO	= 4.3
Nitrogen	= 17.6			N_2	= 28.8
	60.9				100.0

At the carbon electrode (the anode) not only chlorine but also a small amount of oxygen is liberated. The latter attacks the carbon of the electrode, forming carbon monoxide, the greater part of which in turn combines with the chlorine, forming phosgene gas, $COCl_2$, but the latter is decomposed by water with the formation of CO_2 and HCl:

$$COCl_2 + H_2O = CO_2 + 2\,HCl.$$

This accounts for the presence of the CO_2 and CO in chlorine which has been prepared electrolytically.

2. Hydrochloric Acid HCl. Mol. Wt. 36.47

Density = 1.2686 (Air = 1).* Weight of one liter = 1.6400 g.
Molar volume = 22.24 l. Critical temperature = +52° C.

Hydrochloric acid is determined in gas mixtures by absorption in standardized alkali hydroxide solution.

---

* Leduc, *Compt. rend.*, **125**, 571 (1897), found the density of hydrogen to be 1.2692 and Busvold, *Inaug. Dissert.* Zurich, 1910, obtained the value 1.2680. The above figure is the mean of these two determinations.

3. Sulfur Dioxide. Mol. Wt. 64.07

Density = 2.2639 (Air = 1).* Weight of one liter = 2.9267 g.
Molar volume = 21.89 l. Critical temperature = +155° C.

For the determination of sulfur dioxide from pyrite burners, F. Reich recommends that the gas should be drawn by means of an aspirator through a measured amount of 0.1 N iodine solution, colored blue with starch, until the latter is decolorized. The amount of the gas is equal to the quantity of water which has flowed from the aspirator + the volume of the absorbed SO_2.

For example, 10 ml. of 0.1 N iodine solution were decolorized after V ml. of water had flowed from the aspirator; the gas was at $t°$ C. and 760 mm. pressure. Since in the absorption of the SO_2 by the iodine the following reaction takes place,

$$SO_2 + H_2O + I_2 = 2\,HI + SO_3,$$

it is evident that the amount of SO_2 absorbed, measured dry at 0° and 760 mm. pressure, was 10.95 ml., for 1 ml. 0.1 N iodine solution corresponds to 1.095 ml. SO_2.

It follows, then, that the volume of gas taken for the analysis equals

$$\frac{V \cdot (B - w) \cdot 273}{760 \cdot (273 + t)} + 10.95 \text{ ml.} = V_1,$$

and the original gas contained $\frac{1095}{V_1}$ per cent SO_2.

Other examples of gas analyses in which the absorbed constituent is estimated by titration are found in the determination of the hydrogen sulfide in gas mixtures (see below) and in the determination of carbonic acid in the atmosphere by the method of Pettenkofer (cf. p. 508).

4. Hydrogen Sulfide, H_2S. Mol. Wt. 34.08

Density = 1.1895 (Air = 1).† Weight of one liter = 1.5378 g.
Molar volume = 22.16 l. Critical temperature = 100° C.

Determination of Hydrogen Sulfide in Gas Mixtures

Hydrogen sulfide, when present in the gases escaping from mineral springs, can be estimated as follows:

Lower a large funnel of 2–3 liters capacity, into the spring and hold it in place by means of a wooden frame B weighted with stones, s (Fig. 151). Remove the rubber tubing d from the flask a, open the stop-

* Leduc, *Compt. rend.*, **117**, 219 (1893).
† Leduc, *Compt.. rend..*, **125**, 571 (1897).

cock h, and fill the funnel T by means of suction, with water up to the stopper, and then close h. As soon as the water in the funnel has been replaced by the ascending bubbles of gas, connect the flask a on one side with the stop-cock tube h and on the other side directly with the aspirator A by means of a long rubber tubing. Start suction by opening H and continue aspirating with h open until the water in the funnel T again reaches the stopper, then close h. Allow the funnel to fill with gas again, and eventually remove this through a by means of suction. Repeat this operation twice more. In this way the neck of the funnel, the glass tube h, the rubber tubing d, and the flask a, all have the air originally present in them replaced by gas from the spring; a few drops of water are carried along mechanically into a. Introduce 10 ml. of 0.01 N iodine solution into the ten-bulb tube b and place 10 ml. of 0.01 thiosulfate solution in the tube c. Quickly connect the flask a with b by

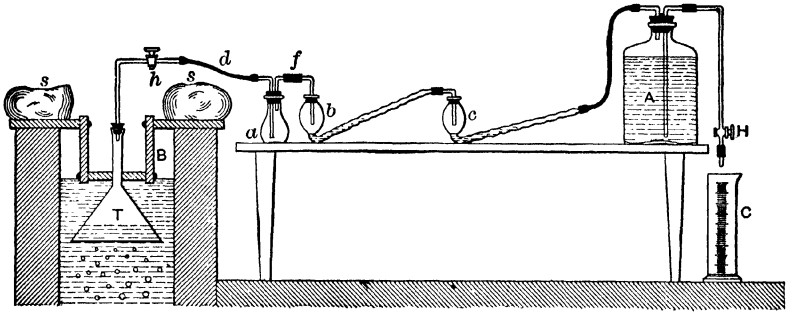


FIG. 151.

means of a short piece of rubber tubing f, and connect c with the aspirator A by means of a longer piece of tubing. Meanwhile the funnel T is again filling with gas. Place a measuring cylinder, C, under the outlet tube of the bottle A, open H, and cautiously turn the stop-cock h. Allow the gas to bubble slowly through b until the iodine solution becomes light yellow, but is not decolorized. Now close H and after about 2 minutes h also. Pour the contents of c into b, add starch and titrate the excess of the thiosulfate with 0.01 N iodine solution (cf. p. 583). The number of milliliters, n, of iodine required for the titration, represents the amount of iodine which reacted originally with the hydrogen sulfide. The position of the water in the graduate (V ml.), the temperature of the room $t°$, and the barometer reading B are all noted; w is the tension of aqueous vapor at the temperature $t°$.

In computing the amount of hydrogen sulfide in the gases escaping from the spring, it is to be remembered that the volume of gas which

is taken for the analysis is equal to the amount of water which has flowed into c plus the volume of hydrogen sulfide which has been absorbed by the iodine in b during the experiment. Inasmuch, however, as the amount of the latter is small in comparison with the total amount of gas taken for analysis, it may be neglected here. Furthermore, it is necessary to call attention to the fact that the volume of gas escaping from the spring is at a different temperature than that of the analysis; all the volumes, therefore, should be reduced to correspond to the temperature at the spring. The amount of hydrogen sulfide present per liter in the spring gases at the temperature $t°$ and the barometric pressure B is

$$308.4 \frac{n\,(273 + t)}{V\,(B - w)} = \text{ml. } H_2S \text{ per liter.}*$$

5. Determination of Ethylene, according to Haber

The principle of this method was discussed on p. 651. The determination is effected in the Bunte buret (cf. p. 681, Fig. 148).

First, determine the contents of the lower portion of the buret from the lowest scale division to the cock by weighing the water drawn from between these points, after allowing the buret to drain. Then introduce about 90 ml. of the gas to be examined into the buret and take the thermometer and barometer readings. Then, exactly as described on p. 681, draw down the liquid by suction to the stop-cock, † pour a little bromine water into a small evaporating-dish, allow about 10 ml. of the liquid to rise into the buret, and, in order to wash the bromine water from the tip into the buret, add 2 or 3 ml. of water.

Thoroughly wet the walls of the buret with the bromine water, by suitably turning and inclining the tube; in this way the ethylene is quickly absorbed. To determine the excess of bromine, allow a strong solution of potassium iodide to rise into the buret and vigorously shake. Run out the liquid into an Erlenmeyer flask, carefully wash the buret with water and titrate the deposited iodine with 0.1 N sodium thiosulfate solution. Determine the titer of the bromine water by pouring a little into a porcelain dish, pipeting off 10 ml. of it, allowing this amount to run into a solution of potassium iodide and titrating the liberated iodine with 0.1 N sodium thiosulfate solution.

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* In this formula the temperature of the spring does not come into consideration because the gas is at the laboratory temperature when measured. The volume V is expressed in liters.

† After about one minute liquid will collect above the stop-cock, owing to the drainage of the liquid from the sides of the buret; this is removed before adding the bromine.

The method of calculating the results will be illustrated best by means of an example.

Example. — A gas consisting of 90 volumes of air and 10 volumes of ethylene was used for the analysis. Taken for analysis, 91.2 ml. of the mixture. Temperature, 18.3°. Barometer reading, 725 mm. Tension of aqueous vapor at 18.3° = 15.6 mm. mercury.

Volume of the ungraduated portion of the buret	6.10 ml.
Reading of the bromine water in the graduated part.....	10.00 ml.
Bromine water used	16.10 ml.

Titer of the bromine water:

10 ml. of the bromine water correspond to 12.0 ml. 0.1 *N* sodium thiosulfate solution, so that 16.10 ml. of bromine water are equivalent to 19.32 ml. of 0.1 *N* sodium thiosulfate.

We have now:

16.1 ml. bromine water.....	= 19.32 ml. 0.1 *N* solution.
16.1 ml. bromine water + ethylene.....	= 12.23 ml. 0.1 *N* solution.
The ethylene corresponds to.....	7.09 ml. 0.1 *N* solution.

Since the absorption of the ethylene by the bromine water takes place according to the equation

$$C_2H_4 + Br_2 = C_2H_4Br_2$$

it follows that

2 Br = 2 I = 20,000 ml. 0.1 *N* sodium thiosulfate solution = 22,270* ml. ethylene gas. Since 1 ml. 0.1 *N* sodium thiosulfate corresponds to 1.114 ml. C_2H_4, the 7.09 ml. of 0.1 *N* solution used represent 7.09 × 1.110 = 7.94 ml. C_2H_4 at 0° C. and 760 mm. pressure, or 9.10 ml. C_2H_4 at 18.3° C. and 725 mm., measured moist.

The gas consists, therefore, of:

C_2H_4 = 9.1		C_2H_4 = 10.0 per cent.	
Air = 82.1	and in per cent	Air = 90.0 per cent.	
91.2		100.0 per cent.	

This method is especially suited for the determination of ethylene present with benzene in illuminating-gas. In one sample the sum of the two gases can be determined by absorption with fuming sulfuric acid or bromine water, and in a second sample the ethylene as described above.

Remark. — Instead of using bromine water, which changes its strength so rapidly, it is better to use a tenth-normal solution of potassium bromate; on acidifying an equivalent quantity of bromine is obtained.

The experiment is carried out as follows: Exactly as described above, introduce 90 ml. of the gas into the Bunte buret, withdraw the water till the lower cock is reached, place some potassium bromate in a small porcelain dish, draw up about 10 ml. of it into the buret

* Cf. p. 647.

and determine the volume. Then, after wiping off the lower capillary, add an excess of concentrated potassium bromide solution and finally introduce an excess of dilute hydrochloric acid. After shaking 8 minutes, all the ethylene will be brominated. At the end of this time, allow 10 per cent potassium iodide solution to enter the buret, shake and empty into an Erlenmeyer flask. Titrate the iodine thus liberated with 0.1 *N* sodium thiosulfate solution. The calculation is carried out as before.

6. Determination of Ethylene in the Presence of Acetylene

In one sample determine the sum of the ethylene and acetylene by absorption in fuming sulfuric acid and determine the ethylene by the bromate-bromide absorption method, just described. In the cold, acetylene is not absorbed by dilute bromine water and this method is suitable for determining ethylene in the presence of small quantities of acetylene. If considerable acetylene is present some acetylene is likely to be absorbed.

The acetylene, however, may be removed by means of a 20 per cent solution of mercuric cyanide in 2 *N* sodium hydroxide. Use 10 ml. of the solution for each 50 ml. of the gas mixture. Have the absorbent over the mercury in an absorption pipet. After the removal of the acetylene, ethylene can be removed by the following reagent: — Dissolve 20 g. $Hg(NO_3)_2$ in 100 ml. of 2 *N* HNO_3 and saturate the solution with $NaNO_3$. Use 5 ml. of the absorbent over mercury for the absorption of ethylene. After this benzene can be absorbed in fuming sulfuric acid and then CO, CH_4 and H_2 in the usual way.

Gas-volumetric Methods

If as a result of a chemical reaction a gas is evolved, from the volume of the latter the weight of the original substance can be computed.

Examples of this sort of an analysis were given under the determination of CO_2 in carbonates (pp. 338, 340, 344, 346), the carbon contents of iron and steel (pp. 358 and 360), and the NO_3 in nitrates (p. 393).

At this place a few more important determinations of the same nature will be described.

1. Determination of Ammonia in Ammonium Salts

The following method, first proposed by Knop* and later modified by P. Wagner,† depends upon the fact that ammonia is oxidized by sodium hypobromite with evolution of nitrogen:

$$2\,NH_3 + 3\,NaOBr = 3\,H_2O + 3\,NaBr + N_2.$$

* *Chem. Centralbl.*, 1860, p. 243.

† *Zeitschr. f. anal. Chem.*, XIII (1874), p. 383; XV (1876), p. 250.

The nitrogen is collected in an azotometer and measured.

If the amount of the ammonia is calculated from the volume of the nitrogen, too low results will be obtained, and this fact was formerly explained by the assumption that a part of the nitrogen was absorbed as such by the alkaline bromite solution. This is not true. At ordinary temperatures all of the ammonia is not oxidized according to the above equation to water and nitrogen, but a small quantity of ammonium hypobromite is formed; for this reason too little nitrogen is obtained in the azotometer. If, on the other hand, the decomposition takes place at 100°, the reaction goes quantitatively according to the equation. It is inconvenient to work at such a high temperature, so that it is more practical to make a correction to the volume of nitrogen obtained at ordinary temperatures.

Reagents and apparatus required:

1. An *ammonium chloride solution*, obtained by dissolving 8.356 g. of the pure sublimed salt in water and diluting to 500 ml. 10 ml. of this solution evolve at 0° C. and 760 mm. pressure 35 ml. of nitrogen.

2. *Sodium hypobromite solution.* Dissolve 100 g. of sodium hydroxide in water, dilute to 1250 ml. and after cooling the flask in cold water, add 25 ml. of bromine, vigorously shake the contents of the flask and again cool.

This solution must be preserved in a stoppered bottle and protected from the action of light.

3. An azotometer. Instead of Wagner's* azotometer Lunge's Universal Apparatus (Fig. 71, *b*, p. 341), or any such measuring instrument may be used.

Procedure. — Place 10 ml. of the standard ammonium chloride solution in the small Wagner decomposition-bottle (Fig. 71, *a*, p. 341) and pour 40–50 ml. of the hypobromite solution into the glass *L* (which is fused to the bottom of the bottle *H*). Then connect the bottle with the measuring-tube *A*,† which is entirely filled with mercury, open *b* and lower the leveling-tube *B*. Incline the bottle *H* so that some of the hypobromite solution comes in contact with the solution of ammonium chloride and mix the two liquids by gentle shaking. A lively evolution of nitrogen at once takes place and the liquid becomes heated. As soon as the action ceases, allow fresh hypobromite solution to act upon the ammonium salt and repeat the process until finally all of the hypobromite is in the outer part of *H*. As soon as no more gas is evolved by shaking, place the decomposition-bottle in water at the room temperature and after allowing it to stand 10 minutes, read the volume of the nitrogen under the conditions described on p. 343. The

* *Loc. cit.*

† The contents of the decomposition-bottle are previously cooled to the room temperature before the cock *b* is connected with it.

volume of nitrogen at 0° and 760 mm. thus found will be smaller than the theoretical value of 35 ml., but it corresponds to the amount of ammonia contained in 10 ml., of the ammonium chloride solution, *i.e.*, 0.05320 g. NH_3.

Carry out a number of several determinations and take the mean of the results obtained for the correct value.

After this, weigh out some of the ammonium salt to be analyzed, dissolve in water, and dilute so that 10 ml. of the solution will contain approximately the same amount of ammonia as in the case of the standard solution. Then if, for example, from a g. of an ammonium salt, V_1 ml. of nitrogen at 0° and 760 mm. pressure were found, and V ml. were obtained from 0.05320 g. of NH_3 in the standardization, then

$$\frac{V_1 \times 5.320}{V \cdot a} = \text{per cent } NH_3.*$$

Remark. — The results obtained by this method agree with those obtained by the distillation method described on p. 483. Only with substances containing thiocyanates are the results obtained too high; in this case the thiocyanate is decomposed by the alkaline hypobromite solution with evolution of nitrogen and carbon monoxide.†

Consequently, the above method affords uncertain results in the analysis of the ammonia in gas liquors.

Urea is decomposed by the alkaline hypobromite solution according to the equation:

$$CO(NH_2)_2 + 3\ NaOBr = 3\ NaBr + CO_2 + N_2 + 2\ H_2O.‡$$

so that it can be determined in the same way as ammonium salts, the carbon dioxide produced by the decomposition being kept back by means of caustic soda solution.

2. Determination of Nitrous and Nitric Acids

Principle. — If a solution of a nitrite or nitrate is shaken with mercury and an excess of sulfuric acid, all of the nitrogen is set free as nitric oxide:

$$2\ HNO_2 + 2\ Hg + H_2SO_4 = 2\ H_2O + Hg_2SO_4 + 2\ NO,$$
$$2\ HNO_3 + 6\ Hg + 3\ H_2SO_4 = 4\ H_2O + 3\ Hg_2SO_4 + 2\ NO.$$

From the volume of the nitric oxide, the weight of the nitrate or nitrite is computed.

---

* Lunge (Lunge-Berl, *Chem. techn. Untersuchungsmethoden*) does not standardize against the solution of ammonium chloride of known strength, but adds 2.2 per cent more ammonia to correspond to the loss of nitrogen. Then $V \times 0.001558$ = g. ammonia.

† Donath and Pollak, *Z. angew. Chem.*, **1897**, 555.

‡ This reaction does not take place as completely as with ammonium salts. Lunge finds in the determination of urea in urine that the nitrogen deficit is 9 per cent. If, therefore, the volume of nitrogen after being reduced to 0° and 760 mm. is multiplied by 2.952, the correct urea value is obtained.

The analysis is best performed in a Lunge nitrometer.* The latter is a Bunte buret in which the lower stop-cock is lacking and the lower end is connected with a leveling-tube containing mercury. By raising the latter, completely fill the nitrometer (which need not be graduated) with mercury and then close the two-way cock under the funnel. Place a weighed amount of the substance dissolved in a little water in the funnel, lower the leveling-tube, and introduce the solution into the nitrometer by carefully opening the cock. Wash out the funnel 4 times with 2–3 ml. of concentrated sulfuric acid. Now remove the decomposition-tube from the frame, place it several times in a nearly horizontal position and then quickly change to a vertical position. By this means the mercury becomes intimately mixed with the acid and the decomposition at once begins. Continue mixing 1–2 minutes until there seems to be no further increase in the volume of the liberated gas. Then connect the decomposition vessel by means of a short piece of rubber tubing with the gas-buret filled with mercury, transfer the nitric oxide to the latter, and read its volume after reducing it to the standard conditions by means of the gas-compensation tube. (Cf. p. 341, Fig. 72, *b*.)

If in an analysis, a g. of a nitrate were taken and V_0 ml. corresponds to the volume of NO at 0° and 760 mm., we have:

$$x = \frac{V_0 \times 62.01}{22391} \text{ g. } NO_3$$

and in per cent:

$$\frac{6201}{22391} \times \frac{V_0}{a} = 0.2769 \times \frac{V_0}{a} = \text{per cent } NO_3.$$

Remark. — For the analysis of "nitrose," the author knows of no method which gives such exact results.

For the determination of nitrous acid in the presence of nitric acid by a gas-volumetric method, P. Gerlinger† treats the neutral solution of the two salts with a concentrated solution of ammonium chloride, whereby the following reaction takes place:

$$NH_4Cl + KNO_2 = 2\,H_2O + KCl + N_2.$$

Half of the nitrogen evolved, therefore, comes from the nitrous acid present.

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* *Ber.*, **1890**, 440, and *Z. angew. Chem.*, **1890**, 139. See also Lunge-Berl, *Chem. techn. Untersuchungsmethoden.*

† *Z. angew. Chem.*, **1901**, 1250. Cf. J. Gaihlot, *J. Pharm. Chem.*, **1900**, 9.

Hydrogen Peroxide Methods

Hydrogen peroxide in many cases acts as an *oxidizing* agent, in other cases it has a marked *reducing* action, and by shaking with inert solids it is decomposed slowly into water and oxygen.

This anomalous behavior can be explained very easily by assuming that one of the oxygen atoms in hydrogen peroxide has one positive and one negative charge as valence bonds.

When hydrogen peroxide decomposes spontaneously on standing, a reaction which is often aided by shaking with an inert substance, such as sand, this neutral oxygen atom is lost and oxygen molecules are formed. When hydrogen peroxide acts as an *oxidizing agent*, this neutral oxygen atom is reduced to its normal negative valence of two. When hydrogen peroxide acts as a *reducing agent*, gaseous oxygen is always one of the products of the reaction. It is usually assumed that half of the evolved oxygen comes from the oxidizing agent and half from the hydrogen peroxide. Thus

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ = 2\,Mn^{++} + 8\,H_2O + 5\,O_2.$$

In the two following methods which involve the use of hydrogen peroxide, a large excess of the peroxide should not be used and long-continued shaking should be avoided.

(a) Standardization of Permanganate Solutions

The determination is best made according to Lunge in a gas volumeter (p. 341, Fig. 72). To obtain correct results, however, it is absolutely necessary that no excess of hydrogen peroxide be present. Consequently it is necessary to determine by means of a preliminary experiment the exact value of the permanganate solution in terms of the H_2O solution used (cf. p. 533). Then place a measured amount of the latter in the outside part of the Wagner decomposition-bottle (Fig. 72*a*, p. 341), and add 30 ml. of 6 *N* sulfuric acid. After this, introduce the exact amount of hydrogen peroxide required for the decomposition of the permanganate into the inner part of the bottle and connect the latter with the measuring-tube, which is filled with mercury, the cock *b* being removed for the time being, but it is replaced at the end of 2–3 minutes and turned to the position shown in the figure.

Then mix the two liquids, taking care to hold the decomposition-flask so that its contents will not be warmed by the heat of the hand, inclining it to an angle of about 90° and shaking for exactly one minute. While the oxygen is being evolved, care must be taken that the gas in the eudiometer is under reduced pressure. After the decomposition

is accomplished, place the gas under atmospheric pressure, close *b*, and by means of the compensation-tube, reduce the volume of the gas to what it would be at 0° C. and 760 mm. pressure, as described on p. 342.

One-half of the observed volume corresponds to the amount of oxygen given up by the potassium permanganate. This number multiplied by 0.001429 gives the *weight* of the oxygen obtained from the permanganate.

Remark. — The volume of permanganate to be taken for the experiment is determined by the size of the measuring-tube. If the latter has a capacity of 150 ml., 15 ml. of a 0.2 *N* solution or 40–50 ml. of a 0.1 *N* solution should be taken.

The hydrogen peroxide used should not be too concentrated; a 2 per cent solution is suitable. The available oxygen present in a sample of pyrolusite* can be determined by the same procedure.

(b) Determination of Cerium in Soluble Ceric Salts

If hydrogen peroxide is added to an acid solution of a soluble ceric salt, the latter is reduced with evolution of oxygen:

$$2\ Ce^{+++} + H_2O_2 = 2\ Ce^{++} + 2\ H^+ + O_2.$$

The determination is accomplished in precisely the same way as was described above in the standardization of the permanganate solution. If the volume of liberated oxygen is multiplied by 0.01538, the product represents the corresponding amount of CeO_2.†

Remark. — If a large excess of hydrogen peroxide is avoided in the above analysis, satisfactory results will be obtained.

Silicon Fluoride, SiF_4. Mol. Wt. = 104.3

Density = 3.605 (Air = 1). Weight of 1 liter = 4.660 g.
Molar volume = 22.40 l.

Determination of Fluorine as Silicon Fluoride (Hempel and Oettel)‡

Principle. — If a mixture of calcium fluoride and powdered quartz is treated with concentrated sulfuric acid in a glass vessel, all of the fluorine will be expelled as silicon fluoride:

$$2\ CaF_2 + SiO_2 + 2\ H_2SO_4 = 2\ CaSO_4 + 2\ H_2O + SiF_4,$$

and this gas can be collected and measured.

One ml. SiF_4 at 0° and 760 mm. pressure corresponds to 0.006978 g. CaF_2, or 0.003395 g. F_2.

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* Lunge's *Alkali Makers' Handbook.*

† Assuming that the atomic weight of Ce = 140.25.

‡ *Gasanalytische Methoden.*

Procedure. — Mix a weighed amount of the very finely-powdered substance, which must not contain any other acid that can be expelled by treatment with concentrated sulfuric acid,* with 3 g. of finely-powdered ignited quartz and introduce into the *dry* decomposition flask *K* (Fig. 152). Evacuate the latter somewhat by twice lowering the leveling-tube *N* with the stop-cock *H* open, closing the cock and expelling the air. At the beginning of the experiment, the buret *H* should not be connected with the Orsat tube *O*. By raising the ground-glass tube *R*, cause about 30 ml. of concentrated sulfuric acid to flow into the flask. This acid must have been previously heated in a porcelain crucible for some time at a temperature near the boiling-point, to destroy every trace of organic matter, and allowed to cool in a desiccator over phosphorus pentoxide. Heat the acid in *K* to boiling with the stop-cock *H* open and frequently shake. During the entire experiment, keep the mercury level in the tube *N* a little lower than that of the mercury in the measuring-tube *M*.†

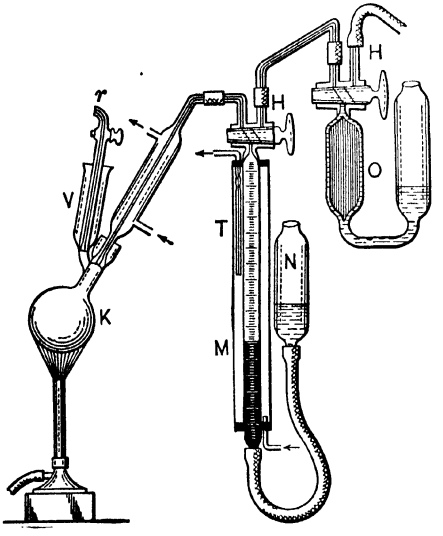


FIG. 152.

At first the sulfuric acid foams considerably, but soon ceases, which is a sure sign that the decomposition is complete. Then remove the flame, allow the sulfuric acid to cool and expel all the gas in *K* by introducing through *V* sulfuric acid, which has been previously heated and cooled as described above. As soon as the sulfuric acid reaches the stop-cock *H*, close it. After waiting 10 minutes more, place the gas under atmospheric pressure, by suitably raising *N*, and note the volume and temperature.

Now drive the gas over into the Orsat tube *O*, containing caustic potash solution (1 : 2). The silicon tetrafluoride is immediately absorbed. Return the residual gas to the tube *M*, and after waiting 15 minutes read the volume. The difference between the two readings gives the volume of silicon tetrafluoride.

* Cf. p. 411.

† To keep the inside of *N* perfectly dry, place 2–3 ml. of concentrated sulfuric acid on top of the mercury.

Remarks. — A. Koch tested this method in the author's laboratory and obtained results varying from 98.97–102.63 per cent with pure calcium fluoride. To obtain this accuracy, however, it is necessary to carry out the decomposition under approximately atmospheric pressure. When working under a vacuum the results were always too low. Thus in one case only 85.70 per cent of the theoretical value was obtained.

During these experiments with reduced pressure, a white sublimate formed at the lower part of the condenser, which on coming in contact with the sulfuric acid that is introduced at the last, caused a strong effervescence. Since, however, all the gas in the buret was replaced, we believed that the low results could be traced to the absorption of silicon fluoride by the sulfuric acid. This idea proved to be false, for a measured volume of silicon fluoride does not change when allowed to stand for 24 hours over concentrated sulfuric acid. The error, therefore, must be caused by the deposit that has condensed in the lower part of the condenser. If the work is carried out under atmospheric pressure as described above, the white deposit is never obtained.

The method can be used for the estimation of fluorine in the presence of carbonates. In this case the silicon fluoride is absorbed by means of a little water and the carbon dioxide by means of caustic potash. As, however, a little of the carbon dioxide is dissolved by the water, the gas residue which has been freed from carbon dioxide is shaken with this water again, whereby this dissolved carbon dioxide is removed and can be absorbed by a further treatment with caustic potash solution. For further details, consult the original paper by Hempel and Scheffler.*

Determination of Water Vapor in Gas Mixtures

In gas analysis it is a common practice to express the results in percentages by volume. Thus if a mixture of oxygen and carbon dioxide measures V_1 ml. under atmospheric pressure and after the carbon dioxide has been absorbed the residual gas measures V_2 ml. under the same pressure, it is customary to assume that the original gas contained $V_1 - V_2$ ml. of CO_2 and V_2 ml. of oxygen. A little consideration will show that this is really an inexact assumption although it is true that the original mixture could be obtained by mixing the indicated volumes of carbon dioxide and oxygen.

When two or more gases are mixed, each occupies the total volume of the mixture. This is an apparent contradiction because two bodies cannot occupy the same space. In the case of a gas, however, the actual volume taken up by the molecules is very small compared to the total volume occupied by the gas and it is customary to neglect it in gas analysis. Thus at 0° and 1 mm. pressure, 1 liter of hydrogen gas contains only 0.16 ml. of space actually occupied by hydrogen molecules. Under higher pressures, the actual volume occupied by the molecules becomes less.

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* *Z. anorg. Chem.*, **20**, 1 (1897).

In V ml. of carbon dioxide and oxygen under atmospheric pressure, therefore, there are present V ml. of carbon dioxide and V ml. of oxygen and the pressure of the mixture is the combined pressures of the two gases. In any gas mixture, *the total pressure is the sum of the partial pressures.*

In a mixture of two gases, the percentage composition can be easily computed if the volume of the gas mixture is known under a definite pressure and temperature and, at the same time, the partial pressure of one of the gases is known. Moreover, the ratio of the partial pressures of the gases shows the relative volumes provided the gases were measured singly under the same pressure and at the same temperature.

Applications. — 1. *Reduction of Volumes of Moist Gases to a dry condition at* 0° *and* 760 *mm.* If a gas is saturated with water vapor at any temperature, the partial pressure exerted by the water is known. Water evaporates until the vapor pressure of the liquid water is exactly balanced by the gas pressure exerted by the evaporated water and this is independent of whether other gases are present or not. The table on pages 728–730 gives the vapor pressures of water at various temperatures. If a gas saturated with water vapor occupies a volume V_t at $t°$ and P mm. pressure (of liquid mercury) and w is the tension of aqueous vapor at this temperature, then the volume occupied by the dry gas at 0° and 760 mm. pressure would be $V_0 = V_t \frac{(P - w)\ 273}{760\ (273 + t)}$.

2. *Calculation of the Moisture in the Air at Normal Pressure* (760 *mm.*) *and Temperature* $t°$.

What is the percentage of moisture (by volume) of air saturated with moisture at 0°, 25° and 35°? According to the table: $w_0 = 4.6$ mm.; $w_{25} = 23.5$ mm.; and $w_{35} = 41.8$ mm. By dividing each of these values by 760 and multiplying by 100, we find the percentage of moisture to be 0.61 per cent at 0°; 3.09 per cent at 25° and 5.50 per cent at 35°.

If the gas is not saturated with moisture, the relation of the dry gas to the moist one can be computed if the degree of saturation, or *humidity* is known. The humidity of the gas expresses the amount of moisture as a percentage of the amount that the gas contains when saturated with moisture. Thus if the humidity is 50 per cent, the gas could take up just as much more water at the prevailing temperature. If the humidity is r, then if the given gas were measured dry at 760 mm. and at the same temperature, its volume would be $\frac{V\ (P - r \cdot w)}{760}$ and if it were possible for the water vapor to exist as gas at 760 mm. pressure and the same temperature, its volume would be $\frac{V \cdot r \cdot w}{760}$.

3. *Calculation of the Weight of Water-vapor in a Given Volume of Air* at $t°$ and P mm. pressure, which is saturated with moisture.

If 1 ml. of water could exist as a gas at 0° and 760 mm. pressure, it ought to weigh 0.000801 g. as an ideal gas. At $t°$ and P mm. pressure, it should weigh

$$\frac{0.000801 \times P \times 273}{760 \times (273 + t)} \text{ g.}$$

If the gas is not saturated with water vapor, but the degree of saturation (the humidity) is known, then the following formula gives the weight of water-vapor present in the volume v_t of the gas,

$$\frac{0.00801 \cdot r \cdot w \cdot v_t \cdot 273}{760\,(273 + t)} \text{ g.}$$

Or, if the weight of vapor present in a given gas volume is known, then from the last equation the humidity, r, of gas may be computed:

$$r = \frac{g \cdot 760\,(273 + t)}{0.000801 \cdot w \cdot v_t \cdot 273}.$$

Density Tables

One of the easiest methods for determining the percentage composition of a solution containing only one dissolved substance is to determine the density of the solution. This, however, is not a reliable method of analysis because the density of a solution is never strictly proportional to the quantity of dissolved substance and if a density curve is plotted for all possible concentrations, it will sometimes be found that there are, at certain parts of the curve, two different concentrations that have the same density.

Instead of determining the *density* of a solution, or weight of the unit volume, it is often customary to determine the weight of the solution as compared to the weight of the same volume of another liquid. Water is commonly taken as the basis of comparison and since 1 ml. of water at 4° weighs 1 g., the specific gravity when referred to water at this temperature is the same as the density, when this is defined as the weight in grams of 1 cubic centimeter of water.

Unfortunately, however, usage has not been uniform in the choice of temperature at which the specific gravities have been taken and the comparison is often made with water at the same temperature.

The extensive application of hydrometers as measuring instruments in the collection of revenues in commerce and for buying and selling certain liquids has led the U. S. Bureau of Standards to define the vari-

ous scales in terms of fundamental units. Some of the tables in this book are taken from this source. About 15 years previously the Manufacturing Chemists' Association of the United States published tables, which have been copied in quite a number of text-books, in which the specific gravities were taken at 60° Fahrenheit and referred to water at the same temperature.

Whenever a specific gravity value is given, the *modulus* should also be stated. Thus a specific gravity at $\frac{60°}{60°}$ F. means that the comparison was made at 60° F. with water at the same temperature and $\frac{15°}{4°}$ C. means that the comparison was made at 15° C. with water at 4° C.

The confusion, however, does not end here. Just as certain civilized countries, particularly England and the United States, have been slow to adopt the metric system, so the people of most countries have held tenaciously to other scales for determining relative masses of equal volumes of liquids. Thus the English Twaddle scale and the various French Baumé scales are still in constant use. Throughout the text of this book, the metric system has been used for the sake of simplicity and, as far as the analytical chemist is concerned, density tables are, on the whole, more satisfactory than specific gravity tables. Data will be given, however, showing how these tables can be translated into other units.

TABLE 1. — DENSITY OF PURE WATER FREE FROM AIR

[Under standard pressure (76 cm.), at every tenth part of a degree of the international hydrogen scale from 0° to 41° C., in grams per milliliter[1]]

Degrees Centigrade	Tenths of Degrees										Mean Differences
	0	1	2	3	4	5	6	7	8	9	
0	0 999 8681	8747	8812	8875	8936	8996	9053	9109	9163	9216	+ 59
1	9267	9315	9363	9408	9452	9494	9534	9573	9610	9645	+ 41
2	9679	9711	9741	9769	9796	9821	9844	9866	9887	9905	+ 24
3	9922	9937	9951	9962	9973	9981	9988	9994	9998	*0000	+ 8
4	1.000 0000	*9999	*9996	*9992	*9986	*9979	*9970	*9960	*9947	*9934	− 8
5	0 999 9919	9902	9884	9864	9842	9819	9795	9769	9742	9713	− 24
6	9682	9650	9617	9582	9545	9507	9468	9427	9385	9341	− 39
7	9296	9249	9201	9151	9100	9048	8994	8938	8881	8823	− 53
8	8764	8703	8641	8577	8512	8445	8377	8308	8237	8165	− 67
9	8091	8017	7940	7863	7784	7704	7622	7539	7455	7369	− 81
10	7282	7194	7105	7014	6921	6826	6729	6632	6533	6432	− 95
11	6331	6228	6124	6020	5913	5805	5696	5586	5474	5362	−108
12	5248	5132	5016	4898	4780	4660	4538	4415	4291	4166	−121
13	4040	3912	3784	3654	3523	3391	3257	3122	2986	2850	−133
14	2712	2572	2431	2289	2147	2003	1858	1711	1564	1416	−145
15	1266	1114	0962	0809	0655	0499	0343	0185	0026	*9865	−156
16	0.998 9705	9542	9378	9214	9048	8881	8713	8544	8373	8202	−168
17	8029	7856	7681	7505	7328	7150	6971	6791	6610	6427	−178
18	6244	6058	5873	5686	5498	5309	5119	4927	4735	4541	−190
19	4347	4152	3955	3757	3558	3358	3158	2955	2752	2549	−200
20	2343	2137	1930	1722	1511	1301	1090	0878	0663	0449	−211
21	0233	0016	*9799	*9580	*9359	*9139	*8917	*8694	*8470	*8245	−231
22	0.997 8019	7792	7564	7335	7104	6873	6641	6408	6173	5938	−232
23	5702	5466	5227	4988	4747	4506	4264	4021	3777	3531	−242
24	3286	3039	2790	2541	2291	2040	1788	1535	1280	1026	−252
25	0770	0513	0255	*9997	*9736	*9476	*9214	*8951	*8688	*8423	−261
26	0 996 8158	7892	7624	7356	7087	6817	6545	6273	6000	5726	−271
27	5451	5176	4898	4620	4342	4062	3782	3500	3218	2935	−280
28	2652	2366	2080	1793	1505	1217	0928	0637	0346	0053	−289
29	0.995 9761	9466	9171	8876	8579	8282	7983	7684	7383	7083	−298
30	6780	6478	6174	5869	5564	5258	4950	4642	4334	4024	−307
31	3714	3401	3089	2776	2462	2147	1832	1515	1198	0880	−315
32	0561	0241	*9920	*9599	*9276	*8954	*8630	*8304	*7979	*7653	−324
33	0.994 7325	6997	6668	6338	6007	5676	5345	5011	4678	4343	−332
34	4007	3671	3335	2997	2659	2318	1978	1638	1296	0953	−340
35	0610	0267	*9922	*9576	*9230	*8883	*8534	*8186	*7837	*7486	−347
36	0.993 7136	6784	6432	6078	5725	5369	5014	4658	4301	3943	−355
37	3585	3226	2866	2505	2144	1782	1419	1055	0691	0326	−362
38	0 992 9960	9593	9227	8859	8490	8120	7751	7380	7008	6636	−370
39	6263	5890	5516	5140	4765	4389	4011	3634	3255	2876	−377
40	2497	2116	1734	1352	0971	0587	0203	*9818	*9433	*9047	−384
41	0.991 8661										

[1] According to P. Chappuis, Bureau international des Poids et Mesures, Travaux et Mémoires, **13**; 1907.

TABLE 2. — WEIGHT OF 1 GALLON OF WATER

[This table is based on the water densities of P. Chappuis (Bureau International des Poids et Mesures, Travaux et Mémoires, XIII; 1907) for 0° to 40° C., and of M. Thiesen (Wiss. Abh. der Physikalisch-Technischen Reichsanstalt, 4, No. 1; 1904) for 41° to 100° C. The weights in air are for dry air at the same temperature as the water up to 40° C. and at a (corrected) barometric pressure of 760 mm. and against brass weights of 8.4 density at 0° C. Above 40° C. the temperature of the air is assumed to be 20° C., *i.e.*, the water is allowed to cool to 20° C. before the weighings are made. The volumetric computations are based on the relation that 1 liter = 61.023378 cubic inches. The weights corresponding to 15⅝° C. (60° F.) and 16⅔° C. (62° F.) have been included in the table because of the frequent use of these temperatures in engineering and industrial work.]

Temperature, °C.	Weight in Vacuo		Weight in Air	
	Grams	Pounds	Grams	Pounds
0	3784 833	8 34412	3780 520	8.33461
1	5 055	.34461	0.758	.33613
2	5 211	34495	0 930	.33551
3	5 303	.34515	1.037	.33575
4	5 332	.34522	1.082	.33585
5	5.302	.34515	1 067	.33582
6	5.212	.34495	0 992	.33565
7	5 066	.34463	0 861	.33536
8	4.864	.34419	0 675	.33495
9	4.610	.34363	0.435	.33442
10	4 303	.34295	0.144	.33378
11	3.943	.34216	3779 798	.33302
12	3.534	.34125	9.403	.33215
13	3.076	.34025	8 960	.33117
14	2.574	.33914	8 472	.33009
15	2 026	.33793	7 939	.32892
(15⅝) 60° F.	(3781 703)	(8.33722)	(3777 623)	(8.32823)
16	1 435	.33663	7 362	32765
(16⅔) 62° F.	(3781 017)	(8.33571)	(3776.953)	(8 32675)
17	0 801	.33523	6 741	32628
18	0.125	.33374	6.080	.32482
19	3779.407	.33216	5.375	.32327
20	8 649	.33049	4 630	.32162
21	7.850	.32872	3 845	.31989
22	7.012	.32688	3 021	.31808
23	6 135	.32494	2 157	.31617
24	5.220	.32293	1.256	.31419
25	4 268	.32083	0 317	.31212
26	3 279	.31865	3769.341	.30996
27	2 254	31639	8.329	30773
28	1 195	.31405	7.283	30543
29	0.100	.31164	6.201	.30304
30	3768 972	.30915	5.086	.30058
31	7 812	.30659	3.938	.29805
32	6 618	.30396	2.757	.29545
33	5 393	.30126	1.545	.29278
34	4 137	.29849	0.301	.29003
35	2.851	.29566	3759.027	.28723
36	1.536	.29276	7.725	.28436
37	0 192	.28979	6 393	.28142
38	3758 820	.28677	5 033	.27842
39	7.420	.28368	3.645	.27536
40	5 995	.28054	2 232	.27225
41	4.52	.2773	0.53	.2685
42	3.04	.2740	3749.05	.2652
43	1.53	.2707	7.54	.2619
44	3749.98	.2673	5 99	.2585

TABLE 2. — WEIGHT OF 1 GALLON OF WATER — *Continued*

Temperature, °C.	Weight in Vacuo		Weight in Air	
	Grams	Pounds	Grams	Pounds
45	3748 39	8.2638	3744 40	8 2550
46	6 80	2603	2 81	.2515
47	5 21	.2568	1 23	.2480
48	3 54	.2531	3739 56	.2443
49	1.88	.2494	7 90	.2407
50	0 17	.2457	6 20	2369
51	3738 47	.2419	4 50	.2332
52	6 69	.2380	2 72	2292
53	4 95	.2341	0 98	2254
54	3.13	.2301	3729 16	.2214
55	1.32	2261	7 35	.2174
56	3729 46	.2220	5 50	2133
57	7 72	.2182	3 76	2095
58	5.71	.2138	1 75	2051
59	3 82	.2096	3719 86	.2009
60	1 89	2054	7 93	1966
61	3719 92	.2010	5 97	1923
62	7 95	1967	4 00	1880
63	5 95	.1923	2 00	.1835
64	3.90	1877	3709 95	1790
65	1 86	1832	7.91	1745
66	3709 82	1787	5 87	.1700
67	7 73	1741	3 79	165ɔ
68	5 61	1695	1 67	.1608
69	3 49	1648	3699 56	.1561
70	1 33	1600	7 40	.1514
71	3699 14	1552	5 21	.1465
72	6 98	.1504	3 05	1418
73	4 75	1455	0 82	.1369
74	2 52	.1406	3688 59	.1319
75	0 28	1357	6 36	.1270
76	3687 97	1306	4 05	1219
77	5 70	1256	1 78	1169
78	3 39	1205	3679 48	.1119
79	1 05	1153	7 13	1067
80	3678 70	1101	4 79	1015
81	6 32	.1049	2 41	.0963
82	3 93	0996	0 02	.0910
83	1 54	0944	3667 64	.0858
84	3669 12	.0890	5 22	0804
85	6 66	0836	2 76	.0750
86	4 20	.0782	0 31	0696
87	1 70	0727	3657 81	0641
88	3659 21	0672	5 31	0586
89	6 67	.0616	2 78	.0530
90	4 13	.0560	0 25	.0474
91	1 60	0504	3647.71	.0418
92	3649 02	.0447	5 14	.0362
93	6 41	.0390	2.53	.0304
94	3 80	0332	3639.92	.0247
95	1 19	.0274	7.32	.0189
96	3638.54	.0216	4 67	.0131
97	5.85	.0157	1 98	.0072
98	3.20	0098	3629 34	0013
99	0.47	0038	6 61	7 9953
100	3627.79	7 9979	3 93	.9894

TABLE 3. — WEIGHT OF 1 CUBIC FOOT OF WATER

[This table is based on the water densities of P. Chappuis (Bureau International des Poids et Mesures, Travaux et Mémoires, **13**; 1907) for 0° to 40° C., and of M. Thiesen (Wis. Abh. der Physikalisch-Technischen Reichsanstalt, 4, No. 1; 1904) for 41° to 100° C. The weights in air are for dry air at the same temperature as the water up to 40° C. and at a (corrected) barometric pressure of 760 mm. and against brass weights of 8.4 density at 0° C. Above 40° C. the temperature of the air is assumed to be 20° C. *i.e.*, the water is allowed to cool to 20° C. before the weighings are made. The volumetric computations are based on the relation that 1 liter = 1.000027 cubic decimeters and 1 cubic decimeter = 61.023378 cubic inches. The weights corresponding to 15⅝° C. (60° F.) and 16⅔° C. (62° F.) have been included in the table because of the frequent use of these temperatures in engineering and industrial work.]

Temperature, °C.	Weight in Vacuo		Weight in Air	
	Grams	Pounds	Grams	Pounds
0	28312 517	62 4183	28280 254	62 3472
1	14 178	4220	82.033	.3511
2	15 345	.4246	83 321	.3540
3	16 033	4261	84 121	.3557
4	16 250	.4266	84 458	.3565
5	16 025	.4261	84 345	.3562
6	15 352	4246	83 784	.3550
7	14.260	.4222	82 804	.3528
8	12 749	.4189	81 413	.3498
9	10 849	4147	79 618	.3458
10	08 552	.4096	77 441	.3410
11	05 859	.4037	74 853	.3353
12	02 800	3969	71.898	.3288
13	28299 374	3894	68 584	.3215
14	95 619	.3811	64.933	.3134
15	91 519	3720	60 946	3046
(15⅝) 60° F.	(28289 103)	(62 3667)	(28258 58)	(62 2994)
16	87.098	3623	56 630	2951
(16⅔) 62° F.	(28283 971)	(62 3554)	(28253.57)	(62.2884)
17	82 356	3518	51 985	.2849
18	77 299	3407	47 040	.2740
19	71.928	.3289	41.766	.2624
20	66 258	.3164	36 193	.2501
21	60 281	3032	30 321	.2371
22	54 012	.2894	24 157	.2235
23	47 452	2749	17 694	.2093
24	40 607	.2598	10 954	.1944
25	33 485	2441	03 930	.1789
26	26 087	2278	28196 629	.1629
27	18 420	.2109	89.059	.1462
28	10 500	.1934	81 234	.1289
29	02 307	.1754	73.140	.1111
30	28193.869	.1568	64 799	.0927
31	85 191	.1376	56 212	.0737
32	76 259	.1179	47 377	.0543
33	67.096	.0977	38 311	.0343
34	57.700	.0770	29.005	.0138
35	48.080	.0558	19.475	61.9926
36	38 243	.0341	09.735	.9713
37	28 190	.0120	28099 771	.9493
38	17.926	61 9893	89 596	.9269
39	07.454	.9663	79.215	.9040
40	28096 794	.9428	68.645	.8807
41	85.76	.918	55 90	.853
42	74.71	.894	44 86	.828
43	63.39	.869	33.55	.803
44	51.78	.844	21 94	.778

TABLE 4. — DEGREES BAUMÉ, POUNDS PER GALLON, AND GALLONS PER POUND CORRESPONDING TO VARIOUS SPECIFIC GRAVITIES

Specific Gravity 60°/60° F.	Degrees Baumé (Modulus 140)	Pounds per Gallon	Gallons per Pound
0.600	103.33	4.993	0.2003
.610	99.51	5.076	.1970
.620	95.81	5.160	.1938
.630	92.22	5.243	.1907
.640	88.75	5.326	.1877
.650	85.38	5.410	.1848
.660	82.12	5.493	.1820
.670	78.96	5.577	.1793
.680	75.88	5.660	.1767
.690	72.90	5.743	.1741
.700	70.00	5.827	.1716
.710	67.18	5.910	.1692
.720	64.44	5.994	.1668
.730	61.78	6.077	.1646
.740	59.19	6.160	.1623
.750	56.67	6.244	.1602
.760	54.21	6.327	.1580
.770	51.82	6.410	.1560
.780	49.49	6.494	.1540
.790	47.22	6.577	.1520
.800	45.00	6.661	.1501
.810	42.84	6.744	.1483
.820	40.73	6.827	.1465
.830	38.68	6.911	.1447
.840	36.67	6.994	.1430
.850	34.71	7.078	.1413
.860	32.79	7.161	.1396
.870	30.92	7.244	.1380
.880	29.09	7.328	.1365
.890	27.30	7.411	.1349
.900	25.56	7.494	.1334
.910	23.85	7.578	.1320
.920	22.17	7.661	.1305
.930	20.54	7.745	.1291
.940	18.94	7.828	.1278
.950	17.37	7.911	.1264
.960	15.83	7.995	.1251
.970	14.33	8.078	.1238
.980	12.86	8.162	.1225
.990	11.41	8.245	.1213
1.000	10.00	8.328	.1201

TABLE 5. — SPECIFIC GRAVITIES, POUNDS PER GALLON, AND GALLONS PER POUND CORRESPONDING TO VARIOUS DEGREES BAUMÉ

Degrees Baumé (Modulus 140)	Specific Gravity 60°/60° F.	Pounds per Gallon	Gallons per Pound	Degrees Baumé (Modulus 140)	Specific Gravity 60°/60° F.	Pounds per Gallon	Gallons per Pound
10 0	1 0000	8 328	0 1201	55 0	0.7568	6 300	0.1587
11.0	.9929	8 269	.1209	56 0	.7527	6 266	.1596
12.0	.9859	8 211	.1218	57 0	.7487	6 233	.1604
13.0	9790	8.153	.1227	58 0	.7447	6 199	.1613
14.0	.9722	8 096	.1235	59 0	.7407	6 166	.1622
15 0	.9655	8 041	.1244	60 0	.7368	6 134	.1630
16 0	9589	7 986	.1252	61 0	.7330	6 102	.1639
17.0	.9524	7 931	.1261	62 0	.7292	6 070	.1647
18 0	.9459	7 877	.1270	63 0	.7254	6 038	.1656
19.0	.9396	7 825	.1278	64 0	7216	6 007	.1665
20.0	.9333	7.772	.1287	65 0	.7179	5 976	.1673
21 0	9272	7 721	.1295	66 0	.7143	5 946	.1682
22 0	.9211	7 670	.1304	67 0	.7107	5 916	.1690
23 0	.9150	7 620	1313	68 0	.7071	5 886	.1699
24 0	.9091	7 570	.1321	69.0	.7035	5 856	.1708
25 0	.9032	7 522	.1330	70 0	.7000	5 827	.1716
26 0	.8974	7 473	.1338	71 0	.6965	5 798	.1725
27.0	8917	7.425	1347	72 0	.6931	5 769	.1733
28 0	.8861	7 378	.1355	73 0	.6897	5 741	.1742
29.0	.8805	7 332	.1364	74.0	.6863	5.712	.1751
30 0	.8750	7 286	1373	75 0	.6829	5 685	.1759
31 0	.8696	7 241	.1381	76 0	.6796	5 657	.1768
32 0	.8642	7 196	.1390	77 0	.6763	5 629	.1776
33 0	.8589	7 152	.1398	78 0	.6731	5 602	.1785
34 0	.8537	7 108	.1407	79.0	.6699	5 576	.1793
35.0	.8485	7.065	.1415	80.0	.6667	5 549	.1802
36 0	8434	7.022	1424	81 0	.6635	5 522	1811
37 0	.8383	6 980	.1433	82.0	.6604	5 497	.1819
38 0	8333	6 939	.1441	83 0	.6573	5 471	.1828
39.0	.8284	6 898	.1450	84.0	.6542	5 445	.1837
40 0	.8235	6 857	.1459	85 0	.6512	5 420	.1845
41 0	.8187	6 817	.1467	86 0	.6482	5 395	1854
42 0	.8140	6 777	.1476	87 0	6452	5.370	1862
43 0	.8092	6 738	.1484	88 0	.6422	5 345	.1871
44.0	.8046	6 699	.1493	89 0	.6393	5 320	.1880
45 0	.8000	6 661	.1501	90 0	.6364	5.296	.1888
46.0	7955	6 623	.1510	91 0	.6335	5 272	.1897
47 0	.7910	6.586	.1518	92.0	.6306	5 248	.1905
48.0	.7865	6 548	.1527	93.0	.6278	5 225	.1914
49.0	.7821	6 511	.1536	94.0	.6250	5 201	.1923
50.0	.7778	6 476	.1544	95.0	.6222	5 178	.1931
51 0	.7735	6 440	.1553	96 0	6195	5 155	.1940
52.0	.7692	6 404	.1562	97 0	6167	5 132	.1949
53 0	.7650	6 369	1570	98 0	6140	5 110	.1957
54 0	.7609	6.334	.1579	99.0	.6114	5.088	.1966
55.0	.7568	6 300	.1587	100 0	.6087	5.066	.1974

TABLE 6. — DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15.056}{15.056}\text{C.}\right)$ FOR LIQUIDS HEAVIER THAN WATER

[Calculated from the formula degrees Baumé = $145 - \frac{145}{D\,\frac{60°}{60°}\,\text{F.}}$ which defines the Baumé scale, in general use in the United States, for liquids heavier than water]

$D\frac{15.056}{15.056}C$	0	1	2	3	4	5	6	7	8	9	Diff.
1.00	0 000	0.145	0 289	0 434	0.578	0 721	0.865	1 008	1.151	1 293	143
1.01	1 436	1 578	1 719	1 861	2 002	2 143	2 283	2 424	2 564	2 704	141
1.02	2 843	2 982	3 121	3 260	3.399	3 537	3 675	3 812	3 950	4 087	138
1.03	4 223	4 360	4 496	4 632	4 768	4 903	5 038	5 174	5 308	5 443	136
1 04	5 577	5 711	5 845	5 978	6 111	6 244	6 377	6 509	6.641	6 773	133
1.05	6.905	7.036	7 167	7 298	7.429	7.559	7.689	7.819	7.949	8.078	130
1.06	8.208	8 336	8 465	8 594	8 722	8 850	8 978	9.105	9.232	9 359	128
1.07	9.486	9 613	9 739	9 865	9 991	10 116	10.242	10 367	10.492	10 616	126
1 08	10 741	10 865	10 989	11 113	11 236	11 359	11 483	11 605	11.728	11 850	124
1 09	11 972	12 094	12 216	12 338	12 459	12 580	12 701	12.821	12 942	13 062	121
1.10	13 182	13.302	13 421	13 540	13.659	13.778	13.897	14.015	14 134	14 252	119
1.11	14.370	14.487	14 604	14.721	14 838	14 955	15.072	15.188	15 304	15.420	117
1.12	15 536	15.651	15 767	15 882	15 997	16 111	16 226	16 340	16.454	16.568	115
1 13	16 682	16 795	16 908	17 021	17.134	17 247	17 359	17 471	17 583	17 695	113
1 14	17 807	17 919	18 030	18 141	18 252	18 363	18 473	18 583	18 693	18 803	111
1.15	18 913	19.023	19 132	19 241	19 350	19.459	19.568	19 676	19 784	19 892	109
1.16	20 000	20 108	20 215	20 322	20 430	20 536	20.643	20.750	20 856	20 962	107
1.17	21 068	21 174	21 280	21 385	21 491	21 596	21 701	21 806	21 910	22 014	105
1.18	22 119	22 223	22 327	22.430	22 534	22 637	22 740	22 843	22 946	23 049	103
1.19	23 151	23 254	23 356	23 458	23 560	23 661	23 763	23 864	23 965	24 066	101
1.20	24.167	24.267	24.368	24 468	24 568	24.668	24.768	24.868	24.967	25.066	100
1.21	25 165	25 264	25.363	25 462	25 560	25 658	25 755	25 855	25 952	26 050	98
1 22	26 148	26 245	26 342	26 439	26.536	26 633	26 729	26 826	26 922	27 018	97
1.23	27 114	27 210	27 305	27.401	27 496	27 591	27 686	27 781	27 876	27 970	95
1 24	28 065	28.159	28.253	28.347	28 441	28 534	28 628	28 721	28 814	28.907	94
1.25	29 000	29 093	29.185	29 278	29.370	29.462	29.554	29 646	29.738	29.829	92
1 26	29 921	30 012	30 103	30.194	30 285	30 376	30 466	30 556	30.647	30.737	91
1 27	30 827	30.917	31 006	31.096	31 185	31 275	31.364	31 453	31 542	31 630	89
1 28	31 719	31 807	31 896	31 984	32 072	32 160	32 247	32 335	32 422	32 510	88
1.29	32 597	32 684	32 771	32 858	32 944	33 031	33 117	33 204	33 290	33.376	87
1.30	33 462	33 547	33 633	33 718	33.804	33 889	33 974	34.059	34.144	34 229	85
1.31	34 313	34 397	34 482	34 566	34 650	34 734	34 818	34 901	34 985	35 068	84
1 32	35.152	35 235	35 318	35 401	35 483	35 566	35 649	35 731	35 813	35 895	83
1 33	35.977	36 059	36 141	36 223	36 304	36 386	36.467	36 548	36 629	36 710	81
1.34	36 791	36 872	36 952	37 033	37 113	37 173	37 273	37 353	37.433	37.513	80
1.35	37 593	37 672	37 751	37 831	37 910	37.989	38 068	38 147	38 225	38.304	79
1.36	38 382	38 461	38 539	38 617	38 695	38 773	38 851	38 928	39.006	39 803	78
1.37	39 161	39 238	39 315	39 392	39 469	39.546	39.622	39.609	39 775	39.851	77
1.38	39.928	40 004	40 080	40.156	40 231	40 307	40 382	40 458	40 533	40.608	76
1.39	40.683	40 758	40 833	40.908	40.983	41.057	41 132	41.206	41.280	41 355	75
1.40	41 429	41.503	41 576	41.650	41 724	41 797	41.871	41.944	42 017	42 090	74
1.41	42 163	42 236	42 309	42 381	42 454	42.527	42.599	42.671	42 743	42 815	73

TABLE 6. — DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15.056}{15.056}\text{ C.}\right)$ FOR LIQUIDS HEAVIER THAN WATER. — *Continued*

D $\frac{15.056}{15.056}$ C	0	1	2	3	4	5	6	7	8	9	Diff.
1.41	42.163	42.236	42 309	42 381	42.454	42 527	42 599	42 671	42.743	42 815	73
1.42	42.887	42.959	43.031	43 103	43 174	43 246	43 317	43 388	43.459	43 530	72
1.43	43.601	43.672	43 743	43 814	43 884	43 955	44 025	44 095	44 166	44 236	71
1.44	44.306	44.376	44 445	44.515	44.585	44 654	44.724	44 793	44 862	44 931	70
1.45	45.000	45.069	45.138	45.207	45 275	45 344	45.412	45.481	45.549	45.617	69
1.46	45.685	45.753	45.821	45.889	45.956	46.024	46 091	46.159	46.226	46.293	67
1.47	46.361	46.428	46.495	46.562	46.628	46 695	46.762	46.828	46.894	46 961	67
1.48	47.027	47.093	47.159	47 225	47 291	47 357	47 423	47 488	47 554	47 619	66
1.49	47.685	47.750	47.815	47 880	47.945	48.010	48.075	48.140	48.204	48.269	65
1.50	48.333	48.398	48.462	48.526	48.591	48 655	48.719	48.782	48.846	48.910	64
1.51	48.974	49.037	49.101	49.164	49.227	49.290	49.354	49.417	49.480	49.543	63
1.52	49.605	49.668	49.731	49.793	49 856	49 918	49 980	50.043	50.105	50 167	62
1.53	50.229	50.291	50 353	50 414	50.476	50 538	50 599	50 660	50.722	50 783	61
1.54	50.844	50.905	50.966	51 027	51.088	51 149	51 210	51 270	51 331	51 391	61
1.55	51.452	51.512	51.572	51.632	51.692	51.752	51.812	51.872	51.932	51.992	60
1.56	52.051	52.111	52.170	52.230	52.289	52.348	52.407	52.467	52 526	52 585	59
1.57	52.643	52.702	52.761	52.820	52.878	52.937	52.995	53.053	53.112	53.170	59
1.58	53.228	53.286	53.344	53.402	53.460	53.517	53 575	53.633	53.690	53.748	58
1.59	53 805	53.862	53.920	53 977	54.034	54 091	54.148	54.205	54.262	54 318	57
1.60	54.375	54.432	54.488	54.545	54.601	54.657	54.714	54.770	54.826	54.882	56
1.61	54.938	54.994	55 050	55.106	55.161	55.217	55.272	55 328	55 383	55.439	56
1.62	55 494	55.549	55.604	55.659	55 714	55.769	55 824	55 879	55 934	55 988	55
1 63	56.043	56 098	56.152	56 206	56 261	56 315	56 369	56 423	56.478	56.531	54
1 64	56.585	56.639	56 693	56.747	56.801	56 854	56.908	56 961	57 015	57.068	54
1.65	57.121	57.175	57.228	57.281	57.334	57.387	57.440	57.493	57 545	57.598	53
1.66	57.651	57.703	57.756	57.808	57.861	57.913	57.965	58.017	58.070	58 122	52
1.67	58.174	58.226	58 278	58 329	58.381	58.433	58.485	58 536	58 588	58 639	52
1.68	58.690	58.742	58.793	58 844	58 896	58 947	58.998	59 049	59 100	59 150	51
1.69	59.201	59.252	59.303	59 353	59.404	59.454	59 505	59.555	59.605	59 656	50
1.70	59.706	59.756	59.806	59.856	59.906	59.956	60.006	60.056	60.105	60.155	50
1.71	60.205	60.254	60 304	60 353	60.403	60 452	60.501	60.550	60.600	60.649	49
1 72	60.698	60.747	60.796	60 844	60.893	60.942	60 991	61.039	61.088	61.136	49
1.73	61 185	61.234	61.282	61 330	61 378	61 427	61.475	61 523	61 571	61.619	48
1.74	61.667	61 715	61 762	61.810	61 858	61 906	61 953	62.001	62.048	62 096	48
1.75	62.143	62.190	62.237	62 285	62.332	62.379	62.426	62.473	62.520	62.567	47
1.76	62.614	62 660	62.707	62.754	62 801	62 847	62.894	62.940	62 987	63.033	46
1.77	63.079	63.125	63.172	63 218	63.264	63 310	63.356	63.402	63 448	63 494	46
1.78	63.539	63.585	63.631	63.676	63.722	63.768	63 813	63.858	63.904	63.949	46
1.79	63.994	64.040	64 085	64.130	64.175	64.220	64.265	64 310	64.355	64.400	45
1.80	64.445	64.489	64.534	64.579	64.623	64.668	64.712	64.757	64.801	64.845	45
1.81	64.890	64.934	64.978	65.022	65.066	65.110	65.154	65 198	65 242	65 286	44
1.82	65 330	65.374	65.417	65 461	65 504	65 548	65 591	65 635	65 678	65 722	43
1.83	65.765	65.808	65.852	65 895	65.938	65.981	66.024	66.067	66.110	66.153	43
1.84	66.196	66.238	66.281	66.324	66 367	66.409	66.452	66.494	66.537	66.579	42
1.85	66.622										

TABLE 7. — SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15.056}{15.056}\text{ C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS HEAVIER THAN WATER

[Calculated from the formula specific gravity $\frac{60°}{60°}$ F. $= \frac{145}{145 - \text{Deg. Baumé.}}$]

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
0	1 0000	1 0007	1.0014	1 0021	1 0028	1 0035	1 0042	1.0049	1 0055	1 0062
1	1 0069	1 0076	1 0083	1 0090	1 0097	1 0105	1 0112	1.0119	1 0126	1 0133
2	1.0140	1 0147	1 0154	1 0161	1 0168	1 0175	1 0183	1 0190	1 0197	1 0204
3	1 0211	1 0218	1 0226	1 0233	1 0240	1 0247	1 0255	1 0262	1 0269	1 0276
4	1 0284	1 0291	1 0298	1 0306	1 0313	1 0320	1 0328	1 0335	1 0342	1 0350
5	1 0357	1 0365	1 0372	1 0379	1 0387	1 0394	1 0402	1 0409	1 0417	1 0424
6	1.0432	1 0439	1 0447	1 0454	1 0462	1 0469	1 0477	1 0484	1 0492	1.0500
7	1 0507	1 0515	1.0522	1 0530	1 0538	1.0545	1 0553	1 0561	1 0569	1.0576
8	1 0584	1 0592	1 0599	1 0607	1 0615	1 0623	1 0630	1 0638	1 0646	1 0654
9	1 0662	1 0670	1 0677	1 0685	1 0693	1 0701	1 0709	1 0717	1 0725	1 0733
10	1.0741	1 0749	1 0757	1 0765	1 0773	1 0781	1 0789	1 0797	1 0805	1 0813
11	1 0821	1 0829	1 0837	1 0845	1 0853	1 0861	1 0870	1 0878	1 0886	1.0894
12	1 0902	1 0910	1 0919	1 0927	1 0935	1 0943	1 0952	1 0960	1 0968	1.0977
13	1 0985	1 0993	1.1002	1.1010	1 1018	1 1027	1 1035	1 1043	1 1052	1.1060
14	1 1069	1.1077	1.1086	1 1094	1 1103	1 1111	1 1120	1 1128	1.1137	1.1145
15	1 1154	1 1162	1.1171	1.1180	1.1188	1 1197	1 1206	1 1214	1 1223	1 1232
16	1.1240	1 1249	1 1258	1.1267	1 1275	1 1284	1 1293	1 1302	1.1310	1.1319
17	1 1328	1 1337	1 1346	1 1355	1 1364	1 1373	1 1381	1 1390	1 1399	1 1408
18	1 1417	1 1426	1 1435	1.1444	1 1453	1 1462	1 1472	1 1481	1.1490	1.1499
19	1 1508	1 1517	1 1526	1 1535	1 1545	1 1554	1 1563	1 1572	1 1581	1 1591
20	1 1600	1 1609	1 1619	1 1628	1 1637	1 1647	1 1656	1 1665	1 1675	1 1684
21	1 1694	1 1703	1 1712	1 1722	1 1731	1 1741	1 1750	1 1760	1 1769	1 1779
22	1 1789	1 1798	1 1808	1 1817	1 1827	1 1837	1 1846	1 1856	1 1866	1 1876
23	1 1885	1 1895	1 1905	1.1915	1 1924	1 1934	1 1944	1 1954	1 1964	1 1974
24	1 1983	1 1993	1 2003	1 2013	1 2023	1 2033	1 2043	1 2053	1 2063	1 2073
25	1 2083	1 2093	1 2104	1 2114	1 2124	1 2134	1 2144	1 2154	1 2164	1 2175
26	1 2185	1 2195	1 2205	1 2216	1 2226	1 2236	1 2247	1 2257	1 2267	1 2278
27	1 2288	1 2299	1 2309	1 2319	1 2330	1 2340	1 2351	1 2361	1 2372	1 2383
28	1 2393	1 2404	1 2414	1 2425	1 2436	1 2446	1 2457	1 2468	1 2478	1 2489
29	1 2500	1 2511	1 2522	1 2532	1 2543	1 2554	1 2565	1 2576	1 2587	1 2598
30	1 2609	1 2620	1 2631	1 2642	1 2653	1 2664	1 2675	1 2686	1 2697	1 2708
31	1 2719	1 2730	1 2742	1 2753	1 2764	1 2775	1 2787	1 2798	1 2809	1.2821
32	1 2832	1 2843	1 2855	1 2866	1 2877	1 2889	1 2900	1 2912	1 2923	1 2935
33	1 2946	1 2958	1 2970	1 2981	1 2993	1 3004	1 3016	1 3028	1 3040	1 3051
34	1 3063	1 3075	1 3087	1 3098	1 3110	1 3122	1 3134	1 3146	1 3158	1 3170
35	1 3182	1 3194	1 3206	1 3218	1.3230	1 3242	1 3254	1 3266	1 3278	1 3291
36	1 3303	1 3315	1 3327	1 3339	1 3352	1 3364	1 3376	1 3389	1 3401	1.3414
37	1 3426	1 3438	1 3451	1 3463	1 3476	1 3488	1 3501	1 3514	1 3526	1.3539
38	1 3551	1 3564	1 3577	1 3590	1 3602	1 3615	1 3628	1 3641	1 3653	1 3666
39	1 3679	1 3692	1 3705	1 3718	1 3731	1 3744	1 3757	1 3770	1.3783	1 3796
40	1.3810	1 3823	1 3836	1 3849	1 3862	1 3876	1 3889	1 3902	1.3916	1 3929
41	1 3942	1 3956	1 3969	1 3983	1 3996	1 4010	1 4023	1 4037	1 4050	1 4064
42	1 4078	1 4091	1 4105	1 4119	1 4133	1 4146	1 4160	1 4174	1.4188	1 4202
43	1 4216	1 4230	1 4244	1 4258	1 4272	1 4286	1 4300	1 4314	1.4328	1 4342
44	1 4356	1 4371	1 4385	1 4399	1 4414	1 4428	1 4442	1 4457	1 4471	1 4486
45	1 4500	1 4515	1 4529	1 4544	1 4558	1 4573	1 4588	1 4602	1 4617	1.4632
46	1 4646	1 4661	1 4676	1 4691	1 4706	1 4721	1 4736	1 4751	1 4766	1.4781
47	1 4796	1 4811	1 4826	1.4841	1.4857	1 4872	1 4887	1 4902	1 4918	1.4933
48	1 4948	1 4964	1 4979	1 4995	1 5010	1 5026	1 5041	1 5057	1 5073	1.5088
49	1 5104	1 5120	1 5136	1 5152	1 5167	1 5183	1 5199	1 5215	1 5231	1 5247
50	1 5263	1 5279	1 5295	1 5312	1 5328	1 5344	1 5360	1 5376	1 5393	1 5409
51	1 5426	1 5442	1 5458	1 5475	1.5491	1 5508	1 5525	1 5541	1 5558	1 5575
52	1 5591	1 5608	1 5625	1 5642	1 5659	1 5676	1 5693	1 5710	1 5727	1 5744
53	1 5761	1 5778	1 5795	1 5812	1 5830	1 5847	1 5864	1 5882	1 5899	1 5917
54	1 5934	1 5952	1 5969	1 5987	1 6004	1 6022	1 6040	1 6058	1 6075	1 6093
55	1 6111	1 6129	1 6147	1 6165	1.6183	1 6201	1 6219	1 6237	1.6256	1 6274
56	1 6292	1 6310	1 6329	1 6347	1 6366	1 6384	1 6403	1.6421	1 6440	1 6459
57	1 6477	1 6496	1 6515	1.6534	1 6553	1 6571	1 6590	1 6609	1 6628	1 6648
58	1 6667	1 6686	1.6705	1 6724	1 6744	1 6763	1 6782	1 6802	1 6821	1 6841
59	1.6860	1.6880	1.6900	1 6919	1 6939	1 6959	1 6979	1 6999	1.7019	1 7039
60	1.7059	1 7079	1 7099	1 7119	1 7139	1 7160	1.7180	1 7200	1 7221	1 7241
61	1.7262	1.7282	1 7303	1.7324	1 7344	1 7365	1.7386	1.7407	1 7428	1.7449
62	1.7470	1.7491	1.7512	1 7533	1.7554	1.7576	1.7597	1.7618	1.7640	1 7661
63	1 7683	1.7705	1 7726	1.7748	1.7770	1 7791	1.7813	1 7835	1.7857	1 7879
64	1 7901	1 7923	1 7946	1 7968	1.7990	1 8012	1.8035	1 8057	1 8080	1 8102
65	1 8125	1 8148	1.8170	1 8193	1 8216	1 8239	1 8262	1 8285	1 8308	1 8331
66	1 8354	1 8378	1 8401	1 8424	1 8448	1 8471	1 8495	1 8519	1 8542	1 8566
67	1 8590	1.8614	1 8638	1 8662	1 8686	1 8710	1.8734	1 8758	1.8782	1 8807
68	1 8831	1 8856	1 8880	1 8905	1.8930	1.8954	1.8979	1.9004	1 9029	1.9054
69	1 9079	1.9104	1 9129	1.9155	1 9180	1 9205	1 9231	1.9256	1.9282	1.9308
70	1.9333									

TABLE 8. — DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15.056}{15.056}\text{C.}\right)$ FOR LIQUIDS LIGHTER THAN WATER

[Calculated from the formula degrees Baumé = $\frac{140}{\text{D}\frac{60°}{60°}\text{F}} - 130$ which defines the Baumé scale, in general use in the United States, for liquids lighter than water]

$\text{D}\frac{15.056}{15.056}\text{C}$	0	1	2	3	4	5	6	7	8	9	Diff.
0.60	103 333	102 945	102.558	102 172	101.788	101 405	101 023	100 642	100.263	99.885	382
.61	99 508	99.133	98 758	98 385	98 013	97.642	97.273	96.904	96.537	96 171	370
.62	95 806	95.443	95 080	94 719	94 359	94 000	93 642	93 285	92.930	92 576	360
.63	92.222	91.870	91.519	91.169	90 820	90 472	90 126	89 780	89 436	89 092	348
.64	88 750	88.409	88.068	87 729	87 391	87 054	86 718	86 383	86.049	85.716	337
.65	85 385	85 054	84 724	84 395	84.067	83 741	83 415	83.090	82 766	82.443	327
.66	82 121	81.800	81 480	81 161	80 843	80 526	80 210	79 895	79 581	79.268	317
.67	78.955	78.644	78 333	78 024	77 715	77 407	77 101	76 795	76 490	76 186	308
.68	75.882	75 580	75 279	74 978	74 678	74 380	74 082	73 785	73 488	73 193	298
.69	72.899	72.605	72.312	72.020	71.729	71 439	71 149	70 861	70 573	70.286	290
.70	70 000	69 715	69 430	69.146	68 864	68 582	68 300	68 020	67.740	67.461	282
.71	67 183	66 906	66 629	66 354	66 078	65.804	65 531	65 258	64 986	64.715	274
.72	64 444	64.175	63 906	63 638	63 370	63 103	62 837	62 572	62 308	62 044	266
.73	61.781	61 518	61 257	60 996	60.736	60.476	60 217	59.959	59.702	59.445	260
.74	59 189	58.934	58.679	58.425	58 172	57.919	57 668	57 416	57 166	56 916	252
.75	56 667	56 418	56.170	55 923	55 676	55.430	55 185	54 941	54 697	54.453	246
.76	54 210	53.968	53 727	53 486	53 246	53 007	52 768	52 529	52.292	52.055	239
.77	51.818	51 582	51.347	51 113	50 879	50 645	50 412	50 180	49.949	49 718	234
.78	49.487	49.257	49 028	48 799	48 571	48 344	48 117	47 891	47 665	47.440	227
.79	47.215	46.991	46 768	46.545	46 322	46.101	45 879	45 659	45 439	45.219	222
.80	45 000	44.781	44 564	44.346	44.129	43 913	43 697	43 482	43.267	43 053	216
.81	42 840	42 626	42 414	42 202	41 990	41 779	41 569	41 359	41 149	40 940	210
.82	40.732	40 524	40 316	40 109	39 903	39.697	39 492	39 287	39 082	38 878	206
.83	38.675	38.472	38 269	38 067	37.866	37.665	37 464	37 264	37 064	36.866	201
.84	36.667	36.469	36 271	36 074	35 877	35 680	35 485	35 289	35 094	34 900	196
.85	34.706	34.512	34 319	34 127	33.934	33.743	33 551	33 361	33 170	32 980	192
.86	32 791	32 602	32 413	32 225	32 037	31 850	31 663	31 476	31 290	31 105	187
.87	30 920	30 735	30 550	30 366	30.183	30.000	29 817	29 635	29 453	29 272	183
.88	29 091	28 910	28 730	28 550	28 371	28 192	28 014	27.835	27 658	27 480	179
.89	27.303	27 127	26 951	26 775	26 600	26.425	26 250	26.076	25 902	25 729	175
.90	25.556	25.383	25 211	25 039	24.867	24 696	24.525	24 355	24 185	24 015	171
.91	23.846	23.677	23 509	23.341	23 173	23 005	22 838	22 672	22 506	22 339	168
.92	22.174	22 009	21 844	21 679	21 515	21 351	21 188	21.025	20.862	20.700	164
.93	20 538	20 376	20 215	20 054	19 893	19 733	19 573	19 413	19 254	19 095	160
.94	18.936	18.778	18 620	18.462	18 305	18 148	17.991	17 835	17.679	17 524	157
.95	17.368	17.214	17 059	16.905	16.751	16 597	16.444	16 290	16.138	15.985	154
.96	15 833	15 682	15 530	15.379	15 228	15.078	14 928	14 778	14 628	14 479	150
.97	14.330	14 181	14.033	13 885	13 737	13 590	13 433	13 297	13 149	13 003	147
.98	12 857	12.712	12.566	12 421	12 276	12 132	11 988	11 844	11.700	11 557	144
.99	11.414	11.271	11.129	10.987	10.845	10.704	10 562	10 421	10 281	10 140	142
1.00	10.000										

TABLE 9. — SPECIFIC GRAVITIES AT $\frac{60°}{60°}$F. $\left(\frac{15.056}{15.056}\text{C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER

[Calculated from the formula, Specific Gravity $\frac{60°}{60°}$ F. $= \frac{140}{130 + \text{Deg. Bé}}$]

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
10	1 0000	0 9993	0.9986	0 9979	0.9972	0.9964	0.9957	0.9950	0 9943	0 9936
11	.9929	.9922	.9915	9908	.9901	.9894	.9887	9880	9873	9866
12	9859	.9852	.9845	.9838	.9831	.9825	.9818	.9811	.9804	9797
13	.9790	.9783	.9777	.9770	.9763	.9756	.9749	9743	.9736	9729
14	.9722	.9715	.9709	.9702	.9695	.9689	.9682	.9675	.9669	.9662
15	.9655	.9649	.9642	.9635	.9629	.9622	.9615	.9609	.9602	.9596
16	.9589	.9582	.9576	.9569	.9563	.9556	.9550	.9543	.9537	9530
17	.9524	.9517	.9511	.9504	.9498	.9492	.9485	.9479	.9472	.9466
18	.9459	.9453	.9447	.9440	.9434	.9428	.9421	.9415	.9409	.9402
19	.9396	.9390	.9383	.9377	.9371	.9365	.9358	.9352	.9346	9340
20	.9333	.9327	.9321	.9315	.9309	.9302	.9296	9290	.9284	.9278
21	.9272	.9265	.9259	.9253	.9247	.9241	.9235	.9229	.9223	9217
22	.9211	9204	.9198	.9192	.9186	.9180	.9174	.9168	.9162	9156
23	.9150	.9144	.9138	.9132	.9126	.9121	.9115	.9109	.9103	9097
24	.9091	.9085	.9079	.9073	.9067	.9061	.9056	.9050	.9044	.9038
25	.9032	.9026	.9021	.9015	.9009	.9003	8997	.8992	.8986	8980
26	.8974	.8969	.8963	.8957	8951	8946	8940	.8934	.8929	8923
27	8917	8912	.8906	.8900	.8895	.8889	.8883	8878	.8872	8866
28	8861	.8855	.8850	.8844	.8838	8833	.8827	.8822	.8816	8811
29	.8805	.8799	.8794	.8788	.8783	.8777	.8772	.8766	.8761	8755
30	.8750	.8745	.8739	.8734	.8728	.8723	.8717	.8712	.8706	.8701
31	8696	.8690	.8685	.8679	.8674	.8669	.8663	.8658	.8653	8647
32	8642	8637	.8631	.8626	.8621	.8615	.8610	.8605	.8600	8594
33	8589	.8584	.8578	.8573	.8568	8563	.8557	.8552	.8547	.8542
34	8537	.8531	.8526	.8521	.8516	.8511	.8505	.8500	.8495	8490
35	8485	.8480	.8475	.8469	.8464	.8459	.8454	.8449	.8444	8439
36	8434	.8429	.8424	.8419	.8413	.8408	.8403	.8398	.8393	8388
37	8383	.8378	.8373	.8368	.8363	.8358	.8353	.8348	.8343	8338
38	.8333	.8328	.8323	.8318	.8314	.8309	.8304	.8299	.8294	8289
39	.8284	.8279	.8274	.8269	.8264	.8260	.8255	.8250	.8245	.8240
40	.8235	.8230	.8226	.8221	.8216	.8211	.8206	.8202	.8197	.8192
41	8187	.8182	.8178	.8173	.8168	.8163	.8159	.8154	.8149	.8144
42	.8140	.8135	.8130	.8125	.8121	8116	.8111	.8107	.8102	.8097
43	.8092	.8088	.8083	.8078	.8074	.8069	.8065	.8060	.8055	.8051
44	.8046	.8041	.8037	.8032	.8028	.8023	.8018	.8014	.8009	.8005
45	.8000	.7995	.7991	.7986	.7982	.7977	.7973	.7968	.7964	.7959
46	.7955	.7950	.7946	.7941	.7937	.7932	.7928	.7923	.7919	.7914
47	.7910	.7905	.7901	.7896	.7892	.7887	.7883	.7878	.7874	.7870
48	.7865	.7861	.7856	.7852	.7848	.7843	.7839	.7834	.7830	7826
49	.7821	.7817	.7812	.7808	.7804	.7799	.7795	.7791	.7786	.7782
50	.7778	.7773	.7769	.7765	.7761	.7756	.7752	.7748	.7743	.7739
51	.7735	.7731	.7726	.7722	.7718	.7713	.7709	.7705	.7701	.7697
52	.7692	.7688	.7684	.7680	.7675	.7671	.7667	.7663	.7659	7654
53	.7650	.7646	.7642	.7638	.7634	.7629	.7625	.7621	.7617	.7613
54	.7609	.7605	.7600	7596	.7592	.7588	.7584	.7580	.7576	.7572
55	.7568	.7563	.7559	.7555	.7551	.7547	.7543	.7539	.7535	.7531

TABLE 10. — SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15.056}{15.056}\text{ C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER — *Continued*

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
55	0.7568	0.7563	0.7559	0 7555	0.7551	0.7547	0 7543	0.7539	0.7535	0 7531
56	.7527	.7523	.7519	.7515	.7511	.7507	.7503	7499	.7495	7491
57	.7487	.7483	.7479	.7475	.7471	.7467	.7463	.7459	.7455	7451
58	.7447	.7443	.7439	.7435	.7431	.7427	7423	.7419	7415	7411
59	.7407	.7403	.7400	.7396	.7392	.7388	.7384	.7380	.7376	.7372
60	.7368	.7365	.7361	.7357	.7353	.7349	7345	.7341	.7338	.7334
61	.7330	.7326	.7322	.7318	.7315	.7311	.7307	.7303	.7299	7295
62	.7292	.7288	.7284	.7280	.7277	.7273	.7269	.7265	.7261	.7258
63	.7254	.7250	.7246	.7243	.7239	.7235	.7231	.7228	.7224	.7220
64	.7216	.7213	.7209	.7205	.7202	.7198	.7194	.7191	.7187	.7183
65	.7179	.7176	.7172	.7168	.7165	.7161	.7157	.7154	.7150	.7147
66	.7143	.7139	7136	.7132	.7128	.7125	.7121	.7117	.7114	.7110
67	.7107	.7103	.7099	.7096	.7092	.7089	.7085	.7081	.7078	.7074
68	.7071	.7067	.7064	.7060	.7056	.7053	.7049	.7046	.7042	.7039
69	.7035	.7032	.7028	.7025	.7021	.7018	.7014	.7011	.7007	.7004
70	.7000	.6997	.6993	.6990	6986	.6983	6979	.6976	.6972	.6969
71	.6965	.6962	.6958	.6955	.6951	.6948	.6944	.6941	.6938	.6934
72	.6931	.6927	.6924	.6920	6917	.6914	6910	.6907	6903	6900
73	.6897	.6893	.6890	.6886	.6883	6880	.6876	.6873	6869	.6866
74	.6863	.6859	.6856	.6853	.6849	.6846	.6843	.6839	.6836	.6833
75	.6829	.6826	.6823	.6819	.6816	.6813	.6809	.6806	.6803	.6799
76	.6796	.6793	.6790	.6786	6783	.6780	.6776	.6773	6770	6767
77	.6763	.6760	.6757	.6753	.6750	6747	.6744	6740	6737	6734
78	.6731	.6728	.6724	.6721	.6718	.6715	6711	.6708	6705	.6702
79	.6699	.6695	.6692	.6689	.6686	.6683	.6679	6676	6673	.6670
80	.6667	.6663	.6660	.6657	.6654	.6651	.6648	.6645	6641	.6638
81	.6635	6632	.6629	.6626	.6623	.6619	.6616	.6613	.6610	6607
82	.6604	6601	.6598	.6594	.6591	.6588	6585	6582	6579	6576
83	.6573	.6570	.6567	.6564	.6560	6557	.6554	.6551	6548	6545
84	.6542	6539	.6536	.6533	.6530	.6527	.6524	6521	6518	6515
85	.6512	.6509	6506	.6503	.6500	6497	.6494	6490	6487	6484
86	.6482	.6479	6476	.6473	.6470	6467	.6464	.6461	6458	6455
87	.6452	.6449	.6446	.6443	.6440	.6437	6434	6431	6428	6425
88	.6422	.6419	.6416	.6413	6410	.6407	.6404	.6401	.6399	6396
89	.6393	.6390	.6387	.6384	.6381	.6378	.6375	.6372	.6369	.6367
90	.6364	.6361	.6358	.6355	.6352	.6349	.6346	.6343	.6341	.6338
91	.6335	.6332	6329	.6326	.6323	.6321	.6318	.6315	6312	.6306
82	.6306	.6303	.6301	6298	.6295	.6292	6289	.6286	6284	.6281
93	.6278	.6275	.6272	.6270	.6267	6264	6261	6258	6256	6253
94	.6250	.6247	.6244	.6242	.6239	.6236	.6233	.6231	.6228	.6225
95	.6222	.6219	.6217	.6214	.6211	.6208	.6206	.6203	6200	6197
96	.6195	.6192	.6189	.6186	6184	.6181	.6178	.6176	.6173	6170
97	.6167	.6165	6162	.6159	6157	.6154	.6151	.6148	6146	.6143
98	.6140	.6138	.6135	.6132	6130	.6127	.6124	.6122	6119	.6116
99	.6114	.6111	.6108	.6106	6103	.6100	.6098	6095	6092	.6090
100	.6087									

TABLE 11. — CONVERSION OF DENSITY BASIS

Prepared for use in reducing readings of a hydrometer graduated to indicate density or specific gravity at a specified standard temperature, T, referred to water at a specified temperature, T′, as unity, to the basis of another standard temperature, t, and reference temperature, t′.

The factor Δ (given in units of the sixth decimal place), multiplied by the density or specific-gravity reading, gives the correction to be applied to the reading to reduce it to the required basis.

Suppose a hydrometer indicates specific gravity at $\frac{20°}{4°}$C., and it is required to know the correction in order that it shall indicate specific gravity at $\frac{15\ 56}{15.56}$ C., then,

$$D\frac{15.56}{15.56} = D\frac{20°}{4°} + \Delta D\frac{20°}{4°}$$

That is, if the hydrometer indicates correctly a specific gravity of 1.5760 at $\frac{20°}{4°}$, then at $\frac{15.56}{15.56}$ the reading of the instrument will be too low by 1.5760 × 0.001062 = 0.0017. A correction of 0.0017 must therefore be added to the indication of the hydrometer.

Or, if a maker using standards indicating $D\frac{15.56}{15.56}$ C. wishes to graduate a hydrometer to indicate density at 20° C. referred to water at 4° C. $\left(D\frac{20}{4}\right)$, the readings of the standard must be corrected by use of the factor + 0.001062.

Suppose the standard reads	1 5760
The corresponding correction is 1.6 × .001062 =	+0 0017
Corrected reading	1 5777

The table is calculated for Jena 16^{III} glass.

Given Basis of Density	Required Basis of Density $\frac{t}{t'}$									
	$D\frac{25°}{4°}$ C	$D\frac{20}{4}$	$D\frac{17\ 5}{4}$	$D\frac{15\ 56}{4}$	$D\frac{15}{4}$	$D\frac{15}{15}$	$D\frac{15\ 56}{15\ 56}$	$D\frac{17\ 5}{17\ 5}$	$D\frac{20}{20}$	$D\frac{25}{25}$
$\frac{T}{T'}$	Δ (In Units of the Sixth Decimal Place)									
$D\frac{25°}{4°}$ C	0	+ 115	+ 172	+ 217	+ 230	+1104	+1177	+1459	+1884	+2931
$D\frac{20}{4}$	− 115	0	+ 58	+ 102	+ 115	+ 989	+1062	+1345	+1769	+2816
$D\frac{17\ 5}{4}$	− 172	− 58	0	+ 45	+ 58	+ 932	+1005	+1287	+1711	+2758
$D\frac{15\ 56}{4}$	− 217	− 102	− 45	0	+ 13	+ 887	+ 960	+1242	+1667	+2713
$D\frac{15}{4}$	− 230	− 115	− 58	− 13	0	+ 874	+ 947	+1229	+1654	+2700
$D\frac{15}{15}$	−1103	− 988	− 931	− 886	− 873	0	+ 73	+ 354	+ 779	+1826
$D\frac{15\ 56}{15.56}$	−1176	−1061	−1004	− 960	− 947	− 73	0	+ 281	+ 706	+1752
$D\frac{17.5}{17.5}$	−1457	−1343	−1285	−1240	−1227	− 354	− 281	0	+ 424	+1471
$D\frac{20}{20}$	−1881	−1766	−1708	−1664	−1651	− 778	− 705	− 423	0	+1046
$D\frac{25}{25}$	−2923	−2808	−2751	−2707	−2694	−1821	−1748	−1468	−1044	0

TABLE 12. — DENSITY OF SOLUTIONS OF SULPHURIC ACID (H_2SO_4) AT 20° C.

Calculated from Dr. J. Domke's table.[1] Adopted as the basis for standardization of hydrometers indicating per cent of sulfuric acid at 20° C.]

Per Cent H_2SO_4	$D\frac{20}{4}$C.	Per Cent H_2SO_4	$D\frac{20}{4}$C.	Per Cent H_2SO_4	$D\frac{20}{4}$C.
0	0 99823	50	1 39505	91.0	1.81950
1	1.00506	51	1 40487	91 2	1 82045
2	1.01178	52	1.41481	91 4	1.82137
3	1.01839	53	1 42487	91.6	1.82227
4	1.02500	54	1.43503	91 8	1.82315
5	1.03168	55	1.44530	92 0	1.82401
6	1.03843	56	1.45568	92.2	1.82484
7	1.04527	57	1.46615	92 4	1 82564
8	1.05216	58	1.47673	92 6	1 82641
9	1.05909	59	1 48740	92 8	1.82717
10	1.06609	60	1.49818	93 0	1 82790
11	1.07314	61	1.50904	93 2	1.82860
12	1.08026	62	1.51999	93 4	1 82928
13	1.08744	63	1.53102	93 6	1 82993
14	1 09468	64	1.54213	93 8	1 83055
15	1 10199	65	1 55333	94 0	1 83115
16	1.10936	66	1.56460	94 2	1.83172
17	1.11679	67	1.57595	94 4	1 83226
18	1 12428	68	1 58739	94 6	1 83276
19	1.13183	69	1.59890	94 8	1 83324
20	1 13943	70	1.61048	95 0	1 83368
21	1.14709	71	1.62213	95 1	1 83389
22	1.15480	72	1 63384	95.2	1 83410
23	1.16258	73	1.64560	95 3	1 83430
24	1.17041	74	1.65738	95 4	1 83449
25	1.17830	75	1 66917	95 5	1 83469
26	1.18624	76	1 68095	95 6	1 83486
27	1.19423	77	1.69268	95 7	1 83503
28	1 20227	78	1.70433	95 8	1 83520
29	1.21036	79	1.71585	95.9	1 83534
30	1 21850	80	1.72717	96.0	1 83548
31	1.22669	81	1.73827	96 1	1 83560
32	1.23492	82	1.74904	96 2	1 83572
33	1.24320	83	1 75943	96 3	1 83584
34	1.25154	84	1.76932	86 4	1 83594
35	1.25992	85	1.77860	96 5	1 83604
36	1.26836	85.5	1 78300	96.6	1.83613
37	1 27685	86	1.78721	96.7	1 83621
38	1 28543	86.5	1 79124	96 8	1.83628
39	1.29407	87	1.79509	96 9	1.83634
40	1 30278	87 5	1 79875	97.0	1 83637
41	1 31157	88	1 80223	97.1	1 83639
42	1.32043	88 5	1.80552	97 2	1.83640
43	1 32938	89	1 80864	97.3	1.83640
44	1.33843	89 5	1 81159	97.4	1.83639
45	1.34759	90	1.81438	97 5	1 83637
46	1.35686	90 2	1.81545	97 6	1.83634
47	1.36625	90 4	1.81650	97 7	1 83629
48	1.37574	90 6	1 81753	97 8	1.83623
49	1.38533	90 8	1.81853	97 9	1.83615
50	1.39505	91.0	1 81950	98 0	1.83605

[1]Wiss. Abh. der Kaiserlichen Normal-Eichungs-Kommission, 5, p. 131; 1900.

TABLE 13. — TEMPERATURE CORRECTIONS TO PER CENT OF SULFURIC ACID DETERMINED BY HYDROMETER (STANDARD AT 20° C.)

[Calculated from the same data as the preceding table, assuming Jena 16^{III} glass as the material used. The table should be used with caution, and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air]

Observed Per Cent H_2SO_4	Temperature in Degrees Centigrade											
	0	5	10	15	25	30	35	40	45	50	55	60
	Subtract from Observed Per Cent				Add to Observed Per Cent							
0					0.16	0 35	0 59	0 86	1.17	1.5	1.9	2.1
5	0 59	0 49	0.36	0 20	0 24	0 50	0 79	1.11	1.45	1 8	2.2	2.6
10	0 92	0.72	0 51	0 27	0 29	0 60	0 93	1 28	1.65	2 0	2 4	2.8
20	1 39	1.06	0.72	0 36	0.37	0 75	1 14	1 53	1 93	2.3	2 7	3.1
30	1 64	1 23	0 82	0 41	0 41	0 82	1 24	1 65	2 07	2.5	2 9	3.3
40	1 65	1 24	0 82	0 41	0 41	0 82	1.22	1.62	2 03	2 4	2.8	3.2
50	1 56	1.17	0 78	0 39	0 38	0 77	1 15	1 52	1 90	2.3	2 6	3.0
60	1 52	1.14	0 76	0.38	0 37	0 74	1 11	1.48	1 84	2 2	2.6	2.9
70	1 54	1 15	0 76	0 38	0 38	0 75	1 13	1 50	1 86	2.2	2.6	3.0
80	1 72	1.30	0 87	0.44	0 45	0 90	1 36	1.83	2.31	2 8	3 3	3.8
81	1 76	1 34	0 92	0 44	0 47	0 93	1 42	1 93	2 44	3 0	3 5	4 0
82	1 84	1 41	0 96	0 47	0 50	1 00	1 51	2 04	2 58	3.1	3.7	4.3
83	1 94	1 48	1.00	0 50	0 53	1.06	1 59	2 18	2 78	3 4	4 0	4.6
84	2 05	1.57	1 06	0 53	0 55	1 12	1 74	2 36	3 0	3 7	4 4	5 1
85	2 20	1 67	1 13	0 57	0 61	1.23	1 88	2 57	3 3	4.0	4 9	5.8
86	2 36	1 80	1 22	0 62	0 66	1.35	2 08	2 84	3 7	4 6	5 5	
87	2 54	1 95	1.32	0 67	0 73	1 50	2 31	3 2	4 1	5 2		
88	2 75	2 12	1 44	0 74	0 81	1 67	2 59	3 6	4 7	6 0		
89	3 01	2 31	1 58	0 82	0 89	1 86	2 91	4 1	5.6			
90	3 27	2.53	1 73	0 91	0 99	2 10	3.4	4 9				
91	3 57	2.78	1 93	1 01	1 13	2 44	4 1					
92	3 91	3.06	2.13	1 12	1 32	3.00						
93	4.29	3 38	2 37	1.26	1.64							
94	4.75	3 77	2 69	1 46								
95	5.29	4.26	3.12	1 76								
96	5 96	4 88	3.65	2 19								
97	6.78	5 68	4.42	2 90								

TABLE 14. — DENSITY OF STRONG ACIDS AT 15° IN VACUO

(According to LUNGE, ISLER, NAEF, and MARCHLEWSKY)*

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205		33.07	27.95	1.440	74.64	54.07
1.210		33.80	28.58	1.445	75.94	54.55
1.215		34.53	29.21	1.450	77.24	55.03
1.220		35.26	29.84	1.455	78.56	55.50
1.225		36.01	30.48	1.460	79.94	55.97
1.230		36.76	31.11	1.465	81.38	56.43

* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

TABLE 14. — DENSITY OF STRONG ACIDS AT 15° IN VACUO — *Continued*

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight		Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight
	HNO_3	H_2SO_4		H_2SO_4		H_2SO_4
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525		62.06	1.665	74.24	1.805	87.60
1.530		62.53	1.670	74.66	1.810	88.30
1.535		63.00	1.675	75.08	1.815	89.16
1.540		63.43	1.680	75.50	1.820	90.05
1.545		63.85	1.685	75.94	1.825	91.00
1.550		64.26	1.690	76.38	1.830	92.10
1.555		64.67	1.695	76.76	1.835	93.56
1.560		65.20	1.700	77.17	1.840	95.60
1.565		65.65	1.705	77.60	1.8405	95.95
1.570		66.09	1.710	78.04	1.8410	96.38
1.575		66.53	1.715	78.48	1.8415	97.35
1.580		66.95	1.720	78.92	1.8410	98.20
1.585		67.40	1.725	79.36	1.8405	98.52
1.590		67.83	1.730	79.80	1.8400	98.72
1.595		68.26	1.735	80.24	1.8395	98.77
1.600		68.70	1.740	80.68	1.8390	99.12
1.605		69.13	1.745	81.12	1.8385	99.31

TABLE 15. — DENSITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS AT 15° C.

Specific Gravity	Per Cent KOH	Per Cent NaOH	Specific Gravity	Per Cent KOH	Per Cent NaOH
1.007	0.9	0.59	1.252	27.0	22.50
1.014	1.7	1.20	1.263	28.2	23.50
1.022	2.6	1.65	1.274	28.9	24.48
1.029	3.5	2.50	1.285	29.8	25.50
1.037	4.5	3.22	1.297	30.7	26.58
1.045	5.6	3.79	1.308	31.8	27.65
1.052	6.4	4.50	1.320	32.7	28.83
1.060	7.4	5.20	1.332	33.7	30.00
1.067	8.2	5.86	1.345	34.9	31.20
1.075	9.2	6.58	1.357	35.9	32.50
1.083	10.1	7.30	1.370	36.9	33.73
1.091	10.9	8.07	1.383	37.8	35.00
1.100	12.0	8.78	1.397	38.9	36.36
1.108	12.9	9.50	1.410	39.9	37.65
1.116	13.8	10.30	1.424	40.9	39.06
1.125	14.8	11.06	1.438	42.1	40.47
1.134	15.7	11.90	1.453	43.4	42.02
1.142	16.5	12.69	1.468	44.6	43.58
1.152	17.6	13.50	1.483	45.8	45.16
1.162	18.6	14.35	1.498	47.1	47.73
1.171	19.5	15.15	1.514	48.3	48.41
1.180	20.5	16.00	1.530	49.4	50.10
1.190	21.4	16.91	1.546	50.6	.....
1.200	22.4	17.81	1.563	51.9	.....
1.210	23.3	18.71	1.580	53.2	.....
1.220	24.2	19.65	1.597	54.5	.....
1.231	25.1	20.69	1.615	55.9	.....
1.241	26.1	21.55	1.634	57.5	.....

TABLE 16. — DENSITY OF AMMONIA SOLUTIONS AT 15° C.

(According to LUNGE and WIERNIK)*

Specific Gravity	Per Cent NH_3	Specific Gravity	Per Cent NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters
−2.0	3.955	+2.0	5.302	+6.0	6.998
1.9	3.985	2.1	5.340	6.1	7.047
1.8	4.016	2.2	5.378	6.2	7.095
1.7	4.047	2.3	5.416	6.3	7.144
1.6	4.078	2.4	5.454	6.4	7.193
1.5	4.109	2.5	5.491	6.5	7.242
1.4	4.140	2.6	5.530	6.6	7.292
1.3	4.171	2.7	5.569	6.7	7.342
1.2	4.203	2.8	5.608	6.8	7.392
1.1	4.235	2.9	5.647	6.9	7.442
1.0	4.267	3.0	5.687	7.0	7.492
0.9	4.299	3.1	5.727	7.1	7.544
0.8	4.331	3.2	5.767	7.2	7.595
0.7	4.364	3.3	5.807	7.3	7.647
0.6	4.397	3.4	5.848	7.4	7.699
0.5	4.430	3.5	5.889	7.5	7.751
0.4	4.463	3.6	5.930	7.6	7.804
0.3	4.497	3.7	5.972	7.7	7.857
0.2	4.531	3.8	6.014	7.8	7.910
0.1	4.565	3.9	6.055	7.9	7.964
0.0	4.600	4.0	6.097	8.0	8.017
+0.1	4.633	4.1	6.140	8.1	8.072
0.2	4.667	4.2	6.183	8.2	8.126
0.3	4.700	4.3	6.226	8.3	8.181
0.4	4.733	4.4	6.270	8.4	8.236
0.5	4.767	4.5	6.313	8.5	8.291
0.6	4.801	4.6	6.357	8.6	8.347
0.7	4.836	4.7	6.401	8.7	8.404
0.8	4.871	4.8	6.445	8.8	8.461
0.9	4.905	4.9	6.490	8.9	8.517
1.0	4.940	5.0	6.534	9.0	8.574
1.1	4.975	5.1	6.580	9.1	8.632
1.2	5.011	5.2	6.625	9.2	8.690
1.3	5.047	5.3	6.671	9.3	8.748
1.4	5.082	5.4	6.717	9.4	8.807
1.5	5.118	5.5	6.763	9.5	8.865
1.6	5.155	5.6	6.810	9.6	8.925
1.7	5.191	5.7	6.857	9.7	8.985
1.8	5.228	5.8	6.904	9.8	9.045
1.9	5.265	5.9	6.951	9.9	9.105

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT
— Continued

Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters
+10.0	9.165	+14.0	11.908	+18.0	15.357
10.1	9.227	14.1	11.986	18.1	15.454
10.2	9.288	14.2	12.064	18.2	15.552
10.3	9.350	14.3	12.142	18.3	15.650
10.4	9.412	14.4	12.220	18.4	15.747
10.5	9.474	14.5	12.298	18.5	15.845
10.6	9.537	14.6	12.378	18.6	15.945
10.7	9.601	14.7	12.458	18.7	16.045
10.8	9.665	14.8	12.538	18.8	16.145
10.9	9.728	14.9	12.619	18.9	16.246
11.0	9.792	15.0	12.699	19.0	16.346
11.1	9.857	15.1	12.781	19.1	16.449
11.2	9.923	15.2	12.864	19.2	16.552
11.3	9.989	15.3	12.947	19.3	16.655
11.4	10.054	15.4	13.029	19.4	16.758
11.5	10.120	15.5	13.112	19.5	16.861
11.6	10.187	15.6	13.197	19.6	16.967
11.7	10.255	15.7	13.281	19.7	17.073
11.8	10.322	15.8	13.366	19.8	17.179
11.9	10.389	15.9	13.451	19.9	17.285
12.0	10.457	16.0	13.536	20.0	17.391
12.1	10.526	16.1	13.623	20.1	17.500
12.2	10.596	16.2	13.710	20.2	17.608
12.3	10.665	16.3	13.797	20.3	17.717
12.4	10.734	16.4	13.885	20.4	17.826
12.5	10.804	16.5	13.972	20.5	17.935
12.6	10.875	16.6	14.062	20.6	18.047
12.7	10.947	16.7	14.151	20.7	18.159
12.8	11.019	16.8	14.241	20.8	18.271
12.9	11.090	16.9	14.331	20.9	18.383
13.0	11.162	17.0	14.421	21.0	18.495
13.1	11.235	17.1	14.513	21.1	18.610
13.2	11.309	17.2	14.605	21.2	18.724
13.3	11.383	17.3	14.697	21.3	18.839
13.4	11.456	17.4	14.790	21.4	18.954
13.5	11.530	17.5	14.882	21.5	19.069
13.6	11.605	17.6	14.977	21.6	19.187
13.7	11.681	17.7	15.072	21.7	19.305
13.8	11.757	17.8	15.167	21.8	19.423
13.9	11.832	17.9	15.262	21.9	19.541

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT
— Concluded

Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters	Degrees, C.	Tension in Millimeters
+22.0	19.659	+26.0	24.988	+30.0	31.548
22.1	19.780	26.1	25.138	30.1	31.729
22.2	19.901	26.2	25.288	30.2	31.911
22.3	20.022	26.3	25.438	30.3	32.094
22.4	20.143	26.4	25.588	30.4	32.278
22.5	20.265	26.5	25.738	30.5	32.463
22.6	20.389	26.6	25.891	30.6	32.650
22.7	20.514	26.7	26.045	30.7	32.837
22.8	20.639	26.8	26.198	30.8	33.026
22.9	20.763	26.9	26.351	30.9	33.215
23.0	20.888	27.0	26.505	31.0	33.405
23.1	21.016	27.1	26.663	31.1	33.596
23.2	21.144	27.2	26.820	31.2	33.787
23.3	21.272	27.3	26.978	31.3	33.980
23.4	21.400	27.4	27.136	31.4	34.174
23.5	21.528	27.5	27.294	31.5	34.368
23.6	21.659	27.6	27.455	31.6	34.564
23.7	21.790	27.7	27.617	31.7	34.761
23.8	21.921	27.8	27.778	31.8	34.959
23.9	22.053	27.9	27.939	31.9	35.159
24.0	22.184	28.0	28.101	32.0	35.359
24.1	22.319	28.1	28.267	32.1	35.559
24.2	22.453	28.2	28.433	32.2	35.760
24.3	22.588	28.3	28.599	32.3	35.962
24.4	22.723	28.4	28.765	32.4	36.165
24.5	22.858	28.5	28.931	32.5	36.370
24.6	22.996	28.6	29.101	32.6	36.576
24.7	23.135	28.7	29.271	32.7	36.783
24.8	23.273	28.8	29.441	32.8	36.991
24.9	23.411	28.9	29.612	32.9	37.200
25.0	23.550	29.0	29.782	33.0	37.410
25.1	23.692	29.1	29.956	33.1	37.621
25.2	23.834	29.2	30.131	33.2	37.832
25.3	23.976	29.3	30.305	33.3	38.045
25.4	24.119	29.4	30.479	33.4	38.258
25.5	24.261	29.5	30.654	33.5	38.473
25.6	24.406	29.6	30.833	33.6	38.689
25.7	24.552	29.7	31.011	33.7	38.906
25.8	24.697	29.8	31.190	33.8	39.124
25.9	24.842	29.9	31.369	33.9	39.344
34.0	39.565	34.4	40.455	34.8	41.364
34.1	39.786	34.5	40.680	34.9	41.595
34.2	40.007	34.6	40.907		
34.3	40.230	34.7	41.135	35.0	41.827

TABLE 18. — HEATS OF COMBUSTION OF 1 LITER OF GAS MEASURED AT 0° AND 760 MM. BAROMETRIC PRESSURE

Gas	Weight of One Liter in Grams	Referred to	
		Gaseous Water Calories	Liquid Water Calories
Carbon monoxide	1.25016	2,560	3,034
Hydrogen	0.09004	2,595	3,077
Methane	0.71488	8,505	9,469
Ethylene	1.25899	14,018	14,989
Propylene	1.93660	21,226	22,720
Benzene-gas	3.48428	(?)33,750	(?)35,198
Acetylene	1.18080	13,582	14,073
Generator-gas	.....	about 900	about 1,000
Water-gas	.....	" 3,386	" 3,700
Dowson gas	.....	" 1,400	.....
Illuminating-gas	.....	" 5,000	" 5,500

The values in the above table are based upon Thomsen's measurements and only in the case of benzene is the theoretical density used.*

* Julius Thomsen, *Thermochem. Untersuchungen* (1882), Vol. II, pp. 56, 85, 107, and Vol. IV, p. 254.

$$CO + O = CO_2 + 67{,}960 \text{ cals.}$$
$$H_2 + O = H_2O + 68{,}357 \text{ cals.}$$
$$CH_4 + 4O = 2H_2O + CO_2 + 211{,}930 \text{ cals.}$$
$$C_2H_4 + 6O = 2H_2O + 2CO_2 + 333{,}350 \text{ cals.}$$
$$C_3H_6 + 9O = 3H_2O + 3CO_2 + 492{,}740 \text{ cals.}$$
$$C_2H_6 + 15O = 3H_2O + 6CO_2 + 787{,}950 \text{ cals.}$$
$$C_2H_2 + 5O = H_2O + 2CO_2 + 310{,}450 \text{ cals.}$$

TABLE 19. — MELTING-POINTS OF THE CHEMICAL ELEMENTS[1]

Element	C.	F.	Element	C.	F.
Helium	<−271	<−456	Neodymium	840?	1544
Hydrogen	−259	−434	Arsenic	850?	1562
Neon	−253?	−423	Barium	850	1562
Fluorine	−223	−369	Praseodymium	940?	1724
Oxygen	−218	−360	Germanium	958	1756
Nitrogen	−210	−346	Silver	960.5	1761
Argon	−188	−306	Gold	1063.0	1945.5
Krypton	−169	−272	Copper	1083.0	1981.5
Xenon	−140	−220	Manganese	1260	2300
Chlorine	−101.5	−150.7	Samarium	1300–1400	2370–2550
Mercury	− 38.9	− 38.0	Beryllium		
Bromine	− 7.3	+ 18.9	(glucinum)	1350?	2462
Caesium	+ 26	79	Scandium	?	
Gallium	30	86	Silicon	1420	2588
Rubidium	38	100	Nickel	1452	2646
Phosphorus	44	111.2	Cobalt	1480	2696
Potassium	62.3	144	Yttrium	1490	2714
Sodium	97.5	207.5	Chromium	1520	2768
Iodine	113.5	236.3	Iron	1530	2786
Sulphur	S_I 112.8	235.0	Palladium	1549	2820
	S_{II} 119.2	246.6	Zirconium	1700?	3090
	S_{III} 106.8	224.2	Columbium		
Indium	155	311	(Niobium)	1700?	3090
Lithium	186	367	Thorium	>1700 <Pt	>3090 <Pt
Selenium	217–220	422–428	Vanadium	1720	3128
Tin	231.9	449.4	Platinum	1755	3191
Bismuth	271	520	Ytterbium	?	
Thallium	302	576	Titanium	1800	3272
Cadmium	320.9	609.6	Uranium	<1850	<3362
Lead	327.4	621.3	Rhodium	1950	3542
Zinc	419.4	786.9	Boron	2200–2500?	4000–4500
Tellurium	452	846	Iridium	2350?	4262
Antimony	630.0	1166	Ruthenium	2450?	4442
Cerium	640	1184	Molybdenum	2500?	4500
Magnesium	651	1204	Osmium	2700?	4900
Aluminum	658.7	1217.7	Tantalum	2850	5160
Radium	700	1292	Tungsten	3000	5430
Calcium	810	1490	Carbon	>3600 for p. = 1 at.	>6500 for p. = 1 at.
Lanthanum	810?	1490			
Strontium	>Ca<Ba?				

[1] Reproduced from Circular No. 35 (2nd edition) of U. S. Bureau of Standards.

TABLE 20. — APPROXIMATE TEMPERATURES BY COLORS

	Cent.	Fahr.
First visible red	525	977
Dull red	700	1292
Cherry red	900	1652
Dull orange	1100	2012
White	1300	2372
Dazzling white	1500	2732

TABLE 21. — DENSITY OF PHOSPHORIC ACID AT 17.5°

Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15 84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

TABLE 22. — DENSITY OF ACETIC ACID AT 15°

Specific Gravity	Per Cent $H.C_2H_3O_2$	Specific Gravity	Per Cent $H.C_2H_3O_4$	Specic Gravity	Per Cent $H.C_2H_3O_2$	Specific Gravity	Per Cent $H.C_2H_3O$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS*

Substance	Formula	Molecular or Atomic Weight	Weight in 1 ml. of *N* solution	Solubility in 100 Gms. Water
Acetic acid	$HC_2H_3O_2$	60.03	.06003	
Aluminium	Al	27.10	.009033	
chloride	Al_2Cl_6	266.96	.04449	$69.87^{15°}$
chloride	$Al_2Cl_6 \cdot 12H_2O$	483.15	.08053	40
oxide	Al_2O_3	102.20	.01703	insol.
sulfate	$Al_2(SO_4)_3$	342.38	.05706	$36.1^{20°}$
sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	666.67	.11111	87
Ammonia	NH_3	17.03	.01703	
Ammonium	NH_4	18.04	.01804	
chloride	NH_4Cl	53.50	.05350	$29.4^{0°}$
hydroxide	NH_4OH	35.05	.03505	
nitrate	NH_4NO_3	80.05	.08005	$118^{0°}$
sulfate	$(NH_4)_2SO_4$	132.14	.06607	$71^{0°}$
Antimony	Sb	120.20	.06010	
Arsenic	As	74.96	.03748	
oxide	As_2O_5	229.92	.03832[1]	150
Arsenous oxide	As_2O_3	197.92	.03299	$1.7^{18°}$
Arsenious oxide	As_2O_3	197.92	.04948[3]	$1.7^{18°}$
Barium	Ba	137.37	.068685	
carbonate	$BaCO_3$	197.37	.098685	$.0022^{20°}$
chloride	$BaCl_2$	208.29	.104145	$30.9^{0°}$
chloride	$BaCl_2 \cdot 2H_2O$	244.32	.12216	$36.2^{0°}$
hydroxide	$Ba(OH)_2$	171.38	.08569	
hydroxide	$Ba(OH)_2 \cdot 8H_2O$	315.51	.15775	$5.56^{15°}$
sulfate	$BaSO_4$	233.44	.11672	$.000172^{0°}$
oxide	BaO	153.37	.076685	$1.5^{0°}$
peroxide	BaO_2	169.37	.08469	insol.
Bromine	Br	79.92	.07992	$4.17^{0°}$
Cadmium carbonate	$CdCO_3$	172.40	.08620	insol.
chloride	$CdCl_2$	183.32	.09166	$140^{20°}$
chloride	$CdCl_2 \cdot 2H_2O$	219.35	.109675	$168^{20°}$
sulfide	CdS	144.47	.072235	insol.
Calcium	Ca	40.00	.020035	
carbonate	$CaCO_3$	100.07	.050035	.0013
chloride	$CaCl_2$	110.99	.055495	$59.5^{0°}$
chloride	$CaCl_2 \cdot 6H_2O$	219.086	.109543	$117.4^{0°}$
hydroxide	$Ca(OH)_2$	74.09	.037045	$.17^{0°}$
oxide	CaO	56.07	.028035	$.13^{0°}$
sulfate	$CaSO_4$	136.14	.06807	$.179^{0°}$
sulfide	CaS	72.14	.03607	$.15^{10°}$
Carbon	C	12.005	.003002	insol.
dioxide	CO_2	44.005	.022003[1]	179.67 ml.$^{0°}$
dioxide	CO_2	44.005	.044005[2]	"
Chlorine	Cl	35.46	.03546	150 ml.$^{0°}$
Chromic anhydride	CrO_3	100.00	.033333[3]	$163.4^{0°}$
oxide	Cr_2O_3	152.00	.025333[3]	insol.
Citric acid	$H_3C_6H_5O_7$	192.06	.06402	133.
Cobalt	Co	58.97	.029485	
Copper	Cu	63.57	.031785	
oxide	CuO	79.57	.07957	
sulfate	$CuSO_4$	159.63	.15963	$20^{0°}$
sulfate	$CuSO_4 \cdot 5H_2O$	249.71	.24971	$31.61^{0°}$
sulfide	CuS	95.63	.047815	.000033

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.

* Compiled and arranged by R. M. Meiklejohn.

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS — *Continued*

Substance	Formula	Molecular or Atomic Weight	Weight in 1 ml. of *N* solution	Solubility in 100 Gms. Water
Cyanogen	CN	26.005	.026005	
Ferric oxide	Fe_2O_3	159.68	.07984[3]	
Ferrous oxide	FeO	71.84	.07184[3]	insol.
sulfate	$FeSO_4$	151.90	.15190[3]	
sulfate	$FeSO_4 \cdot 7H_2O$	278.01	.27801[3]	32.8°
ammon'm sulfate	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	392.14	.39214	18°
Hydrobromic acid	HBr	80.928	.08093	221.2°
Hydrochloric acid	HCl	36.47	.03647	82.5[10]°
Hydrocyanic acid	HCN	27.02	.02702	
Hydrofluoric acid	HF	20.01	.02001	264
Hydroiodic acid	HI	127.93	.12793	
Hydrogen peroxide	H_2O_2	34.016	.017008	
Hydrogen sulfide	H_2S	34.076	.017038	437 ml.[0]°
Iodine	I	126.92	.12692	.0182[11]°
Iron	Fe	55.84	.05584	
Lead	Pb	207.20	.10360	
carbonate	$PbCO_3$	267.20	.13360	.00198
chromate	$PbCrO_4$	323.20	.16160	.00002[18]°
oxide	PbO	223.20	.11160	
peroxide	PbO_2	239.20	.11960	
sulfide	PbS	239.26	.11963	.0001
Magnesium	Mg	24.32	.01216	
carbonate	$MgCO_3$	84.32	.04216	.0106
chloride	$MgCl_2$	95.24	.04762	52.2°
chloride	$MgCl_2 \cdot 6H_2O$	203.34	.10167	167
oxide	MgO	40.32	.02016	00062
sulfate	$MgSO_4$	120.38	.06019	26.9°
sulfate	$MgSO_4 \cdot 7H_2O$	246.49	.123245	76.9°
Malic acid	$H_2C_4H_4O_5$	134.06	.06703	
Manganese	Mn	54.93	.027465	
chloride	$MnCl_2$	125.85	.062925	62.16[10]°
peroxide	MnO_2	86.93	.043465	insol.
sulfate	$MnSO_4$	150.99	.075495	53.2°
Mercuric chloride	$HgCl_2$	271.52	.13576	5.73°
Nickel	Ni	58.68	.02934	
Nitric acid	HNO_3	63.02	.06302[2]	
Nitric acid	HNO_3	63.02	.021006[3]	
Nitrogen trioxide	N_2O_3	76.02	.019005[3]	
pentoxide	N_2O_5	108.02	.05401[2]	
pentoxide	N_2O_5	108.02	.018033[3]	
Nitrous acid	HNO_2	47.02	.04702	
Nitrogen	N	14.01	.01401	
Oxalic acid	$H_2C_2O_4$	90.02	.04501	
Oxalic acid	$H_2C_2O_4 \cdot 2H_2O$	126.05	.063025	4.9°
Phosphoric acid	H_3PO_4	98.06	.09806[2]	v. sol.
Phosphoric acid	H_3PO_4	98.06	.04903[2]	v. sol.
Phosphoric acid	H_3PO_4	98.06	.03268	v. sol.
Potassium	K	39.10	.3910	
bicarbonate	$KHCO_3$	100.11	.10011	22.4°
bitartrate	$KHC_4H_4O_6$	188.14	.18814	.37°
bromide	KBr	119.02	.11902	53.48°
carbonate	K_2CO_3	138.20	.06910	89.4°
chlorate	$KClO_3$	122.56	.0204[27][3]	3.3[0]4

[1] Precipitation reagents. M Methyl orange.

[2] Acids and bases. P. Phenolphthalein.

[3] Oxidizing and reducing agents. Temp. C.

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS — *Concluded*

Substance	Formula	Molecular or atomic weight	Weight in 1 ml. of *N* solution	Solubility in 100 Gms. Water[4]
Potassium chloride	KCl	74.56	.07456	$28.5^{0°}$
chromate	K_2CrO_4	194.20	.06473[3]	$61.5^{0°}$
cyanide	KCN	65.11	.6511[1]	v. sol.
dichromate	$K_2Cr_2O_7$	294.20	.14710[2]	$4.9^{0°}$
dichromate	$K_2Cr_2O_7$	294.20	.04903[3]	$4.9^{0°}$
ferrocyanide	$K_4Fe(CN)_6$	368.30	.36830	
ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	422.35	.42235	$27.8^{12°}$
hydroxide	KOH	56.11	.05611	$107^{15°}$
iodate	KIO_3	214.02	.03567	$4.74^{0°}$
iodide	KI	166.03	.16603	$126.1^{0°}$
nitrate	KNO_3	101.11	.033703	$13.3^{0°}$
nitrite	KNO_2	85.11	.08511	$300^{15.5°}$
oxide	K_2O	94.20	.04710	v. sol.
permanganate	$KMnO_4$	158.03	.031606	$2.83^{0°}$
sulfide	K_2S	110.26	.05513	sol.
sulfocyanate	$KCNS$	97.18	.09718	$177.2^{0°}$
tartrate	$K_2H_4C_4O_6$	226.23	.11312	sol.
Silver	Ag	107.88	.10788	
nitrate	$AgNO_3$	169.89	.16989	$122^{0°}$
Sodium	Na	23.00	.02300	
bromide	$NaBr$	102.92	.10292	$79.5^{0°}$
bicarbonate	$NaHCO_3$	84.01	.08401	$6.90^{0°}$
carbonate	Na_2CO_3	106.00	.05300	$7.1^{0°}$
chloride	$NaCl$	58.46	.05846	$35.7^{0°}$
cyanide	$NaCN$	49.01	.04901	sol.
hydroxide	$NaOH$	40.01	.04001	$133.3^{18°}$
iodide	NaI	149.92	.14992[1]	$158.7^{0°}$
nitrate	$NaNO_3$	85.01	.02834	$72.9^{0°}$
nitrite	$NaNO_2$	69.01	.06901	$83.3^{20°}$
oxalate	$Na_2C_2O_4$	134.00	.06700	$3.22^{15.5°}$
oxide	Na_2O	62.00	.03100	decomp.
phosphate (mono)	NaH_2PO_4	120.06[2]	.12006	v. sol.
phosphate (disod)	Na_2HPO_4	142.05[2]	.14205	
phosphate (disod)	$Na_2HPO_4 \cdot 12H_2O$	358.24[2]	.35824	$6.3^{0°}$
phosphate (trisod)	Na_3PO_4	164.04[2]	.16404	
sulfide	Na_2S	78.06	.03903	$15.4^{10°}$
thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	248.20	.24820	$74.7^{0°}$
Stannous chloride	$SnCl_2$	189.62	.09481	$83.9^{0°}$
chloride	$SnCl_2 \cdot 2H_2O$	225.65	.112825	$118.7^{0°}$
oxide	SnO	134.70	.06735	insol.
Sulfur dioxide	SO_2	64.06	.03203	7979 ml.$^{0°}$
trioxide	SO_3	80.06	.04003	
Sulfuric acid	H_2SO_4	98.076	.049038	
Tartaric acid	$H_2C_4H_4O_6$	150.05	.075025	$115^{0°}$
Tin	Sn	118.70	.05935	
Zinc	Zn	65.37	.037685	
carbonate	$ZnCO_3$	125.37	.062685	$.001^{15°}$
chloride	$ZnCl_2$	136.29	.068145	$209^{0°}$
oxide	ZnO	81.37	.040685	.001
sulfate	$ZnSO_4$	161.43	.080715	$43.02^{0°}$
sulfate	$ZnSO_4 \cdot 7H_2O$	287.54	.14377	$115.2^{0°}$
sulfide	ZnS	97.43	.048715	.00069

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.

[4] The small superior numbers in the last column refer to the temperature in degrees Centigrade.

TABLE 24. — COMPARISON OF METRIC AND CUSTOMARY UNITS (U. S.)

LENGTH

1 millimeter, mm.	= 0.03937 inch.	1 inch	= 2.5400 millimeters.
1 centimeter, cm.	= 0.39371 inch.	1 inch	= 2.5400 centimeters.
1 meter, m.	= 3.2808 feet.	1 foot	= 0.30480 meter.
1 meter	= 1.0936 yards.	1 yard	= 0.91440 meter.
1 kilometer	= 0.62137 (U.S.) mile.	1 mile	= 1.6094 kilometers.

AREAS

1 square millimeter, sq. mm.	= 0.00155 sq. in.	1 sq. in.	= 645.16 sq. mm.
1 square centimeter, sq. cm.	= 0.1550 sq. in.	1 sq. in.	= 6.452 sq. cm.
1 square meter, sq. in.	= 10.764 sq. ft.	1 sq. ft.	= 0.0929 sq. m.
1 square meter	= 1.196 sq. yd.	1 sq. yd.	= 0.8361 sq. m.
1 square kilometers	= 0.3861 sq. mi.	1 sq. mi.	= 2.5900 sq. km.
1 hectare	= 2.471 acres.	1 acre	= 0.4047 hectare.

VOLUMES

1 cubic millimeter, cu. mm.	= 0.000061 in.	1 cu. in.	= 16,387 cu. mm.
1 cubic centimeter, ml.	= 0.06103 cu. in.	1 cu. in.	= 16.387 ml.
1 cubic meter	= 35.314 cu. ft. = 61,028 cu. in.	1 cu. ft.	= 0.02832 cu. m. = 28.32 liters.
1 cubic meter	= 1.3079 cu. yd.	1 cu. yd.	= 0.7645 cu. m.

CAPACITIES

1 cubic centimeter, ml.	= 0.03381 (U.S.) liquid oz.	1 ounce	= 29.574 ml.
1 cubic centimeter	= 0.2705 (U.S.) apothecaries' dram.	1 dram	= 3.6967 ml.
1 cubic centimeter	= 0.8115 (U.S.) apothecaries' scruple.	1 scruple	= 1.2322 ml.
1 liter	= 1.05668 (U.S.) liquid qts.	1 quart	= 0.94636 liter.
1 liter	= 0.26417 (U.S.) gallon.	1 gallon	= 3.78543 liters.
1 liter	= 0.11351 (U.S.) peck.	1 peck	= 8.80982 liters.
1 hectoliter	= 2.83774 (U.S.) bushels.	1 bushel	= 0.35239 hectoliter.

MASSES

1 gram	= 15.432 grains.	1 grain	= 0.06480 gram.
1 gram	= 0.03527 avoirdupois ounce.	1 ounce (av.)	= 28.350 grams.
1 gram	= 0.03215 troy ouuce.	1 ounce (troy)	= 31.103 grams.
1 kilogram	= 2.2046 pounds (av.)	1 pound (av.)	= 0.4536 kilogram.
1 kilogram	= 2.6792 pounds (troy).	1 pound (troy)	= 0.37324 kilogram.

AVOIRDUPOIS WEIGHT

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams	= 1 ounce	= 28.35 grams.
16 ounces	= 1 pound	= 453.59 grams.
25 pounds	= 1 quarter	= 11.34 kilograms.
4 quarters	= 1 hundred weight	= 45.359 kilograms.

1 avoirdupois pound contains 7000 grains.

1 avoirdupois ounce contains 437.5 grains.

APOTHECARIES' WEIGHT

The system of weights sometimes employed in weighing medicines.

1 grain		= 0.0648 gram.
20 grains	= 1 scruple	= 1.296 grams.
3 scruples	= 1 drachm	= 3.888 grams.
8 drachms	= 1 ounce	= 31.10 grams.
12 ounces	= 1 pound	= 373.23 grams.

1 apothecaries' (or troy) pound contains 5760 grains.

1 apothecaries' (or troy) ounce contains 480 grains.

FLUID MEASURE

1 minim		= .06161	cubic centimeter.
60 minims	= 1 fluid drachm	= 3.696	cubic centimeters.
8 fluid drachms	= 1 fluid ounce	= 29.573	cubic centimeters.
16 fluid ounces	= 1 pint	= 473.18	cubic centimeters.
8 pints	= 1 gallon	= 3.785	liters.

1 gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures sometimes employed by apothecaries.

TABLES FOR CALCULATING ANALYSES

DIRECTIONS FOR USING THE TABLES

Computations of Gravimetric Analysis. — The methods of computing the results in gravimetric work were outlined on pp. 1 to 2. In the so-called *direct analysis* it is assumed that all of the desired element in the original substance is converted into a weighed precipitate of which a known fraction consists of the element in question. The fraction, usually expressed as a decimal, which represents the amount of an element A in one of its compounds is commonly called the *chemical factor:* It represents the weight of A in one part by weight of the compound, independent of what unit of weight is used.

Thus, to be specific, 1 g. of silver chloride contains 0.7526 g. of silver; 1 lb. of silver chloride contains 0.7526 lb. of silver. If p g. of silver chloride are obtained from s g. of original substance, then $0.7526\ p$ is the weight of silver in the sample taken and $\frac{0.7526\ p \times 100}{s}$ = per cent of silver in the substance analyzed. The general rule for computing a direct gravimetric analysis is as follows: Multiply the weight of the precipitate by 100 times the chemical factor and divide by the weight of the original substance. Using the notation as above:

$$\frac{p \times \text{chem. factor} \times 100}{s} = \text{desired percentage.}$$

A table of chemical factors is given on the following pages. The use of the table may be illustrated by an example:

From 0.5 g. of arsenic ore, 0.4761 g. of $Mg_2As_2O_7$ was obtained. What is the per cent of arsenic in the ore?

In the table (p. 746) we seek As under the heading "Sought" and $Mg_2As_2O_7$ under the heading "Found," and we find on the same line that the chemical factor is 0.4827. Finally, in the fourth column we find that the logarithm of this number multiplied by 100 is 1.6837. The computation is as follows:

log factor × 100	1.6837
log 0.4761	9.6777 − 10
colog 0.5	0.3010
	1.6624 log of 45.96

The ore contains 45.96 per cent of arsenic.

If the weight of ore had been 0.4827 g. (a so-called *factor* weight) the per cent of arsenic would have been found by multiplying the weight of precipitate by 100.

This table of factors is convenient, but every chemist should know how to compute any factor. As this often causes trouble for beginners, the method of computing the factors will be discussed.

Computing the Factor. — The symbol AgCl shows that one atomic weight of silver, 107.88, is present in 1 molecular weight of silver chloride, 143.34. This ratio of weights is independent of the unit of weight used and is just as true of tons, pounds, ounces or grains as it is of grams. Using the conception of the gram-molecular weight, the formula shows that 107.88 g. of silver are present in 143.34 g. of silver chloride. If 143.34 g. of silver chloride contain 107.88 g. of silver, 1 g. of silver chloride will contain $\frac{107.88}{143.34} = 0.7526$ g. silver. In other words, the chemical

factor for silver in silver chloride is found by dividing the atomic weight of silver by the molecular weight of silver chloride. Using symbols, the chemical factor in this case is $\frac{Ag}{AgCl}$. It represents the ratio of *what is sought* to *what has been found.*

In the case of the arsenic analysis referred to above, the symbol for magnesium pyroarsenate, $Mg_2As_2O_7$, shows that 2 atoms of arsenic are present in the molecule. The chemical factor is $\frac{2As}{Mg_2As_2O_7} = \frac{149.9}{310.6} = 0.4827.$

As a still more complicated case, assume that a sample of magnetite is analyzed in such away that all of the iron is converted into Fe_2O_3 and it is desired to know the weight of Fe_3O_4 originally present. The chemical factor for converting a weight of Fe_2O_3 into the equivalent weight of Fe_3O_4 is $\frac{2Fe_3O_4}{3Fe_2O_3} = \frac{463.1}{479.1} = 0.9666.$

The concept of the *chemical factor* may be applied to any chemical equation as well as to any precipitate. The following equation represents the reaction between ferrous ions and dichromate ions:

$$6Fe^{++} + Cr_2O_7^{--} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O.$$

On the basis of this equation we can compute the weight of ferrous ammonium sulfate which will react with a given weight of potassium dichromate. The chemical factor is

$$\frac{6[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]}{K_2Cr_2O_7} = \frac{6 \times 392.1}{294.2} = 7.998.$$

If the weight of dichromate is multiplied by this factor the product will be the equivalent of ferrous ammonium sulfate. If a weight of ferrous ammonium sulfate is divided by 7.998, the quotient is the equivalent weight of dichromate.

It is possible to arrive at the same result by a slightly different method of reasoning and this other method is more like the method used in volumetric computations. If the weight of ferrous ammonium sulfate, p, is divided by the molecular weight of ferrous ammonium sulfate, the quotient represents the number of moles of ferrous ammonium sulfate present. The equation, however, shows that one-sixth as many moles of dichromate are required so that by dividing by six and multiplying by the molecular weight of dichromate the weight of dichromate is obtained. In each case the computation may be expressed as follows:

$$\frac{p \times K_2Cr_2O_7}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \times 6} = \text{weight of dichromate.}$$

The fraction $\frac{K_2Cr_2O_7}{6FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$ represents the weight of dichromate which corresponds to 1 g. of ferrous ammonium sulfate, the fraction

$$\frac{p}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

represents the number of moles of ferrous ammonium sulfate present.

It is evident from the foregoing discussion that ordinary chemical arithmetic is really very simple. Formerly the so-called "rule of three" was used more in elementary texts on arithmetic than it is to-day. In Germany it is still used more than in the United States. Most text books on analytical chemistry have been influenced by German practice and beginners in chemistry have been taught to use proportions in chemical arithmetic instead of reasoning out unit values as

they have been taught before studying chemistry. In the above discussion not a single proportion has been written out to be solved mechanically by the rule that "the product of the means is equal to the product of the extremes."

Computations of Volumetric Analysis. —

1. *Relative Strength of Solutions.*

   (*a*) If a ml. of solution $A = b$ ml. of solution B, then

   $$1 \text{ ml. of solution } A = \frac{b}{a} \text{ml. solution } B;\ 1 \text{ ml. of } B = \frac{a}{b} \text{ml. of } A.$$

   (*b*) If solution A is N-normal, then solution B is $\frac{a}{b} \times N$-normal.

   (*c*) If solution A is N-normal and solution B is M-normal, then 1 ml. of $A = N/M$ ml. of B; 1 ml. of $B = M/N$ ml. of A.

2. *Normal Strength or Normality.*

   The *normal strength* gives the number of milli-equivalents contained in one milliliter of solution. Thus, one milliliter of a normal solution contains one milli-equivalent in each milliliter.

   (*a*) To find the normality, divide the value of 1 ml. in terms of any pure substance by the milli-equivalent of that substance. Thus, if *ml.* represents the number of milliliters of solution that contain or are equivalent to g grams of a pure substance (of which the milli-equivalent is e), then the normality, N, is $\frac{g}{ml. \times e} = N$.

   (*b*) If N be the normality, and e the milli-equivalent, then 1 ml. of the solution $= e \times N$ g. of the substance in question.

   The milli-equivalent may be part of the molecule: thus 1 ml. of 0.3 Normal acid $= 0.3 \times 0.031$ g. of Na_2O.

3. *General Method of Finding the Per Cent by Weight.*

   Let ml. represent the net volume of reagent required, N the normality of the reagent, s the weight of substance taken, and e the milli-equivalent weight of the constituent whose percentage is required.

   Then $\frac{\text{ml.} \times N \times e \times 100}{s} = \text{per cent.}$

   Note that if $s = N \cdot e \cdot 100$, then ml. = per cent.

4. *Equivalent Weights.*

   (*a*) Acids. Let M = molecular weight, MO = methyl orange, P = phenolphthalein. The first three acids may be titrated with either indicator.

Acid	*Equivalent*
HCl	M
HNO_3	M
H_2SO_4	M/2
$HC_2H_3O_2$	M (With P)
$H_2C_4H_4O_6$	M/2 (With P)
H_2CO_3	M (With P)
$KHC_4H_4O_6$	M (With P)

$H_2C_2O_4 \cdot 2H_2O$	M/2 (With P)
KHC_2O_4	M (With P)
$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	M/3 (With P)
H_3PO_4	M (With MO)
H_3PO_4	M/2 (With P)
H_3BO_3	M (With P and glycerol, not acid to MO)

(*b*)

Bases	*Equivalent*
KOH	M
NaOH	M
NH_4OH	M (With MO)
$Ba(OH)_2$	M/2

(*c*) SALTS OF WEAK ACIDS

Salts of carbonic and boric acids may be titrated with methyl orange as if the free base were present. With phenolphthalein the end-point is reached when the carbonate is completely changed to bicarbonate. Thus $BaCO_3$ titrates as if it were $Ba(OH)_2$ with methyl orange but reacts with only one (1) equivalent of acid if phenolphthalein be used in the cold.

(*d*) OXIDIZING AGENTS:

Substance	*Reduction Change*	*Equivalent*
$K_2Cr_2O_7$	Each Cr loses 3 charges	M/6
$KMnO_4$	Mn^{+vii} to Mn^{+ii}	M/5
$KMnO_4$	Mn^{+vii} to MnO_2	M/3
MnO_2	Mn^{+iv} to Mn^{+ii}	M/2
$KBrO_3$ or KIO_3	(Br or I)$^{+v}$ to (Br or I)$^{-i}$	M/6
Free Cl, Br, I	To (Cl, Br, or I)$^{-i}$	At. Wt.
Cu++ (Iodide method)	To Cu^+	At. Wt.
Na_2O_2	O± to O=	M/2

(*e*) REDUCING AGENTS:

Substance	*Reduction Change*	*Equivalent*
H_2S	S= to S^0	M/2
$SnCl_2$	Sn^{++} to Sn^{++++}	M/2
HI	I^- to I^0	M
Zn	Zn^0 to Zn^{++}	M/2
Fe	Fe^0 to Fe^{++}	M/2
Fe (After solution in acid)	Fe^{++} to Fe^{+++}	At. Wt.
Fe (Any ferrous salt containing 1 Fe)	Fe^{++} to Fe^{+++}	M
H_2O_2 (With $KMnO_4$)	O± to O^{++}	M/2
$K_4Fe(CN)_6$	To $[Fe(CN)_6]^=$	M
$H_2C_2O_4 \cdot H_2O$ or KHC_2O_4 or $Na_2C_2O_4$	To 2 CO_2	M/2
$KHC_2O_4 \cdot H_2C_2O_4 \cdot H_2O_2$	To 4 CO_2	M/4
$Na_2S_2O_3$	To $\frac{1}{2}$ $Na_2S_4O_6$	M
As_2O_3	To $2AsO_3^=$ or $2AsO_3^-$	M/4

5. *Equivalent weight depends on the reaction.*

Considered as a salt (that is, as if it were a precipitant) the equivalent weight of $KMnO_4 = M$. A solution of $KMnO_4$ which is normal as a salt would be 5-normal in a reaction with a ferrous salt whereby the Mn loses 5 valence charges, and would be 3-normal in a reaction whereby the $KMnO_4$ is only reduced to MnO_2.

Similarly the equivalent weight of potassium binoxalate, KHC_2O_4, or of potassium tetroxalate $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, depends upon the replaceable hydrogen when considered as an acid, but as reducing agents the oxalate content alone is to be considered. A solution of tetroxalate which is normal as an acid is four-thirds normal as a reducing agent. Arsenic acid is like phosphoric acid as an acid, but in the reaction with hydriodic acid the As is reduced from the quinquevalent to the tervalent state (cf. pp. 457–461).

INTERNATIONAL ATOMIC WEIGHTS, 1923

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminium	Al	27.0	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.0
Bismuth	Bi	209.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	45.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.1
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium	Ge	72.1	Sulfur	S	32.06
Glucinum*	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.3	Tellurium	Te	127.5
Helium	He	4.0	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.9
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139 0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2.
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	89.33
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

* Also called *Beryllium*.

CHEMICAL FACTORS*

Sought	Found	Factor	Log
Ag	AgBr	0.5744	9.7593
	AgCl	0.7526	9.8766
	AgCN	0.8055	9.9060
	AgI	0.4595	9.6622
	$AgNO_3$	0.6350	9.8028
	Ag_2O	0.9310	9.9689
	Ag_2S	0.8706	9.9398
	Ag_3PO_4	0.7731	9.8882
	$Ag_4P_2O_7$	0.7125	9.8528
Ag_2O	AgCl	0.8084	9.9076
Al	Al_2O_3	0.5294	9.7238
	$AlPO_4$	0.2212	9.3449
Al_2O_3	$AlPO_4$	0.4179	9.6211
AlF_3	CaF_2	0.7173	9.8557
$AlCl_3$	Al_2O_3	2.615	0.4175
$Al_2(SO_4)_3$	Al_2O_3	3.356	0.5257
$Al_2(SO_4)_3.18H_2O$	Al_2O_3	6.534	0.8152
As	As_2O_3	0.7575	9.8794
	As_2O_5	0.6521	9.8143
	As_2S_3	0.6091	9.7847
	As_2S_5	0.4832	9.6841
	I_2	0.2953	9.4703
	$Mg_2As_2O_7$	0.4827	9.6837
	$Mg_2P_2O_7$	0.6731	9.8281
	$(NH_4MgAsO_4)_2, H_2O$	0.3939	9.5953
As_2O_3	As_2O_5	0.8609	9.9349
	As_2S_3	0.8041	9.9053
	As_2S_5	0.6378	9.8047
	$2I_2$	0.3900	9.5909
	$Mg_2As_2O_7$	0.6372	9.8043
	$Mg_2P_2O_7$	0.8887	9.9487
	$(NH_4MgAsO_4)_2, H_2O$	0.5199	9.7160
AsO_3	As_2S_3	0.9992	9.9996
	As_2S_5	0.7926	9.8991
AsO_3	$Mg_2As_2O_7$	0.7919	9.8987
	$Mg_2P_2O_7$	1.104	0.0430
	$(NH_4MgAsO_4)_2, H_2O$	0.6460	9.8103
As_2O_5	As_2S_3	0.9341	9.9704
	As_2S_5	0.7410	1.8698
	$2I_2$	0.4529	9.6560
	$Mg_2As_2O_7$	0.7403	1.8694
	$Mg_2P_2O_7$	1.032	0.0138
	$(NH_4MgAsO_4)_2, H_2O$	0.6040	9.7810
AsO_4	As_2S_3	1.129	0.0528
	As_2S_5	0.8957	9.9522
	I_2	0.5473	9.7383
	$Mg_2As_2O_7$	0.8949	9.9518
	$Mg_2P_2O_7$	1.2477	0.0962
	$[NH_4MgAsO_4]_2., H_2O$	0.7301	9.8634
Au	$AuCl_3$	0.6496	9.8126
	$HAuCl_4.4H_2O$	0.4785	9.6799
	$KAu(CN)_4.H_2O$	0.5500	9.7403
B	B_2O_3	0.3123	9.4946
	KBF_4	0.08651	8.9371
	H_3BO_3	0.1761	9.2456
	$Na_2B_4O_7.10H_2O$	0.1142	9.0577
B_2O_3	KBF_4	0.2770	9.4425
	H_3BO_3	0.5636	9.7510
	$Na_2B_4O_7.10H_2O$	0.3657	9.5631
BO_2	B_2O_3	1.229	0.896
BO_3	B_2O_3	1.689	0.2273
B_4O_7	B_2O_3	1.114	0.0471
Ba	$BaCl_2.2H_2O$	0.5621	9.7498
	$BaCO_3$	0.6961	9.8426
	$BaCrO_4$	0.5422	9.7341
	$BaSO_4$	0.5885	9.7697
	$BaSiF_6$	0.4912	9.6913
BaO	$BaCO_3$	0.7771	9.8905
	$BaCrO_4$	0.6053	9.7820
	$BaSO_4$	0.6570	9.8176

* The use of the table will be illustrated by two examples. (1) What weight of silver corresponds to p g. of silver bromide? For computation with a slide rule, use column 3, $p \times 0.5744$ = weight of Ag. With logarithms, log p + 9.7593 = log weight of Ag. (2) What weight of silver bromide corresponds to q g. of silver? Use the same factor as before but *divide* by it or *subtract* the logarithm.

Strictly speaking, the logarithm in the above case is not 9.7593 but 9.7593 − 10 or $\bar{1}$ 7593, in which the characteristic is a negative number and the mantissa a positive fraction. It is a little easier to use the first expression and in chemical computations it is not necessary to write out the − 10 each time because there is never any doubt whether a characteristic of 7, 8 or 9 represents a very large number or a number less than unity.

In computing the weight of silver bromide instead of subtracting the logarithm 9.7593 it is more convenient to add the co-logarithm 0.2407 which is obtained quickly by subtracting each digit of 9.7593 from 9 except the last one which is subtracted from 10. It gives the logarithm of $\frac{1}{0.5744} = 0.2417$.

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
BaO	$BaSiF_6$	0.5484	9.7391
BaO_2	Ba	1.233	0.0909
	$BaCrO_4$	0.6685	9.8251
	$BaSO_4$	0.7256	9.8607
$BaCO_3$	$BaSO_4$	0.8458	9.9272
$BaCl_2.2H_2O$	$BaSO_4$	1.047	0.0198
$BaCrO_4$	$BaSO_4$	1.085	0.0356
BaF_2	$BaSiF_6$	0.6271	9.7973
$Ba(NO_3)_2$	$BaSO_4$	1.120	0.0491
$Ba_3(PO_4)_2$	$BaSO_4$	0.8599	9.9345
BaS	$BaSO_4$	0.7258	9.8608
Be	BeO	0.3625	9.5594
BeO	$BeCl_2$	0.3141	9.4970
BeO	$BeSO_4.4H_2O$	0.1416	9.1512
Bi	Bi_2O_3	0.8970	9.9528
	BiOCl	0.8024	9.9044
	$BiPO_4$	0.6874	9.8372
	Bi_2S_3	0.8129	9.9101
	$BiAsO_4$	0.6006	9.7786
Bi_2O_3	Bi	1.115	0.0472
	BiOCl	0.8946	9.9516
	$BiPO_4$	0.7663	9.8844
	Bi_2S_3	0.9063	0.9573
	$BiAsO_4$	0.6696	9.8258
	$BiONO_3$	0.8118	9.9095
	$Bi(NO_3)_3.5H_2O$	0.4803	9.6815
Br	Ag	0.7408	9.8697
	AgBr	0.4256	9.6290
	AgCl	0.5576	9.7463
	HBr	0.9874	9.9945
BrO_3	Ag	1.186	0.0740
	AgBr	0.6812	9.8332
Br_2O_5	Ag	1.111	0.0459
	AgBr	0.6386	9.8052
C	CO_2	0.2727	9.4357
	$BaCO_3$	0.0608	8.7839
CO_2	$BaCO_3$	0.2231	9.3486
	BaO	0.2872	9.4582
	$Ba(HCO_3)_2$	0.3395	9.5309
	$CaCO_3$	0.4396	9.6430
	$Ca(HCO_3)_2$	0.5431	9.7349
	CaO	0.7844	9.8946
	CO_3	0.7333	9.8653
	Cs_2CO_3	0.1353	9.1312
	$FeCO_3$	0.3801	9.5799
	$Fe(HCO_3)_2$	0.4951	9.6947
	K_2CO_3	0.3186	9.5033
CO_2	$KHCO_3$	0.4400	9.6439
	Li_2CO_3	0.5958	9.7751
	$LiHCO_3$	0.6478	9.8115
	$MgCO_3$	0.5214	9.7178
	$Mg(HCO_3)_2$	0.6016	9.7793
	MgO	1.093	0.0384
	$MnCO_3$	0.3831	9.5833
	$Mn(HCO_3)_2$	0.4976	9.6969
	Na_2CO_3	0.4154	9.6184
	$NaHCO_3$	0.5241	9.7194
	Na_2O	0.7105	9.8516
	$(NH_4)_2CO_3$	0.4582	9.6611
	$PbCO_3$	0.1648	9.2170
	Rb_2CO_3	0.1907	9.2804
	$Rb(HCO_3)$	0.3007	9.4781
	$SrCO_3$	0.2983	9.4746
	$Sr(HCO_3)_2$	0.4200	9.6233
	SrO	0.4251	1.6285
	$ZnCO_3$	0.3514	9.5458
CO_3	CO_2	1.364	0.1347
Ca	$CaCl_2$	0.3612	9.5577
	$CaCO_3$	0.4005	9.6025
	CaF_2	0.5133	9.7103
	CaO	0.7146	9.8541
	$CaSO_4$	0.2944	9.4689
	CO_2	0.9093	9.9587
CaO	$CaCO_3$	0.5603	9.7484
	CaF_2	0.7182	9.8563
	$Ca(HCO_3)_2$	0.3459	9.5389
	$Ca(H_2PO_4)_2$	0.2394	9.3791
	$CaH_2P_2O_7$	0.2594	9.4140
	$Ca(HSO_3)_2$	0.2773	9.4430
	$Ca_3(PO_4)_2$	0.5421	9.7341
	$CaSO_3$	0.4667	9.6691
	$CaSO_4$	0.4120	9.6149
	$CaSO_4.2H_2O$	0.3257	9.5128
	CO_2	1.274	9.1053
$Ca_3(PO_4)_2$	$Mg_2P_2O_7$	1.393	0.1440
CaS	$BaSO_4$	0.3091	9.4901
$CaSO_4$	$BaSO_4$	0.5832	9.7658
$CaSO_4.2H_2O$	CaO	3.071	0.4872
CaF_2	$CaSO_4$	0.5735	9.7586
Cb	Cb_2O_5	0.7004	9.8453
Cd	CdO	0.8754	9.9422
	CdS	0.7780	9.8910
	$CdSO_4$	0.5392	9.7317
CdO	CdS	0.8888	9.9488
	Cd	1.142	0.0578
	$CdSO_4$	0.6159	9.7895

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
CdS	Cd	1.2853	0.1090
	CdO	1.1252	0.0512
	$CdSO_4$	0.6930	9.8407
Ce	$Ce(NO_3)_4$	0.3612	9.5577
	Ce_2O_3	0.8539	9.9314
	CeO_2	0.8142	9.9107
	$Ce(SO_4)_3$	0.4932	9.6930
Ce_2O_3	CeO_2	0.9536	9.9794
Cl	Ag	0.3287	9.5168
	AgCl	0.2474	9.3934
	$AgNO_3$	0.2088	9.3198
	HCl	0.9724	9.9879
	I	0.2794	9.4462
	KCl	0.4756	9.6772
	MnO_2	0.8158	9.9116
	NaCl	0.6066	9.7829
	NH_4Cl	0.6628	9.8214
	RbCl	0.2933	9.4673
ClO_3	AgCl	0.5823	9.7651
	KCl	1.119	0.0490
	NaCl	1.428	0.1546
ClO_4	AgCl	0.6939	0.8413
	KCl	1.334	0.1251
	NaCl	1.701	0.2308
CN	AgCN	0.1943	9.2884
	Ag	0.2411	9.3822
	KCN	0.3999	9.6020
	NaCN	0.5313	9.7253
	HCN	0.9627	9.9835
CNS	AgCNS	0.3500	9.5440
	$Cu_2(CNS)_2$	0.4774	9.6789
	$BaSO_4$	0.2488	9.3959
	KCNS	0.5974	9.7765
	NH_4CNS	0.7632	9.8825
Co	$Co(NO_3)_2.6H_2O$	0.2026	9.3066
	$K_3Co(NO_2)_6$	0.1304	9.1152
	CoO	0.7866	9.8957
	Co_3O_4	0.7344	9.8659
	$CoSO_4$	0.3804	9.5802
	$CoSO_4.7H_2O$	0.2097	9.3216
CoO	Co	1.2713	0.1043
	$Co(NO_3)_26H_2O$	0.2575	9.4109
	$K_3Co(NO_2)_6$	0.1657	9.2194
	Co_3O_4	0.9336	9.9702
	$CoSO_4$	0.4836	9.6844
	$CoSO_4.7H_2O$	0.2667	9.4259
Cr	$BaCrO_4$	0.2052	9.3125
	Cr_2O_3	0.6842	9.8352
Cr	$PbCrO_4$	0.1609	9.2067
	$K_2Cr_2O_7$	0.3535	9.5484
	K_2CrO_4	0.1768	9.2474
Cr_2O_3	$BaCrO_4$	0.3000	9.4771
	$PbCrO_4$	0.2352	9.3715
	CrO_3	0.7602	9.8809
CrO_3	$BaCrO_4$	0.3947	9.5963
	Cr_2O_3	1.3158	0.1192
	$PbCrO_4$	0.3095	9.4907
	K_2CrO_4	0.5152	9.7120
	$K_2Cr_2O_7$	0.6800	9.8325
CrO_4	$BaCrO_4$	0.4578	9.6607
	Cr_2O_3	1.5263	0.1837
	$PbCrO_4$	0.3589	9.5550
Cs	CsCl	0.7893	9.8973
	Cs_2O	0.9432	9.9746
	Cs_2CO_3	0.8157	9.9116
	Cs_2SO_4	0.7340	9.8657
	Cs_2PtCl_6	0.3945	9.5960
Cs_2O	CsCl	0.8370	0.9227
	Cs_2CO_3	0.8650	9.9370
	Cs_2SO_4	0.7782	9.8911
	Cs_2PtCl_6	0.4182	9.6214
Cu	Cu_2O	0.8882	9.9485
	CuO	0.7989	9.9025
	Cu_2S	0.7986	9.9023
	$Cu_2(CNS)_2$	0.5226	9.7181
	$CuSO_4$	0.3982	9.6001
	$CuSO_4.5H_2O$	0.2546	9.4058
CuO	Cu	1.252	0.0975
	Cu_2O	1.113	0.0463
	Cu_2S	0.9996	9.9998
	$Cu_2(CNS)_2$	0.6541	9.8156
	$CuSO_4$	0.4985	9.6976
	$CuSO_4.5H_2O$	0.3186	9.5032
Er_2O_3 Er	Er	1.143	0.0582
	Er_2O_3	0.8746	9.9418
F	$BaSiF_6$	0.4076	9.6102
	CaF_2	0.4866	9.6872
	$CaSO_4$	0.2791	9.4457
	HF	0.9496	9.9776
	H_2SiF_6	0.7910	9.8982
	K_2SiF_6	0.5170	9.7135
	NaF	0.4524	9.6555
	SiF_4	0.7302	9.8634
Fe	Fe_2O_3	0.6994	9.8447
	$FeCl_2$	0.4405	9.6440

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Fe	$FeCl_3.6H_2O$	0.2066	9.3152
	$Fe(HCO_3)_2$	0.3140	9.4969
	FeO	0.7773	9.8906
	Fe_3O_4	0.7236	9.8595
	$FePO_4$	0.3701	9.5683
	FeS	0.6352	9.8029
	$FeSO_4$	0.3676	9.5654
	$FeSO_4.7H_2O$	0.2008	9.3027
	$FeSO_4(NH_4)_2$, $SO_4.6H_2O$	0.1424	9.1536
	$K_2Cr_2O_7$ (titration)	1.139	0.0564
FeO	Fe	1.287	0.1094
	$FeCO_3$	0.6202	9.7925
	$Fe(HCO_3)_2$	0.4039	9.6063
	Fe_2O_3	0.8998	9.9542
	$FePO_4$	0.4761	9.6777
	FeS	0.8172	9.9123
	$FeSO_4$	0.4729	9.6747
	$FeSO_4.7H_2O$	0.2584	9.4123
	$FeSO_4(NH_4)_2$, $SO_4.6H_2O$	0.1832	9.2630
Fe_2O_3	Fe	1.430	0.1553
	$FeCl_3$	0.4922	9.6922
	$FeCO_3$	0.6892	9.8383
	Fe_3O_4	1.035	0.0149
	$FePO_4$	0.5292	9.7237
	FeS	0.9082	9.9582
	FeS_2	0.6655	9.8231
	$Fe_2(SO_4)_3$	0.3993	9.6013
	$(NH_4)_2SO_4.Fe_2$, $(SO_4)_3.24H_2O$	0.1656	9.2190
FeS_2	$BaSO_4$	0.2570	9.4099
H	H_2O	0.1119	9.0488
H_3BO_3	B_2O_3	1.774	0.2490
HBr	Ag	0.7505	9.8754
	AgBr	0.4311	9.6346
HCl	Ag	0.3380	9.5290
	AgCl	0.2544	9.4056
	$CaCO_3$	0.7288	9.8626
	KCl	0.4891	9.6894
	K_2O	0.7743	9.8889
	NaCl	0.6239	9.7951
	Na_2O	1.176	0.0705
	NH_4Cl	0.6817	9.8335
	$SnCl_4$	0.5600	9.7480
	Na_2CO_3 methyl orange	0.6881	9.8377
	$Na_2C_2O_4$ standardization	0.5442	9.7358
HF	$BaSiF_6$	0.4292	9.6327
	CaF_2	0.5126	9.7098
	$CaSO_4$	0.2939	9.4682
	F	1.053	0.0224
	K_2SiF_6	0.5449	9.7363
HI	Ag	1.186	0.0742
	AgI	0.5448	9.7362
	Pd	2.398	0.3799
	PdI_2	0.7097	9.8510
HNO_2	$AgNO_2$	0.3055	9.4850
	NO	1.567	0.1950
HNO_3	KNO_3	0.6233	9.7947
	N	4.498	0.6530
	$NaNO_3$	0.7413	9.8700
	NH_3	3.701	0.5683
	NH_4Cl	1.178	0.0711
	$(NH_4)_2PtCl_6$	0.2838	9.4530
	NO	2.100	0.3222
	N_2O_3	1.658	0.2196
	N_2O_4	1.370	0.1367
	N_2O_5	1.167	0.0671
	$C_{20}H_{16}N_4HNO_3$	0.1680	9.2252
	Pt	0.6457	9.8100
H_3PO_4	HPO_3	1.225	0.0881
	$H_4P_2O_7$	1.101	0.0457
	$Mg_2P_2O_7$	0.8806	9.9448
	P	3.159	0.4995
	P_2O_5	1.380	0.1399
H_2PtCl_6., $6H_2O$	Pt	2.656	0.4242
H_2S	$BaSO_4$	0.1460	9.1644
	CdS	0.2360	9.3729
	FeS	0.3877	9.5885
	S	1.063	0.0265
H_2SeO_3	Se	1.632	0.2126
H_2SiF_6	$BaSiF_6$	0.5157	9.7124
	CaF_2	1.846	0.2662
	F	1.264	0.1018
	2HF	3.607	0.5571
	6HF	1.202	0.0799
	K_2SiF_6	0.6545	9.8159
	SiF_4	1.384	0.1412
H_2SO_4	$Al_2(SO_4)_3$	0.8594	9.9342
	$Ba(OH)_2$	0.5723	9.7576
	$BaSO_4$	0.4133	9.6163
	$K_2Al_2(SO_4)_4$., $24H_2O$	0.3101	9.4915
	K_2O	1.041	0.0174

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
H_2SO_4	KOH	0.8740	9.9415
	K_2SO_4	0.5628	9.7503
	Na_2CO_3	0.9252	9.9662
	$Na_2C_2O_4$	0.7320	9.8645
	$(NH_4)_2SO_4$	0.7422	9.8705
Hg	Hg_2Cl_2	0.8495	9.9292
	$HgCl_2$	0.7388	9.8686
	HgO	0.9261	9.9666
	HgS	0.8620	9.9355
HCNS	AgCNS	0.3560	9.5515
	$Cu_2(CNS)_2$	0.4857	9.6864
	$BaSO_4$	0.2531	9.4033
Hg_2Cl_2	$SnCl_2$	2.486	0.3956
$HgCl_2$	Hg_2Cl_2	1.150	0.0607
	HgS	1.167	0.0671
HgO	Hg_2Cl_2	0.8455	9.8272
HgS	$Hg(CN)_2$	0.9208	9.9642
	$HgNO_3$	0.8857	9.9472
	$Hg(NO_3)_2$	0.7162	9.8550
	Hg_2O	1.116	0.0476
	HgO	1.074	0.0311
	$HgSO_4$	0.7838	9.8942
I	Ag	1.177	0.0706
	AgI	0.5406	9.7328
	KI	0.7645	9.8834
	Pd	2.379	0.3764
	PdI_2	0.7041	9.8476
	$Na_2S_2O_3.5H_2O$	0.5113	9.7087
	AgCl	0.8855	9.9472
In	In_2O_3	0.8271	9.9176
	In_2S_3	0.7047	9.8480
Ir	Ir_2O_3	0.8894	9.9491
K	KCl	0.5244	9.7197
	K_2O	0.8300	9.9191
	K_2SO_4	0.4487	9.6520
	$KClO_4$	0.2822	9.4505
	K_2PtCl_6	0.1609	9.2064
	Pt	0.4006	9.6027
KCl	Ag	0.6911	9.8396
	AgCl	0.5202	9.7162
	K_2SO_4	0.8557	9.9323
	$KClO_4$	0.5381	9.7309
	K_2PtCl_6	0.3067	9.4868
	Pt	0.7640	9.8831
K_2O	KCl	0.6317	9.8005
	K_2SO_4	0.5405	9.7328
	$KClO_4$	0.3399	9.5314
	K_2PtCl_6	0.1938	9.2873
	Pt	0.4826	9.6836
$KClO_3$	AgCl	0.8550	9.9320
	KCl	1.6438	0.2158
$KClO_4$	AgCl	0.9667	9.9853
	KCl	1.858	0.2691
KCN	AgCN	0.4863	9.6869
	$AgNO_3$ (Liebig method)	0.7665	9.8845
	AgCl	0.4542	9.6573
K_2SO_4	K	2.229	0.3481
	KCl	1.169	0.0679
	K_2O	1.850	0.2672
	K_2PtCl_6	0.3585	9.5545
	SO_3	2.177	0.3379
	$BaSO_4$	0.7465	9.8731
La	La_2O_3	0.8527	9.9308
Li	LiCl	0.1637	9.2140
	Li_2O	0.4643	9.6669
	Li_3PO_4	0.1797	9.2545
	Li_2SO_4	0.1262	9.1012
Li_2O	LiCl	0.3524	9.5470
	Li_2SO_4	0.2718	9.4342
	Li_3PO_4	0.3870	9.5877
Mg	MgO	0.6032	9.7804
	$MgSO_4$	0.2020	9.3054
	$Mg_2P_2O_7$	0.2184	9.3392
	$MgSO_4$	0.2020	9.3054
MgO	$MgSO_4$	0.3349	9.5249
	$Mg_2P_2O_7$	0.3621	9.5588
	$MgCO_3$	0.4782	9.6796
Mn	$MnCO_3$	0.4779	9.6793
	MnO	0.7744	9.8889
	Mn_2O_3	0.6959	9.8426
	Mn_3O_4	0.7203	9.8575
	$MnSO_4$	0.3638	9.5608
	$Mn_2P_2O_7$	0.3869	9.5876
	MnS	0.6314	9.8003
MnO	$MnCO_3$	0.6172	9.7904
	Mn_3O_4	0.9301	9.9685
	$MnSO_4$	0.4697	9.6719
	MnS	0.8153	9.9113
	$Mn_2P_2O_7$	0.4998	9.6988

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Mo	MoO_3	0.6667	9.8239
	MoS_3	0.4995	9.6985
	MoS_2	0.5996	9.7779
	$PbMoO_4$	0.2615	9.4174
MoO_3	MoS_3	0.7492	9.8746
	$(NH_4)_2MoO_4$	0.7344	9.8659
	$(NH_4)_3PO_4(Mo_2O_3)_{12}$	0.9205	9.9640
	$PbMoO_4$	0.3923	9.5936
N	HNO_3	0.2223	9.3470
	NO_2	0.3045	9.4835
	N_2O_3	0.3686	9.5665
	N_2O_4	0.3045	9.4835
	N_2O_5	0.2594	9.4140
	$NaNO_3$	0.1648	9.2169
	NH_3	0.8225	9.9151
	Pt	0.1435	9.1570
	NH_4Cl	0.2619	9.4181
Na	NaCl	0.3934	9.5949
	Na_2SO_4	0.3238	9.5103
	NaBr	0.2235	9.3493
	Na_2CO_3	0.4340	9.6375
	NaF	0.5476	9.7385
	$NaHCO_3$	0.2740	9.4375
	NaI	0.1534	9.1858
	Na_2O	0.7419	9.8704
	NaOH	0.5750	9.7597
	Na_2SO_4	0.3238	9.5103
$Na_2B_4O_7$	B_2O_3	1.443	0.1593
	H_3BO_3	0.8142	9.9107
$Na_2B_4O_7.10H_2O$	B_2O_3	2.735	0.4369
	H_3BO_3	1.540	0.1872
	KBF	0.7577	9.8795
NaBr	Ag	0.9562	9.9806
	AgBr	0.5480	9.7388
NaCl	Ag	0.5418	9.7338
	AgCl	0.4078	9.6105
	$AgNO_3$	0.3441	9.5367
	Na_2O	1.886	0.2756
NaF	CaF_2	1.076	0.0317
Na_2HAsO_3	$Mg_2As_2O_7$	1.095	0.0395
	I	0.6697	9.8259
Na_2HAsO_4	$Mg_2As_2O_7$	1.198	0.0785
	I	0.7328	9.8650
$NaHCO_3$	CO_2	1.909	0.2808
$NaHCO_3$	$KHC_4H_4O_6$	0.4465	9.6498
Na_2O	NaCl	0.5303	9.7245
	Na_2SO_4	0.4364	9.6399
	Na_2CO_3	0.5849	9.7671
	$NaHCO_3$	0.3690	9.5670
	Na_2HPO_4	0.4365	9.6400
	NaH_2PO_4	0.2582	9.4119
	$Na_2H_2P_2O_7$	0.2792	9.4459
	$NaHSO_3$	0.2979	9.4741
	$NaNO_3$	0.3647	9.5619
	NaOH	0.7748	9.8891
	Na_2SO_4	0.4364	9.6399
Na_2SO_3	$BaSO_4$	0.5401	9.7325
$Na_2S_2O_3$	$BaSO_4$	0.3387	9.5298
	$Na_2S_2O_3.5H_2O$	0.6371	9.8042
Na_2SO_4	$BaSO_4$	0.6086	9.7843
Nd	Nd_2O_3	0.8572	9.9332
NH_3	HNO_3	0.2704	9.4320
	H_2SO_4	0.3473	9.5407
	N	1.216	0.0849
	$NaNO_2$	0.2468	9.3923
	$NaNO_3$	0.2005	9.3021
	NH_4Cl	0.3184	9.5023
	$(NH_4)_2HPO_4$	0.2578	9.4113
	$(NH_4)H_2PO_4$	0.1480	9.1703
	$(NH_4)OH$	0.4860	9.6866
	$(NH_4)_2PtCl_6$	0.07670	8.8848
	$(NH_4)_2SO_4$	0.2578	9.4113
	N_2O_5	0.3153	9.4987
	Pt	0.1745	9.2418
NH_4	NH_3	1.059	0.0250
	NH_4Cl	0.3372	9.5279
	$(NH_4)_2PtCl_6$	0.08125	8.9099
	Pt	0.1848	9.2668
NH_4Cl	AgCl	0.3732	9.5719
	NH_3	3.141	0.4971
	$(NH_4)_2PtCl_6$	0.2410	1.3820
	Pt	0.5482	9.7389
$(NH_4)_2SO_4$	$BaSO_4$	0.5661	9.7529
Ni	NiO	0.7858	9.8953
	$NiC_8H_{14}N_4O_4$	0.2032	9.3079
	$NiSO_4$	0.3792	9.5788
	$Ni(NO_3)_2.6H_2O$	0.2018	0.3049
	$Ni_2SO_4.7H_2O$	0.2089	9.3200
NO_3	NO	2.066	0.3152
	NH_3	3.640	0.5612

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
NO_3	NH_4Cl	1.159	0.0641
	$(NH_4)_2PtCl_6$	0.2793	9.4461
	Pt	0.6354	9.8030
	$C_{20}H_{17}N_5O_3$	0.1653	9.2182
N_2O_5	NO	1.800	0.2552
	NH_3	3.171	0.5012
	NH_4Cl	1.010	0.0041
	$(NH_4)_2PtCl_6$	0.2433	9.3861
	Pt	0.5534	9.7430
	$C_{20}H_{17}N_5O_3$	0.1440	9.1582
NO_2	NO	1.533	0.1856
N_2O_3	NO	1.267	0.1026
Os	OsO_4	0.7489	9.8744
P	$Mg_2P_2O_7$	0.2787	9.4452
	$P_2O_5.24MoO_3$	0.0173	8.2368
	$(NH_4)_3PO_4.$, $12MoO_3$	0.0165	8.2184
	P_2O_5	0.4369	9.6404
PO_4	$Mg_2P_2O_7$	0.8535	9.9312
	$P_2O_5.24MoO_3$	0.05283	8.7229
	$(NH_4)_3PO_4.$, $12MoO_3$	0.05063	8.7044
P_2O_5	$Mg_2P_2O_7$	0.6379	9.8048
	$P_2O_5.24MoO_3$	0.03947	8.5963
	$(NH_4)_3PO_4.$, $12MoO_3$	0.03785	8.5780
Pb	PbO	0.9283	9.9677
	PbO_2	0.8662	9.9376
	PbS	0.8659	9.9375
	$PbSO_4$	0.6831	9.8345
	$PbCrO_4$	0.6410	9.8068
	$PbCl_2$	0.7449	9.8721
	$PbMoO_4$	0.5642	9.7515
PbO	PbO_2	0.9331	9.9699
	PbS	0.9328	9.9698
	$PbSO_4$	0.7359	9.8668
	$PbCrO_4$	0.6905	9.8392
	$PbCl_2$	0.8025	9.9044
	$PbCO_3$	0.8353	9.9219
	$Pb(NO_3)_2$	0.6738	9.8285
PbS	$PbSO_4$	0.7889	9.8970
	Pb	1.155	0.0626
	PbO	1.072	0.0302
	$BaSO_4$	1.025	0.0109
$PbSO_4$	$BaSO_4$	1.299	0.1137
$PbSO_4$	$Pb(C_2H_3O_2)_2.$, $3H_2O$	0.7995	9.9028
	$(PbCO_3)_2.Pb$, $(OH)_2$	1.173	0.0693
Rb	AgCl	0.3820	9.7753
	Cl	2.410	0.3820
	RbCl	0.7067	9.8492
	Rb_2CO_3	0.7402	9.8693
	Rb_2O	0.9144	9.9611
	Rb_2SO_4	0.6403	9.8064
	Rb_2PtCl_6	0.2952	9.4701
Rb_2O	RbCl	0.7729	9.8881
	Rb_2SO_4	0.7001	9.8452
RbCl	Rb_2PtCl_6	0.4178	9.6209
S	$BaSO_4$	0.1374	9.1379
	H_2S	0.9408	9.9735
	H_2SO_4	0.3270	9.5145
	FeS	0.3648	9.5621
	FeS_2	0.5346	9.7280
	Na_2S	0.4108	9.6136
SO_2	$BaSO_4$	0.2745	9.4385
	S	1.998	0.3007
SO_3	$BaSO_4$	0.3430	9.5353
	$CaSO_4$	0.5881	9.7695
	H_2SO_4	0.8163	9.9119
	K_2SO_4	0.4595	9.6623
	Na_2SO_4	0.5636	9.7510
SO_4	$BaSO_4$	0.4115	9.6144
Sb	$KSbOC_4H_4O_6.$, $\frac{1}{2}H_2O$	0.3617	9.5583
	$SbCl_3$	0.5305	9.7247
	Sb_2O_3	0.8336	9.9209
	Sb_2O_5	0.7503	9.8753
	Sb_2O_4	0.7898	9.8975
	Sb_2S_3	0.7142	9.8538
	Sb_2S_5	0.5998	9.7780
Sb_2O_3	Sb_2O_4	0.9475	9.9766
	Sb_2S_3	0.8568	9.9239
	Sb_2S_5	0.7196	9.8571
SeO_2	Se	1.405	0.1474
SeO_3	Se	1.606	0.2058
Si	SiO_2	0.4676	9.6698
	SiO_3	0.3693	9.5673
	SiO_4	0.3051	9.4844
SiO_3	SiO_2	1.266	0.1025

CHEMICAL FACTORS — *Concluded*

Sought	Found	Factor	Log
SiO_4	SiO_2	1.532	0.1854
Sn	SnO_2	0.7881	9.8966
	SnO	0.8812	9.9451
	$SnCl_2$	0.6261	9.7967
	$SnCl_2.2H_2O$	0.5260	9.7210
Sr	SrO	0.8456	9.9272
	$SrCO_3$	0.5936	9.7735
	$SrSO_4$	0.4770	9.6785
	$Sr(NO_3)_2$	0.4140	9.6170
SrO	$SrCO_3$	0.7020	9.8463
	$SrSO_4$	0.5641	9.7514
	$Sr(NO_3)_2$	0.4896	9.6899
Ta	$TaCl_5$	0.5059	9.7041
	Ta_2O_5	0.8194	9.9135
Te	TeO_2	0.7994	9.9027
	TeO_3	0.7265	9.8612
Th	ThO_2	0.8790	9.9440
	$Th(NO_3)_4.6H_2O$	0.3947	9.5962
	$ThCl_4$	0.6207	9.7929
ThO_2	$Th(NO_3)_4.6H_2O$	0.4490	9.6523
Ti	TiO_2	0.6005	9.7785
Tl	TlCl	0.8519	9.9304
	Tl_2CO_3	0.8718	9.9404
	TlI	0.6165	9.7900
Tl	$TlNO_3$	0.7669	9.8847
	Tl_2O	0.9623	9.9833
	Tl_2CrO_4	0.7786	9.8913
	Tl_2SO_4	0.8094	9.9081
	$TlHSO_4$	0.6775	9.8309
Tl_2O	Tl_2PtCl_6	0.5196	9.7157
U	U_3O_8	0.8482	9.9285
	UO_2	0.8817	9.9453
	$(UO_2)_2P_2O_7$	0.6670	9.8242
V	V_2O_5	0.5605	9.7485
	V_2O_4	0.6144	9.7885
W	WO_3	0.7931	9.8993
	$PbWO_4$	0.4435	9.6469
Yt	Yt_2O_3	0.7883	9.8967
Yb	Yb_2O_3	1.8785	9.9437
Zn	ZnO	0.8034	9.9049
	$ZnNH_4PO_4$	0.3663	9.5639
	$Zn_2P_2O_7$	0.4290	9.6324
	ZnS	0.6709	9.8266
ZnO	ZnS	0.8351	9.9217
	$ZnNH_4PO_4$	0.4561	9.6590
	$Zn_2P_2O_7$	0.5340	1.7275
Zr	ZrO_2	0.7390	9.8686

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts							
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2605	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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