Representative Procedures
in
Quantitative Chemical Analysis

BY

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PREFACE

THIS introduction to representative procedures in quantitative chemical analysis is an out-growth of long experience in the teaching of that subject. Inevitably it must reflect some characteristics of many predecessors, and to all of these the author desires to make every due acknowledgment of indebtedness.

Procedures have been discussed in relation to their essential features, underlying principles, and varied applications.

A large amount of space has been devoted to iodometric processes both on account of the beauty and accuracy of these methods, constantly growing in recognition, and because the treatment in the more elementary text-books is usually scanty.

The arrangement of the subject matter is such as to permit the selection of a narrower course or a broader course, as may be desired, without detriment to the logical sequence of topics. Explicit directions are given for certain representative experimental processes, but if wider practice is desired the general description of related processes should make it possible to adapt to these the specific directions given for the representative experimental processes.

The value of collateral reading in stimulating interest and in amplifying information is recognized, and, inasmuch as access to the periodical literature is frequently difficult, references in respect to further information have been made, so far as seemed practicable, to a few easily accessible books, in which further reference to original sources may usually be found, if needed.

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REPRESENTATIVE PROCEDURES
IN
QUANTITATIVE CHEMICAL ANALYSIS

CHAPTER I

PROCESSES OF ANALYSIS

THE methods of *Quantitative Chemical Analysis* are generally based upon definite chemical transformations. In *Gravimetric Processes* products of reaction are isolated and *weighed;* in *Volumetric Processes* transformations are brought about by means of *measured* solutions of known content by weight. A few processes of quantitative determination depend upon the measurement of certain physical characteristics, such as the volume filled under determined conditions of temperature and pressure by gaseous substances or the effect of light upon solutions — color, opalescence, refractive power, polarization.

Analytical Reactions

Not all the reactions which are useful in identifying individual elements (*elementary analysis*) or compounds (*proximate analysis*) are adapted to quantitative determinations. Reactions must be so chosen, and so utilized, that substances may either be separated in definite condition for weighing or measurement, or else may be made to react in well-determined ways with known amounts of the reagents. In choosing and applying reactions for the purposes of *quantitative analysis* it is, of course, important to keep in mind the fundamental and general principles of chemical reaction.

The Course of Chemical Action. — When chemical systems undergo change the tendency to reaction is directed in lines which correspond to the development of *free energy* — that is, energy available for the performance of work. The changes of energy which accompany chemical reaction may involve internal changes in the system as well as the evolution of free energy. As heat becomes latent in the change from ice to liquid water, or of liquid water to water vapor, so some of the chemical energy of reaction may disappear in the internal rearrangement of the system. But it appears that all processes which proceed spontaneously after having been started — that is, processes which proceed without continual supplying of energy from without the system — are accompanied by the evolution of free energy, the least stable condition of a system undergoing spontaneous reaction being that in which the system is capable of evolving the greatest amount of free energy, and the most stable condition that which corresponds to the greatest evolution of free energy. If it be assumed, as is probable, that the free energy and the total heat of reaction have the same value in the neighborhood of the absolute zero of temperature, then, all reactions, once started, should proceed at such temperatures with evolution of heat; and, at such temperatures, the amount of heat evolved should measure the resultant of the chemical affinities, or the tendency to reaction. The interval between the ordinary atmospheric temperature and the absolute zero is, however, not very great in comparison with the entire available range of reaction temperatures, and so it is to be expected that *reactions at ordinary temperatures will generally proceed in a way to produce the maximum evolution of heat.* As a matter of fact, heats of reaction may often be used to indicate the direction in which a reaction involving certain elements or ions will move.

For example, amounts of heat evolved in the neutralization of a gram-equivalent of hydrochloric acid and of a gram-equivalent of acetic acid by the action of sodium hydroxide are, respectively, 13,700 calories and 13,400 calories. It is, therefore, natural to suppose that upon gradually adding the water solution of a gram-equivalent of sodium hydroxide to the water solution containing a gram-equivalent of hydrochloric acid and a gram-equivalent of acetic acid the hydrochloric acid will be neutralized before the acetic acid, and this expectation is very closely realized. The residue left after the evaporation of such a solution consists almost entirely of sodium chloride.

Similarly, when a mixture of two gram-molecules of hydrogen and one gram-molecule of oxygen is acted upon at the ordinary temperature by enough outside energy to start the combination of these elements, the reaction

$$2\,H_2 + O_2 = 2\,H_2O$$

(which evolves 68,360 calories, assuming that the water formed is allowed to condense to the liquid phase) proceeds to completion with evolution of heat unless the resulting temperature of the mass be cooled artificially below a definite point (about 560 degrees) at which the chemical change is spontaneous.

On the other hand, reactions may proceed in the direction which implies absorption of heat when heat is supplied at sufficiently high temperatures from without the system; and at intermediate temperatures an equilibrium between opposite tendencies may be established. For example, the reaction in which hydrogen and oxygen form water with evolution of heat at 560 degrees,

$$2\,H_2 + O_2 \rightleftarrows 2\,H_2O,$$

shows a reversal at temperatures of about 1000 degrees, and it proceeds equally in opposite directions at about 2500 degrees.

Similarly, the reaction between a gram-equivalent of hydrochloric acid and a gram-equivalent of sodium hydroxide, which results at ordinary temperatures in practically complete mutual neutralization, is markedly reversible at temperatures approaching low red heat:

$$NaOH + HCl \rightleftarrows NaCl + H_2O.$$

Successive Reactions. — When a system is undergoing transformation, reactions yielding systems of successively greater degrees of stability may intervene between the initial condition and the final condition. For example, the reactions in a system made up of barium dioxide, potassium dichromate, sulphuric acid and water may take place in successive stages.

First, there is the production of hydrogen dioxide and chromic acid in presence of sulphuric acid; secondly, the formation of perchromic acid; and, thirdly, the reduction of the perchromic acid with formation of chromic sulphate.

$$\begin{aligned} BaO_2 + K_2Cr_2O_7 + 6\,H_2SO_4 \\ &= BaSO_4 + 2\,KHSO_4 + 3\,H_2SO_4 + H_2Cr_2O_7 + H_2O_2 \\ &= BaSO_4 + 2\,KHSO_4 + 3\,H_2SO_4 + H_2Cr_2O_8 + H_2O \\ &= BaSO_4 + 2\,KHSO_4 + Cr_2(SO_4)_3 + 5\,H_2O + 2\,O_2. \end{aligned}$$

In exact quantitative analysis it is important to make use of reactions and conditions which result in the establishment of definite and stable systems at once, or at least within a reasonable time.

Non-Reversible and Reversible Reactions. — Processes which result in the formation of inactive products and which are non-reversible proceed to completion, when once started, without regard to the presence of reaction products. On the other hand, processes in which all products are active, and which are therefore reversible, are affected not only by adjustment of conditions or by the increase of a factor but by the removal of an active product.

Examples of processes which rest upon non-reversible reactions and which proceed to completion uninfluenced by the amounts of the products of reaction are the ignition of silicon, aluminium, and iron hydroxides, and of ammonium magnesium phosphate,

$$\begin{aligned} SiO_2 \cdot nH_2O &= SiO_2 + nH_2O, \\ 2\,(AlO)OH &= Al_2O_3 + H_2O, \\ 2\,FeO_3H_3 &= Fe_2O_3 + 3\,H_2O, \\ 2\,NH_4MgPO_4 &= Mg_2P_2O_7 + 2\,NH_3 + H_2O; \end{aligned}$$

the bleaching of iodine by sodium thiosulphate,

$$I_2 + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_2O_6;$$

the precipitation of manganic hydroxide in the reaction between manganese sulphate, and ammonium hydroxide, and bromine,

$$2\,MnSO_4 + 8\,NH_4OH + 2\,Br_2 = H_2Mn_2O_5 + 4\,NH_4Br + 2\,(NH_4)_2SO_4 + 3\,H_2O;$$

and the reduction of ferric chloride by oxalic acid,

$$2\,FeCl_3 + H_2C_2O_4 = 2\,FeCl_2 + 2\,HCl + 2\,CO_2.$$

Velocity of Non-Reversible Reactions. — The velocity with which a non-reversible reaction reaches its end depends upon the masses of the reacting substances and the affinity factors involved. *The rate of a non-reversible reaction, when slow enough to be measurable, is generally accelerated by elevation of temperature, and at each instant it is found to be proportional to the concentration of the reacting substances.* For example, the reaction between iodine and sodium thiosulphate, mentioned above, is practically immediate at the ordinary atmospheric temperature; that between ferric chloride and oxalic acid at a similar temperature and in dilute solution may require years for its completion, but this reaction may be pushed to completion in a few minutes by raising the temperature to 100 degrees. The proper conditions in respect to the times and the temperatures required to effect as completely as possible the transformation of a system must be found experimentally in each individual case.

As the non-reversible process advances the velocity of reaction diminishes, and sometimes to such an extent that it is not feasible, in an analytical process, to continue the reaction to completion. In the case of such a slow non-reversible reaction it is sometimes possible to push the velocity of reaction by adding a large excess of the active reagent and then to determine by some suitable process the amount of that excess. For example, in the reaction between potassium permanganate and selenious acid (in solution with dilute sulphuric acid) the rate of the reaction

$$5\,H_2SeO_3 + 2\,KMnO_4 + 3\,H_2SO_4 = 5\,H_2SeO_4 + K_2SO_4 + 2\,MnSO_4 + 3\,H_2O$$

is exceedingly slow and the straight course of the reaction is complicated by the intervention of a secondary reaction in which a portion of the permanganate acts upon the manganous salt with formation of higher oxides of manganese. By adding a large excess of the permanganate the selenious acid may be more rapidly oxidized, and that excess together with any higher oxides of manganese may then be reduced by a known amount of oxalic acid, leaving an excess of the last to be destroyed by the direct action of more of the permanganate.

The Completion of Reversible Reactions. — *In reversible reactions, the result is influenced by the concentrations of the products as well as by the concentrations of the factors, in accordance with the* LAW OF MASS-ACTION.

When two substances A and B react to form two other substances C and D, the resulting concentrations of the substances expressed in terms of gram-molecules may be represented by the terms C_A, C_B, C_C and C_D. When the reaction takes place in single molecular proportions (mols) the forward action and the reverse action may be represented by the expression $k \cdot C_A \cdot C_B$ and $k_1 \cdot C_C \cdot C_D$, respectively, in which k and k_1 stand for affinity constants, and the equation of equilibrium is

$$\frac{C_A \cdot C_B}{C_C \cdot C_D} = \frac{k_1}{k} = K.$$

When the substances A and B react in multiple molecular proportions the numbers representing molecules n_1, n_2, n_3 and n_4, respectively, appear as exponents, and the equation takes the form

$$\frac{C_A^{n_1} \cdot C_B^{n_2}}{C_C^{n_3} \cdot C_D^{n_4}} = \frac{k_1}{k} = K.$$

When the molecular units of substances are subject to change apart from the chemical reaction (as by dissociation, hydrolysis, polymerization, or depolymerization in solution) so that the numbers of active units are changed, such changes affect the conditions of equilibrium. Representing the coefficients of unitary change (as determined by osmotic, cryoscopic, ebullioscopic, or conductivity measurements) as i_1, i_2, i_3, and i_4, the equation of equilibrium, at constant temperature and volume, takes for the substances reacting in single molecular proportions the form

$$\frac{C_A^{i_1} \cdot C_B^{i_2}}{C_C^{i_3} \cdot C_D^{i_4}} = \frac{k_1}{k} = K;$$

and for cases of reaction in multiple molecular proportions, represented by n_1 and n_2, etc., the expression takes the form

$$\frac{C_A{}^{n_1 i_1} \cdot C_B{}^{n_2 i_2}}{C_C{}^{n_3 i_3} \cdot C_D{}^{n_4 i_4}} = \frac{k_1}{k} = K.$$

The validity of these expressions has been shown experimentally in a number of cases. For example, it has been found that when solutions of sodium sulphate and nitric acid are brought together in a calorimeter the reaction

$$Na_2SO_4 + HNO_3 \rightleftarrows NaHSO_4 + NaNO_3,$$

when interpreted in accordance with the heat effects, proceeds in accordance with the expression

$$\frac{C_A{}^{i_1} \cdot C_B{}^{i_2}}{C_C{}^{i_3} \cdot C_D{}^{i_4}} = \frac{C^{1.91}_{Na_2SO_4} \cdot C^{1.94}_{HNO_3}}{C^{1.88}_{NaHSO_4} \cdot C^{1.82}_{NaNO_3}} = K$$

where the numerical exponents represent the coefficients of unitary change of the individual substances in solution.

Since the concentrations of insoluble substances may be regarded as practically constant, terms relating to them may be eliminated from the equation of equilibrium. For example, in the reaction which takes place between dissolved carbon dioxide and insoluble barium carbonate,

$$BaCO_3 + (CO_2 + nH_2O) \rightleftarrows BaH_2(CO_3)_2 + (n - 1)H_2O,$$

the amount of the solvent (water) being large and practically constant, the equation of equilibrium may be written

$$\frac{C_A{}^{i_1}}{C_C{}^{i_3}} = \frac{C^{1}_{CO_2}}{C^{2.66}_{BaH_2(CO_3)_2}} = K,$$

and this is found to be in accord with the results of experiment.

Similarly, in the reaction between insoluble zinc sulphide and sulphuric acid with the production of zinc sulphate and hydrogen sulphide,

$$ZnS + H_2SO_4 \rightleftarrows ZnSO_4 + H_2S,$$

the value of i for the soluble substances being respectively 2.06, 0.98, and 1.04, under the conditions of action, the equation is

$$\frac{C^{2.06}_{H_2SO_4}}{C^{0.98}_{ZnSO_4} \cdot C^{1.04}_{H_2S}} = K,$$

and since the zinc sulphate and hydrogen sulphide are always produced in equal molecular concentrations, the expression takes the form

$$\frac{C^{2.06}_{H_2SO_4}}{C^{2.02}_{ZnSO_4+H_2S}} = K,$$

which agrees with the experimental results.*

In practical analysis, exact knowledge is often, and indeed generally, wanting in respect to the data necessary for the expression of quantitative effects under given conditions; but the general form of the equation will indicate qualitatively the directions in which changes of concentration take effect.

For example, in the reaction between barium chloride and sulphuric acid,

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2\,HCl,$$

it is obvious that an increase in the concentration of sulphuric acid will tend to make the reaction complete in respect to the removal of barium chloride, and that an increase in the concentration of barium chloride will tend to complete the reaction in respect to the removal of sulphuric acid, and that an increase in the concentration of hydrochloric acid will tend to render each of these reactions less complete. Experience shows that the concentration of the barium sulphate in solution is very small (0.0023 grm. in 1 liter of water), remaining practically constant and being only slightly affected by small changes in the concentration of the hydrochloric acid. Moreover, it is found that the solvent effect of very large concentrations of hydrochloric acid may be balanced by comparatively small concentrations of sulphuric acid, which means, of course, that the tendency toward the reverse action ($2\,HCl : BaSO_4$) is very small in comparison with the tendency toward the forward action ($BaCl_2 : H_2SO_4$).

A similar case is that involving the precipitation of silver chloride by the reaction between sodium chloride and silver nitrate for the purpose of determining either the silver of the

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* Chesneau: Theoretical Principles, trans. Lincoln and Carnahan, p. 79.

silver nitrate or the chlorine of the sodium chloride. These processes are based upon the reversible reaction

$$AgNO_3 + NaCl \rightleftarrows AgCl + NaNO_3.$$

The concentration of the nearly insoluble silver chloride is very small and practically constant, but a slight increase in the amount of either sodium chloride or silver nitrate will determine further precipitation of silver chloride.*

The Principle of Le Chatelier. — *In respect to the effect which may be induced by variations of temperature or pressure or concentration in reversible reactions, the Principle of Le Chatelier affords a useful criterion.* According to this generalization any change made from the outside in the factors of equilibrium of a balanced system is followed by a change of the opposite sort in the similar factors of equilibrium within the system. Thus, an increase in the external temperature will favor a reaction in which heat disappears within the system and will oppose an action in which heat is evolved; while a lowering of the temperature will tend to turn the reaction in the direction which implies evolution of heat. An increase of pressure upon the system will favor the course of reaction in which the pressure (or volume under constant pressure) of the system will be lessened; while diminution of pressure upon the system will aid the course of reaction in which the pressure (or volume under constant pressure) of the system tends to increase.

For example, in an equilibrium between calcium carbonate, calcium oxide, and carbon dioxide in the reversible reaction

$$CaCO_3 \quad \underset{\text{With evolution of heat}}{\overset{\text{With absorption of heat}}{\rightleftarrows}} \quad CaO + CO_2$$

the application of heat will tend to break up the carbonate, while cooling will favor the reaction by which the carbonate is formed from the oxides. In this reaction, in which the heat effect is considerable, the attainment of equilibrium is rapid and markedly dependent upon the temperature; but when the heat of a reaction is small the influence of heating or cooling is not

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* See pp. 67, 69.

immediate or marked, as in the esterification of alcohol with acetic acid,

$$C_2H_5OH + HOC_2H_3O \rightleftarrows C_2H_5OC_2H_3O + H_2O,$$

the final equilibrium of this reaction being attained at the atmospheric temperature only after several days, and at 100 degrees only after some hours.

Similarly, in the adjustment of equilibrium, under changing external pressure an increase of pressure upon the system will favor that process which implies diminution of pressure (or volume) of the system while relief of pressure upon the system will tend to promote the action by which greater pressure (or volume) of the system will be produced. For example, in the equilibrium between calcium carbonate, calcium oxide, and carbon dioxide increase of pressure promotes the formation of the solid carbonate while relief of pressure favors the decomposition of the carbonate into calcium oxide and gaseous carbon dioxide.

$$CaCO_3 \quad \underset{\text{With increased pressure}}{\overset{\text{With diminished pressure}}{\rightleftarrows}} \quad CaO + CO_2$$

The reaction between alcohol and acetic acid, which involves no significant change in volume, is independent of the pressure.

Furthermore, as has been illustrated in the previous discussion of mass-action in relation to reversibility, an increase in the concentration of one component favors the formation of another component (or phase) involving a decrease in the concentration of the first, and a decrease in the concentration of a component favors the formation of another component (or phase) involving an increase in the concentration of the first.

Empirical Processes. — Sometimes it is a matter of convenience to make use of a process for which it has been established that correct results may be indicated under a definite set of empirical conditions rather than a process which depends upon the completion of a definite reaction in accordance with underlying theory; but such processes are employed only when speed rather than the highest accuracy is the object in view or as a last resort in operations demanding exactness.

CHAPTER II

WEIGHING AND MEASURING

The fixing of the amount of a substance taken for analysis, or found in the course of analysis, depends either directly upon an exact process of weighing or, in the case of a liquid or gas for which the relation of weight to volume is known, upon the measurement of volume. Excepting processes of gas-analysis, in which the proportionate composition of a substance is often stated in volumes, the results of analysis are ultimately stated in terms of weight, and generally in percentages by weight.

The Process of Weighing

The Analytical Balance. — The analytical balance (Fig. 1), by which weights are determined, has as essential parts a *beam* which is supported at its middle point by a *knife-edge* set perpendicularly and resting upon a plane *bearing* at the top of a supporting *pillar*, a pan suspended at each end of the beam from an upturned knife-edge fixed in the beam and parallel to the middle knife-edge, and a *pointer* reaching perpendicularly from the middle knife-edge to a *divided scale* so as to show the movements of the beam. A case with glass sides protects the balance from dust and disturbing currents of air during the process of weighing, and a *beam-support* and *pan-supports* which may be set and released by suitable mechanism are important adjuncts. Constancy and sensitiveness are characteristics necessary to good service on the part of the balance; and these essentials are secured by proper attention to details of construction and adjustment, such as rigidity and lightness of the beam, the preservation of a proper relation between the center of gravity of the loaded beam and the plane of the supporting knife-edge, and the proper placing of the knife-edges in respect to one another.

The beam must be rigid enough to keep its shape under the stress of all reasonable loading and light enough to respond to slight variations in the load. The center of gravity of the beam with pans attached should fall below the horizontal plane in which the supporting knife-edge lies, practically the plane of the bearing; for otherwise the balance will be unreliable, being unstable when the center of gravity lies above the plane of the knife-edge, and indifferent when the center of gravity lies in the plane of the knife-edge. But the distance between the plane of the knife-edge and the center of gravity should be very small, else small variations in the load will be without appreciable effect; while it must not be too small lest the oscillations of the beams be tediously slow. In a reasonably sensitive instrument the distance between the center of gravity of the beam and the plane of the knife-edge probably approximates 0.0025 mm.

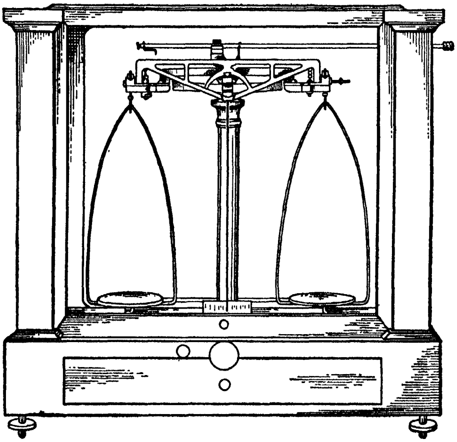

Fig. 1.

The terminal knife-edges for pan suspension and the middle knife-edge for the beam-suspension, all parallel to one another and perpendicular to the beam, should lie in the same plane; for otherwise, with the beam rigid, the relation between the position of the center of gravity and the plane of the beam knife-edge will be subject to change with variation of the load upon the pans. The balance will lose sensitiveness as the load increases, the center of gravity moving downward, in case the plane of the pan knife-edges is lower than the plane of the middle knife-edge; it will become inert and then unstable as the load increases and moves the center of gravity upward in case the plane of the pan knife-edges is above the plane of the middle knife-edge. It is to be noted, however, that lack of perfect rigidity of beam and imperfect adjustment of the knife-edges to the same plane may to some extent be mutually corrective, and that varying sensitiveness, due to flexure of the beam under an increased load, may be counteracted by judicious misplacing of the knife-edges. For if the pan knife-edges be placed so as to lie in a plane slightly above the plane of the middle knife-edge when the pans carry no load the flexure of the beam when under the maximum load may serve to bring them into the plane of the middle knife-edge, and the sensitiveness of the instrument under heavy loading will be thus improved.

In a perfect balance the distance between the beam knife-edge and the two-pan knife-edges should be equal, in order that the leverage of equal masses placed upon the pans may exert equal effects upon the oscillation of the beam, but this is a condition very difficult to fulfill absolutely under varying conditions of temperature. It is possible, however, as will be shown, to determine and eliminate the effect of inequality in the arms of the balance.

Determination of the Zero-Point. — The balance-case having been leveled by means of supporting screws, and the pans lightly dusted with a fine brush, the first step in the process of weighing is the adjustment of the balance to a suitable equilibrium. With the eye directly in front of the middle of the scale, the pans and beam are released by a slow even motion of the releasing mechanism. Should the beam fail to oscillate when set free it may be put in motion by touching it gently with the *rider* which hangs above it on the sliding *rider-rod.* The pan-supports and the beam-support of some balances are moved by the same milled-head, the pans being released slightly in advance of the beam; sometimes the spring-support of the pans and the beam-support are controlled by independent mechanisms. When the pans and the beam-supports are controlled separately the beam begins to oscillate more readily if set free after the lowering of the pan-supports, but extreme care should always be taken to avoid jarring when the beam knife-edge comes in contact with the bearing.

The exact limits to which the pointer moves for an amplitude of four or five divisions on either side of the center of the scale are observed for an uneven number of swings from the center, and the mean of each set is noted; then, counting the excursions to the left − and those to the right +, half the algebraic sum of the means is taken as the center of oscillation or the *zero-point* of the balance. Suppose, for example, successive readings to be noted and recorded as follows:

Divisions to left.	Divisions to right.
− 5	+ 5.2
− 4.6	+ 4.8
− 4.3	......
sum −13.9	+10
Mean− 4.63	+ 5

Then $\frac{-4.63 + 5}{2} = +0.18$ and the zero-point, or point of equilibrium of the balance without load, will fall 0.18 of a division on the right of the center. When the balance is in perfect adjustment its zero-point should coincide with the middle-point of the scale, and if the displacement of the zero-point is more than a division of the scale the balance should be readjusted. But for ordinary weighing it is generally preferable to take slight displacements of the zero-point into account in the weighings rather than to disturb the beam by touch or by changes of temperature due to the insertion of the hand within the balance case.

The Operation of Weighing. — In the operation of weighing, the material to be weighed is usually put upon the left pan of the balance and the weights required to bring about equilibrium are put upon the right pan, down to the limit at which the rider may be used upon the right arm of the beam, precaution being taken never to put corrosive substances directly upon the balance-pan. Crucibles, dishes, weighing bottles, pieces of massive metal, etc., may be placed upon the pan, but ordinary materials for analysis are usually weighed in an exactly counterpoised watch-glass, or in a suitable weighed container such as a crucible or thin glass weighing-tube, the weight of the material being shown by the difference between the weights of the container with and without the material. With the material placed upon the left pan of the balance the counterpoising is begun by the systematic trial of weights upon the right pan in the order of their arrangement in the box. It is easy to find the lightest single weight which, when placed upon the middle of the right pan, makes the pointer move to the left upon cautiously releasing the beam and pans. With balances which have separate pan-supports, about a gram in excess of the weight necessary to produce equilibrium is needed to move the pan, so that weights down to the limit of a gram may be found without releasing the pan-supports. After finding the lightest single weight which is just too heavy, this weight is returned to the box and replaced by the next smaller weight in the box, and this second weight is supplemented by weights taken in order, with necessary replacements and additions, until the limit is reached at which the rider may be used upon the beam. This limit may be 5, 6, 10, or 12 mgrm., according to the division of the beam. Thereafter, the rider is used to indicate milligrams and fractions of a milligram. Throughout the process, unused weights are returned to their places in the box, so that the first reading of the weight used may be made from the vacancies in the box and the reading checked by noting the weights themselves as they are taken subsequently from the pan and returned to their places in the box.

The Method of Equal Swings.—A simple method of weighing and one sufficiently accurate for ordinary analytical processes is the method of equal swings. If the balance is so adjusted that the zero-point is displaced by half the amount lost on each swing from left to right and back to left the pointer will stop at the end of each swing to the right on the division which corresponds to the starting point at the left. Then, if the weights used are so taken that, at the end of each swing to the right, the pointer stops on the division corresponding to the starting point on the left the amount of the weights as read will need no correction.

Suppose, for example, that the pointer loses 0.3 of a division on each swing of moderate amplitude from left to right and the reverse. Then, if the balance is adjusted so that the zero-point shall fall at 0.15 of a division to the right of the center, the pointer will stop in successive excursions to the right at a division which corresponds to the starting point on the left. This is shown in the following example.

Distance from the zero-point on the left.	Zero-point.	Distance from the zero-point on the right.	Loss on the swing from left to right and the reverse.
−6.15	0	+6.0	....
−5.85	0	+5.7	0.30
−5.55	0	+5.4	0.30

Starting-point on the left.	Zero-point.	Stopping-point on the right.
−6.0	+0.15	+6.0
−5.7	+0.15	+5.7
−5.4	+0.15	+5.4

When the weighing is made by the method of equal swings any necessary correction for a known imperfect adjustment of the zero-point may be made mentally by adding to, or subtracting from, the weights used, as the case may be, the weight which would be necessary to adjust the zero-point.

The Method of Oscillations. — In processes demanding the most exact weighing the equilibrium is found just as in the determination of the zero-point of the unloaded balance, by a method of oscillations. If the *point of equilibrium under the load* and the counterpoising weights were to be determined in the same way that the zero-point was determined, and made to coincide exactly with the zero-point, the weights used would indicate at once the weight of the load. This process, however, is unnecessarily tedious. It is more convenient to determine a point of equilibrium not very far removed from the zero-point and then to make a correction for the deviation; and this may be readily done, provided the *sensitiveness of the balance* (that is, the weight which corresponds to a deviation of one scale division) is known.* This correction is to be added when the point of equilibrium under the load lies to the right of the zero-point and to be subtracted when the point of equilibrium lies to the left of the zero-point. For example: Suppose the weights used, the zero-point of the unloaded balance, the point of equilibrium of the loaded balance, and the value of one scale division to be as given in the tabular statement following.

Weights used, grm.	Scale divisions.	
20	Zero-point	+ 0.2
1	Point of equilibrium	− 0.4
0.5	Deviation	0.6 to the left
0.1		
0.02	Value of 1 scale division† = 0.00043 grm.	
0.0057 (rider)		
21.6257		

Then,

the correction for deviation = 0.6 × 0.00043 = 0.00026 grm.
and the corrected weight of load = 21.6257 − 0.00026
= 21.62544 grm.

The Sensitiveness of the Balance.—To find the sensitiveness of the balance when carrying no load it is sufficient to note the change in weight indicated by the rider for a change of 1 scale division in the point of equilibrium; and the sensitiveness of a loaded balance may be similarly indicated by the weight which must be added to, or subtracted from, the counterpoising weights in order to change the point of equilibrium by 1 scale division. With increasing loads the friction on the knife-edge increases and the sensitiveness of the balance decreases. So it is important to know the sensitiveness for various loads. With any given load, or no load, the sensitiveness may be found by determining the variation made in the center of oscillations (the point of equilibrium or the zero-point) by moving the rider so as to change by 1 mgrm. the counterpoising weights, noting

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* For the determination of the *sensitiveness of the balance,* see the next paragraph.

† See p. 18.

the effect upon the point of equilibrium, and then calculating the weight which would produce a variation of 1 scale division.

Suppose, for example, that the zero-point has been found to be at 0.18 of a division to the right of the center, and that the placing of the rider on the 1-mgrm. mark will cause the oscillations shown in the following table.

Divisions to left.	Divisions to right.
− 6	+0.46
− 5.4	+0.42
− 5.1	......
Sum −16.5	+0.88
Mean− 5.5	+0.44

Then $(-5.5 + 0.44) \div 2 = -2.53$ = Point of equilibrium. The addition of 1 mgrm. moves the point of equilibrium of the balance from +0.18 to −2.53 on the scale, and the weight of 1 mgrm. corresponds to 2.7 divisions. The value of 1 scale division for the balance without load will, therefore, be found by solving the proportion $2.7 : 1 = 1 : x$, and $x = 0.37$ mgrm.

The sensitiveness of the balance for varying loads may be found similarly. Thus, if the movement of the rider by an amount corresponding to a change of 1 mgrm. in weight produces variation of 2.7 divisions with a load of 1 grm., 2.7 division with 5 grm., 2.6 divisions with 10 grm., 2.3 divisions with 20 grm., 2.2 divisions with 50 grm., these figures may be used to find the sensitiveness of the balance under loads ranging from 1 grm. to 50 grm. It is convenient to tabulate the results as follows and to place the record upon a card, always visible in the balance-case.

Load.	Value of scale division.
grm.	grm.
0	0.00037
1	0.00037
5	0.00037
10	0.00038
20	0.00043
50	0.00045

In ordinary analytical processes the determination of weights to the fourth decimal place is quite as exact as the conditions warrant. If the fifth decimal, derived by calculation, is less than 5 it should be dropped; if 5, or more than 5, it should be replaced by 1 added to the fourth decimal.

Correction for Inequality in the Arms of the Balance. — The method of weighing, according to which the material to be weighed is always placed on the same pan, gives the ratio of weights compared in successive weighings independently of the slight inequality in arms of the balance which may be due to faulty construction or to existing conditions of temperature, and for most analytical processes this method is sufficient. Sometimes, however, the determination of weights must be absolute, as, for example, in the testing of an untried gram weight against a standard gram. In such cases the effect of inequality in the lengths of the arms of the balance must be eliminated by the method of *weighing by substitution* or by the method of *double weighing.*

Weighing by Substitution. — If the material to be weighed is placed upon the one pan of the balance and counterpoised exactly, the weights which will, when substituted for the material, exactly balance the counterpoise will be the exact measure of the weight of the material independently of inequality in the balance arms. In this process it is more convenient to place the material on the right side of the balance so that the rider may be used in the final adjustment of the substituting weights. The material on the right pan may then be counterpoised by any suitable material placed upon the left pan, but the most convenient material for the counterpoise is a set of weights. The counterpoised material is removed from the right pan, and replaced by exact weights until, with the help of the rider, the balance is brought to an equilibrium.

Double Weighing. — By weighing material in the usual manner, then making another weighing similarly but with the material and weights interchanged upon the pans, and taking the arithmetical mean of the sum of the weights obtained in the two weighings, the effect of any reasonable inequality in the arms of the balance may also be eliminated sufficiently. Theoretically, it is the geometrical mean, or the square root of the product of the two weights, which gives the real weight, but the arithmetical mean gives a sufficiently near approximation.

Corrections for Buoyancy of the Air. — In weighings made by any of the processes described both weights and the material weighed are affected by the buoyancy of the air, and such weighings fail to give a perfect comparison between weights and material by just the difference between the buoyant effect exerted upon the weights and that exerted upon the material. When the amounts of material weighed are as small as they usually are in analysis the difference is not appreciable for ordinary purposes; but when the amounts of material are considerable, or when the materials are weighed in a large container, account must be taken of the atmospheric buoyancy in order that the weights handled may be known with a reasonable degree of exactness. The effects of buoyancy upon materials and weights, measured by the weights of air displaced by each, may be determined exactly if the volume of each is known together with the weight of a cubic centimeter of air under the prevailing conditions of temperature, pressure, and moisture. For all ordinary work, the corrections for apparent weights and materials may be determined accurately enough from the average weight of a cubic centimeter of air under laboratory conditions and the approximate specific gravities of materials and weights. The average weight of 1 $cm.^3$ of air may be taken as 0.0012 grm. and the specific gravity of the weight, or the weights which fill 1 $cm.^3$, as 8.4 for brass and 21.5 for platinum. The corrections to be subtracted from the indicated weight are therefore $0.0012 \div 8.4 = 0.00014$ grm. for every gram of brass, $0.0012 \div 21.5 = 0.00005$ grm. for every gram of platinum; and the correction to be added to the indicated weight will be 0.0012 grm. ÷ sp. gr. of material for every gram. Suppose, for example, that a mass of silver placed upon the left pan of the balance is exactly counterpoised by 15.6875 grm. upon the right pan. From this indicated weight, which is too large by the amount of the buoyancy of the air exerted upon the weights and too small by the buoyancy exerted upon the silver, must be subtracted for the brass weights $15 \times 0.00014 = 0.0024$ grm., and for the platinum weights $0.68 \times 0.00005 = 0.00003$ grm., or 0.00243 grm. in all; and to it must be added $(15.6875 - 0.00243)$* $\times 0.0012 \div 10.15$ (the sp. gr. of silver) $= 0.00179$. The indicated weight of the silver is, therefore, 0.00064 grm. too large, and the true weight is 15.68686 grm.

It is obvious that in a very exact analysis in which large amounts of material are involved correction for the buoyancy of the air upon weights and material is essential. The buoyant effect upon the container of the material is best eliminated by counterpoising with another similar container. In ordinary analysis, in which the amounts of material used rarely exceed

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* In the present case, the subtraction of the buoyancy of air upon the weights at this point is, of course, insignificant.

a gram, and generally are less, the correction for the buoyancy of air is superfluous.

The Analytical Weights. — The set of analytical weights usually consists of individual weights aggregating 100 grm. beside the fraction of a gram. Generally there is one weight of 50 grm., one of 20 grm., two of 10 grm., one of 5 grm., one of 2 grm., three of 1 grm., all of brass; and smaller weights of platinum, one of 500 mgrm., one of 200 mgrm., two of 100 mgrm., one of 50 mgrm., one of 20 mgrm., two of 10 mgrm., one of 5 mgrm., one of 2 mgrm., and three of 1 mgrm.; with a rider of 12 mgrm., 10 mgrm., 6 mgrm., or 5 mgrm., according as the beam is divided between the middle point and the pan knife-edge into 12, 10, 6, or 5 large divisions, respectively. In practice, the rider takes the place of the weights smaller than its own weight. Weights of the same denomination; the two 10-grm. weights, the three 1-grm. weights, the two 100-mgrm. weights and the two 10-mgrm. weights should be distinguished by one, two, or three dots made with a fine round-pointed punch, and should stand in the box, and be used in the weighings, in the order indicated by the marks of identification.

In a perfect set of weights the 1-grm. weights will represent exactly standard grams, the multiple weights will be the real multiples, and the fractional weights the real fractions of the standard gram which are indicated by their denominations. For most purposes of analysis it is not essential that the gram weight be exactly the standard gram with the other weights exact multiples and fractions of the standard gram; but it is essential that the weights throughout the series represent with a high degree of accuracy the exact ratios indicated by their designations. Generally, weights of first quality, when new, are accurate enough for ordinary work, but it is desirable, and for the most accurate work essential, that the degree of error affecting the weights be known, and determined from time to time.

The Testing of Weights. — In testing the analytical sets it is convenient to have at hand a small set of testing weights, with which the regular analytical weights may be compared. Such a set of testing weights may conveniently consist of weights of 500 mgrm., 200 mgrm., 100 mgrm., 50 mgrm., 20 mgrm., 10 mgrm., and 5 mgrm., each of exactly standard weight or of known error. With such a set of testing weights the operation of correcting the analytical weights by the method of substitutional weighing against counterpoises is a simple matter.

Let us suppose, for example, that the standard 500-mgrm. weight is placed upon the left pan of the balance and counterpoised by weights from another set and the rider. If now the standard 500-mgrm. weight is replaced by the 500-mgrm. weight of the set to be corrected, it is easy to determine, by moving the rider or by noting the variation in the swing of the pointer, just how the tested weight compares with the standard 500 mgrm. The smaller weights may be compared in precisely the same manner with the small testing weights. A similar counterpoising of the first gram weight of the set and substitution by the two 500-mgrm. weights, now both of known value, will fix the value of that weight; and similar operations with the second and third 1-grm. weights will determine their values in terms of the standard gram; and for the weights heavier than 1-grm., the corrections may be determined successively by substitutional comparison with the weights already corrected. Thus, the 2-grm. weight may be compared with two corrected 1-grm. weights; the 5-grm. weight with the three 1-grm. weights and the 2-grm. weight; the 10-grm. weight with the 5-grm., the 2-grm., and the three 1-grm. weights; and so on.

In case such a set of small standard weights is not at hand, it is possible, also, to correct the *ratios* of the individual weights of a set by systematic comparisons with one another either by the method of double weighing* or much more simply by substitutional weighing against counterpoises.† Such an operation is best begun by counterpoising exactly (by weights and rider) an extra weight a trifle lighter than 0.01 grm. and then substituting for it the 0.01′-grm. weight of the set to be tested,

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* Ostwald: Physico-Chemical Measurements, trans. Walker, p. 41.

† Richards: Jour. Am. Chem. Soc., **22**, 144 (1900).

determining the relative values of these weights by means of the rider. Next may be found similarly the relation between the 0.01″-grm. weight and the 0.01′-grm. weight; then the relation between the 0.02-grm. weights and the 0.01′-grm. and 0.01″-grm. weights together; then the relation between the 0.05-grm. weight and the sum of the 0.01′-grm., 0.01″-grm., 0.02′-grm. and the extra 0.01-grm. weights, and so on. In this manner a statement of ratios may be constructed, like that given in the first and second columns of the following table. In making use of a small weight as the standard of comparison the errors of the large weights are made to appear very large; but these relative values once determined, more convenient ratios may be found by making a large weight the standard and redetermining the ratios. For example, if the 10-grm. weight is now taken as the standard, the ideal aliquot parts of it represented by the smaller denominations will be shown in the third column, and the difference between these ideal aliquot parts and the corresponding values of the second column will measure the errors of the individual weights.

Denomination of weight.	Ratios with the extra 0.01-grm. weight as a standard.	Weights of each denomination calculated from the 10-grm. weight taken as a standard.	Correction.
Grm.	Grm.	Grm.	Grm.
0.01	0.01006	0.01002	+0.00004
0.01	0.01005		+0.00003
0.02	0.02005	0.02004	+0.00001
0.05	0.05009	0.05009	+0.00000
0.1	0.10019	0.10018	+0.00001
0.1	0.10020		+0.00002
0.2	0.20035	0.20035	±0.00000
0.05	0.50088	0.50088	±0.00000
1	1.00183	1.00177	+0.00006
1	1.00181		+0.00004
1	1.00177		+0.00000
2	2.00383	2.00354	+0.00029
5	5.00884	5.00884	±0.00000
10	10.01768	10.01768	Standard

In making use of such a table of corrections, + corrections are, of course, to be added to the respective weights and − corrections subtracted.

Generally, analytical processes deal with amounts of materials which do not weigh more than a gram or two, the higher weights being used simply as counterpoises of crucibles or other containers. For such processes, therefore, it is not necessary to use, or even to know, the true values of the higher weights, provided identical counterpoises are used throughout a process.

The Measurement of Volume

Volumetric Apparatus. — In order that measurements of volumes of liquids and gases, for which volumetric measurements are feasible, may be exact, it is obvious that accurately graduated and strictly comparable measuring vessels are requisite. At the present time measuring instruments are procurable which are certified by responsible governmental authority.* These instruments are graduated with reference to the liter defined as the volume occupied by one kilogram of pure water at 4 degrees, the temperature of its greatest density; and this is the system of graduation to which it is advisable that all instruments employed in the measurements of volumetric analysis should conform. The measuring vessels commonly used in volumetric analysis are *flasks*, Fig. 2, graduated for contents or for delivery; *single-volume pipettes*, Fig. 3*a* (for the delivery of one definite volume); and *divided pipettes*, Fig. 3*b*, without stop-cocks; *burettes*, Fig. 4*a* and Fig. 4*b*, provided with stop-cocks, or pinch-cocks, or with the Bunsen tap (consisting of a bead within a rubber tube, which by gentle manipulation between the thumb and forefinger allows the passage of liquid in regulated amount), for the delivery of various volumes throughout the range of graduation; and *gas-burettes*, Fig. 5, fitted with stop-cocks and leveling tubes for the adjustment of pressure.

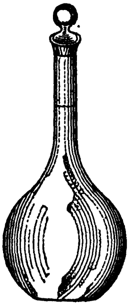
FIG. 2.

It is, of course, necessary in all exact processes that readings should be made with the eye on a level with the reading mark in order to avoid parallax, and the graduation of the tube by lines entirely encircling it is the best aid to a correct placing of the eye in reading. In determining the volumes of liquids the

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* Die Physikalische-Technische Reichsanstalt of Germany and the National Bureau of Standards of the United States.

reading is made from the upper boundary when they are opaque and preferably from the bottom of the meniscus when they are transparent. In the former case, a white card held behind the graduation helps to define the reading boundary; in the latter, a white card striped horizontally with a broad band of black and held so that the darkened meniscus may be defined clearly is an efficient aid.

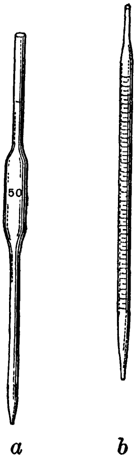

Fig. 3.

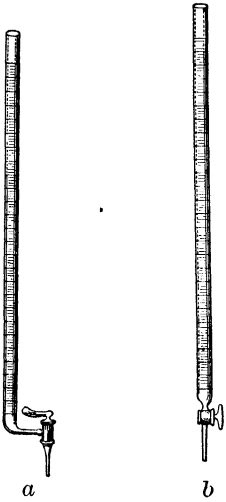

Fig. 4.

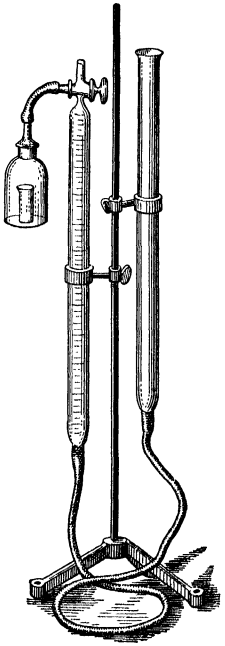

Fig. 5.

Variations of Volume with Changing Temperature. — *Gases* expand and contract regularly with changes in temperature and volumes of gases measured at known temperatures and pressures may be reduced to normal or definite conditions by application of the laws of Boyle and Charles.

Liquids and solutions expand or contract with changes in temperature by amounts which vary with different ranges of temperature as well as with the nature and concentrations of the substances. For example, a liter of pure water expands 2.05 cm.^{3} in the range of 10 degrees from 15 degrees to 25 degrees, and 2.55 cm.^{3} in the range from 20 degrees to 30 degrees. In the range from 15 degrees to 25 degrees, the expansion of a liter of a solution containing 3.16 grm. of potassium permanganate * amounts to 2.13 cm.^{3}, and that of a liter of a solution containing 17 grm. of silver nitrate † amounts to 2.16 cm.^{3}; that of a liter of hydrochloric acid containing 36.5 grm. of that reagent ‡ amounts to 2.42 cm.^{3}, and that of a liter of a solution containing 46 grm. of sodium hydroxide ‡ amounts to 3.15 cm.^{3}.

The measuring vessels are also subject to variations of volume with changing temperatures. In the average, glass vessels expand or contract by about 0.000026 of their volume for every degree of rise or fall in temperature, respectively. The expansion or contraction of a liter flask for a range of 10 degrees may be taken as $1000 \times 10 \times 0.000026 = 0.26$ cm.^{3}.

It is plain, therefore, that graduated apparatus should be used for the determination of volumes of a solution at a temperature not very different from the temperature of standardization, usually 15 degrees, unless correction is made for the variations of the volumes with changing temperature.

Correction of the Indicated Volume. — For change in the volume of the apparatus, the average expansion of glass for a rise of 1 degree (the coefficient of expansion) and the range of temperature afford the data necessary to make due correction; and a correction of the indicated volume for change in the solution itself may, if the coefficient of expansion of the solution be known, be similarly applied. The coefficients of expansion of very dilute solutions generally do not vary much from that of pure water. For such solutions containing only water and the solute at very low concentration, the corrected volume V' may be found by adding to the observed volume V the product obtained by multiplying the observed volume by a factor a depending upon the temperature of observation, this factor bearing the + sign for observations made below 15 degrees (the ordinary temperature of graduation) and the − sign for observations made above 15 degrees. That is, $V' = V + Va$.

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* 0.02 grm. mol. † 0.1 grm. mol. ‡ 1 grm. mol.

The approximate values of this factor for solutions containing 0.1 grm. mol. of a single reagent in 1 liter are shown in the following table.

Temperature	10°	11°	12°	13°	14°	15°
Factor = +0.001 ×	0.46	0.40	0.33	0.22	0.12	0
Temperature	....	16°	17°	18°	19°	20°
Factor = −0.001 ×	....	0.13	0.37	0.42	0.59	0.76
Temperature	....	21°	22°	23°	24°	25°
Factor = −0.001 ×	....	0.95	1.14	1.35	1.56	1.79
Temperature	....	26°	27°	28°	29°	30°
Factor = −0.001 ×	....	2.02	2.27	2.52	2.75	3.06

For example, according to a computation made by the aid of this table, a volume of 50 cm.^{3} of a 0.1 grm. mol. solution of a reagent (and no other dissolved material) if measured at 25 degrees, would measure

$$50 - 50 \times 0.001 \times 1.79 = 49.91 \text{ cm.}^3 \text{ at 15 degrees;}$$

and a volume of 50 cm.^{3} at 10 degrees would measure

$$50 + 50 \times 0.001 \times 0.46 = 50.02 \text{ cm.}^3 \text{ at 15 degrees.}$$

Frequently, however, solutions are employed of much greater concentration in respect to the active reagent or to all the dissolved substances; and solutions are often standardized at a temperature different from the temperature of graduation. In general, therefore, corrections of volume for varying temperatures of solutions may be based preferably upon an experimental determination of the ratio of the concentration of the solution at the temperature of standardization to the concentration at any temperature of use. The Sprengel pyknometer (Fig. 6) as modified by Ostwald * serves the purpose.

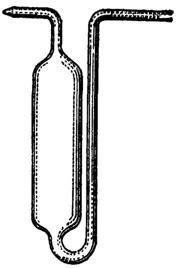

Fig. 6.

The pyknometer, of about 10 cm.^{3} capacity, washed with water, alcohol, and ether, applied successively, and dried by drawing air through it, is first weighed empty. Next,

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* Ostwald: Physico-Chemical Measurements, trans. Walker, p. 92.

the pyknometer is filled with the solution at the temperature of standardization; the volume of the solution is adjusted to the mark by touching the narrowed end of the tube with filter-paper to withdraw liquid, or with a drop of solution on a rod to introduce liquid; and the pyknometer and solution are weighed. The difference between the weight of the empty instrument and the full instrument is the weight of a definite volume of the solution at the temperature of standardization. Similarly, the difference between the weight of the empty pyknometer and the weight of the pyknometer filled to the mark with the solution at the temperature of use gives the weight of a pyknometerful of the solution for the two temperatures.

Suppose, for example, that a solution of silver nitrate is made to contain 17 grm. of that reagent in the liter, or 1.7 grm. in 100 cm.^{3}, at 20 degrees, and that the pyknometer contains 10.1780 grm. at 20 degrees and 10.1680 grm. at 25 degrees, then the amount of silver nitrate contained in the volume indicated as 100 cm.^{3} by a glass measuring instrument at 25 degrees will be given by the proportion

$$10.1780 : 10.1680 = 1.7 : x, \qquad x = 1.6983 \text{ grm.}$$

Calibration of Instruments.—It is often desirable to calibrate graduated instruments, or to graduate less expensive apparatus, and this may be accomplished by means of the relation which exists between the weight of water and the volume which it occupies at given temperatures.

In weighing the water it is necessary to take into consideration the buoyancy of the air both upon the brass weights and upon the corresponding mass of water; but weights of less than 1 grm. may be safely left out of account. The average buoyancy exerted upon 1 grm. of brass amounts to 0.00014 grm. and that exerted upon 1 grm. of water to 0.0012 grm. To obtain the true weight of the water weighed in air, the sum of the weights actually used must be increased by 0.00106 grm., the difference between 0.0012 grm. and 0.00014 grm., for every gram. On the other hand, to find the weight which must be used in air to counterpoise an amount of water which weighs a given number of grams in a vacuum, the given weight must be diminished by 0.00106 grm. for every gram.

The following table gives the actual weights (in a vacuum) of 1 cm.^{3} of water at ordinary laboratory temperatures and the weights which must be used to counterpoise in air the actual weights.

Temperature, Deg. C.	Weight of 1 cm.³ of pure water in a vacuum.	Counterpoising weights in air for 1 cm.³ of water.
	Grm.	Grm.
4	1.000000	0.998940
15	0.999126	0.998066
16	0.998970	0.997910
17	0.998801	0.997741
18	0.998622	0.997562
19	0.998432	0.997372
20	0.998230	0.997170
21	0.998019	0.996959
22	0.997797	0.996737
23	0.997565	0.996505
24	0.997323	0.996263
25	0.997071	0.996011
26	0.996810	0.995750
27	0.996539	0.995479
28	0.996259	0.995199
29	0.995971	0.994911
30	0.995673	0.994613

These relations of the weights of pure water to the volumes make it easy to determine or adjust the accuracy of measuring apparatus at any convenient temperature.

Flasks. — The calibration or testing of a flask graduated for *contents* may be accomplished by counterpoising the dry flask, filling it with water until the bottom of the meniscus of liquid touches the mark upon the neck, finding the weight of the flask with the water, and, by difference, the weight of the water, and then comparing the apparent weight of the water with the actual weight in air of the indicated volume of water for the temperature at the time. For example, if the weight of water required to fill to the mark a liter flask proves to be 997.37 grm. at 20 degrees, the error of the graduation will, according to the table, be the difference between this weight and 997.170 grm., the weight in air of 1000 cm.³ of water at 20 degrees, or +0.20 cm.³.

In calibrating a flask for *delivery* it is first weighed full of water to the mark and then emptied, drained in an inclined position for a definite period (one minute) and weighed again. The difference between the weights noted measures the contents of the flask for delivery. In using the flask for measurements it is allowed to drain for the same definite period.

Ungraduated flasks may be graduated by counterpoising dry or after draining, according as they are to be used for contents or for delivery, and then filling them with exactly the amount of water which has the weight of the desired volume of water at the given temperature, and marking.

Pipettes. — For the delivery of liquids in exact work calibrated pipettes are preferable to flasks. The pipette is filled by suction until the bottom of the meniscus of liquid is a little above the mark upon the stem and closed at the top with the finger. By moving the finger across the tube held in a vertical position and with the lower end touching the side wall of a glass beaker, the meniscus is adjusted exactly to the mark. In using a single-volume pipette the liquid is allowed to run out entirely into a counterpoised flask, and with the point in contact with the neck of the flask the pipette is drained for fifteen seconds. From divided pipettes the liquid is run into the flask to the desired point and drained for fifteen seconds, and the meniscus is again adjusted. The increase in the weight of the flask measures the volume of the water delivered.

In graduating unmarked pipettes, the upper point of marking is first determined approximately by filling the pipette, from the orifice or from a fixed mark, as the case may be, with a volume of water slightly larger than that for which the graduation is to be made, and the level of the meniscus is marked upon a paper scale pasted upon the stem. Then two weighings, one of the volume delivered from a noted point above the mark, and one from a noted point below the mark, to the orifice or to the fixed mark, will give the data for determining the exact point of graduation. For example, if one weighing of water, at 18 degrees, from a pipette designed to deliver 10 cm.^{3} proves to be 10.032 grm. and the other from a point 10 mm. lower proves to be 9.892 grm., then, $10.032 - 9.892 : 10.032 - 9.976$ (the weight of 10 cm.^{3} of water in air at 18 degrees) $= 10 : x$, and $x = 4$; and the graduation mark should be made at the point 4 mm. below the uppermost mark. If the weighings were made at 20 degrees, the mark of graduation should be placed 4.3 mm. below the uppermost point, since $10.032 - 9.892 : 10.032 - 9.972 = 10 : x$, and $x = 4.3$ mm.

Burettes and Divided Pipettes. — Burettes for the measurement of liquids or gases, and the divided pipette, may be tested by weighing, to 0.01 grm., carefully measured portions of water drained successively into a counterpoised flask, and comparing the weights of the indicated volumes with the weights which such volumes should have at the temperatures of the experiment. The corrections of readings once determined may be made easily available for practical application by plotting the readings as abscissæ and the corrections as ordinates, so that the correction for any reading may be seen at a glance.

A more convenient method of testing burettes and divided pipettes involves the use of a small pipette, conveniently of 5 cm.^{3} capacity and calibrated in the manner previously described.* The pipette is attached to the instrument to be tested, in the manner shown in the accompanying figure, and the water-levels are adjusted to the zero-points. Then with the flow cut off from the instrument to be tested, the water is drawn from the calibration pipette to the lower mark, the cock is closed, and the liquid allowed to run from the tested instrument into the calibration-pipette until the latter is again filled to the upper mark. The difference between the reading of the tested instrument at the start and the reading at the end of this operation will show the volume which for the temperature of the experiment equals the capacity of the calibration pipette. In this manner the entire instrument may be calibrated. When much calibration of apparatus is to be done it is most convenient to make use of comparison pipettes with stems graduated and calibrated to deliver exact volumes for any convenient temperature.† The limits within which errors of graduation may be regarded as reasonable may be stated as follows:‡

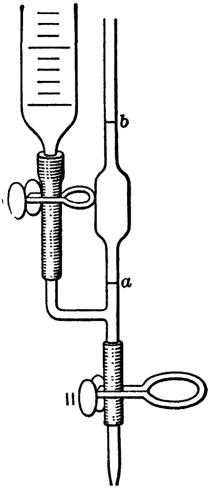

Fig. 7.

	Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}
Capacity	1 to 2	10	50	100	250	500	1000	2000
Limit of error, flasks:								
for contents	......	0.01	0.05	0.08	0.10	0.15	0.30	0.50
for delivery	......	0.03	0.10	0.15	0.20	0.30	0.50	1.00
Limit of error, undivided pipettes	0.01	0.02	0.05	0.10	....	....	....	....
Limit of error, divided pipettes	0.02	0.04	0.10	0.20	....	....	....	....
Limit of error, burettes	......	0.02	0.05	0.10	....	....	....	....

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* Ostwald: Physico-Chemical Measurements, trans. Walker, p. 87.

† Morse and Blalock: Amer. Chem. Jour., **16,** 479.

‡ Further discussion of specifications, marks, graduation, precautions in use, and allowable error in volumetric apparatus may be found in the report of the Committee for Coöperation with the National Bureau of Standards. Jour. Amer. Chem. Soc., **26;** Proc., p. (17), 1904.

CHAPTER III

PROCEDURES IN GRAVIMETRIC ANALYSIS

In processes of Gravimetric Analysis both the substances analyzed and the products of analysis are determined by weighing. When exposed to ordinary air, some substances prove to be hygroscopic (that is, they take up moisture from the air); others give up water to ordinary air; while others assume fairly definite conditions when exposed in an ordinarily dry atmosphere. The water content of every substance exposed to air and capable of taking up or of losing water depends upon an equilibrium between the vapor pressure of the water in the substance and that of the water in the air, and the condition of equilibrium varies with temperature and pressure. It is necessary, therefore, to make sure that the substances determined, and generally the material subjected to analysis, ordinarily weighed in contact with air, shall be definite in respect to content of moisture; and the means of attaining this end, by regulation of the condition of temperature and pressure, must be chosen with a knowledge of the special characteristics of the substances.

Preparation for Weighing

Air-Drying. — Some substances may be brought to a fairly definite condition by simple air-drying — that is, by exposing them to ordinary air for a suitable period at the ordinary atmospheric temperature. Of such substances, crystallized barium chloride, $BaCl_2 \cdot 2\,H_2O$, and crystallized copper sulphate, $CuSO_4 \cdot 5\,H_2O$, which lose hygroscopic water while retaining their water of crystallization in ordinarily dry air, may serve as examples.

Drying in Desiccators. — Some substances are best prepared for weighing by exposing them in closed chambers, at the ordinary temperature, to air which is artificially dried by contact with some strongly hygroscopic substance, like calcium chloride, concentrated sulphuric acid, or phosphorus pentoxide; so that the water of the substance may come to an equilibrium with water vapor at inappreciable concentration in the drying atmosphere. Sometimes to promote the drying effect the air pressure and vapor pressure are reduced in the chamber by means of the vacuum pump. Many forms of these *desiccators* are in common use, but the essential characteristics of every desiccator are the closed chamber and a dehydrator suited to the occasion, and in certain cases, means for exhausting the chamber (Fig. 8).

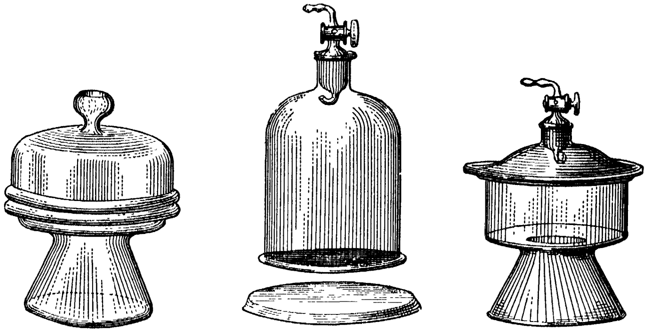
a *b* *c*

FIG. 8.

Dehydration by Heat. — To bring some substances to a definite condition of hydration or dehydration, it is necessary to change the condition of equilibrium by heating them in the hot air chamber (the *air-bath*), or by "igniting" them — that is, heating them in the flame of the Bunsen burner or the blast-lamp or other source of a high degree of heat, as the case may require; and when a substance has been properly dehydrated by heat it is usual to place it in a desiccator in order that it may be protected against the possibility of taking up water by exposure to the ordinary atmosphere while cooling completely to the atmospheric temperature, at which it must be weighed.

PROCESSES DEPENDING UPON THE FORMATION OF VOLATILE PRODUCTS

Like the processes of dehydration used in the preparation of substances for weighing, some procedures of gravimetric analysis rest upon *the fixing of conditions of temperature (and pressure) so that the substances to be analyzed shall yield a volatile constituent and leave a definite and weighable residue,* or upon *the expulsion of the volatile constituent by a reaction resulting in the formation of a definite and weighable residue. Other gravimetric procedures involve the collection and weighing of the volatile constituent, after its expulsion from the substance analyzed.*

The Determination of Water of Composition

The water content of certain hydroxides and many hydrous salts may be expelled by simply submitting these substances to suitable conditions of temperature with the formation of a definite and weighable residue. The difference between the weight of the substance taken and that of the residue will then be the weight of the water evolved.

From certain refractory salts, minerals, and rocks from which the water is expelled with difficulty by heat alone, the evolution of the water may be facilitated by heating with a suitable flux of unchanging weight; and from certain other substances which when heated by themselves evolve beside the water content other volatile matter the water may be evolved alone if a suitable flux be used as a retainer of the volatile constituents other than water. In either case the loss of weight on the part of the mixture of substance and flux will measure the water evolved.

When the residue left after heating, either with or without the aid of a flux, is not sufficiently definite the determination must be made by the direct weighing of the evolved water usually collected in a suitable absorbent.

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* For the description of a special device by which substances may be dried and securely bottled without contact with the ordinary air, see Richards: Methods Used in Precise Chemical Investigation, Publication No. 125 of the Carnegie Institution of Washington, p. 97.

Determination of Water by Loss on Heating. — Hydrous barium chloride, $BaCl_2 \cdot 2\,H_2O$, and hydrous copper sulphate, $CuSO_4 \cdot 5\,H_2O$, both crystallized from water and air-dried under ordinary atmospheric conditions, lose their water of crystallization when suitably heated for a sufficient length of time under conditions which permit the escape of water from the system. From the hydrous barium chloride all the water may be easily expelled at a temperature of 100 degrees. To remove the water entirely from the hydrous copper sulphate prolonged heating at a much higher temperature (200° or more) is required.

Experimental Process: Determination of Water in Barium Chloride. — Clean a crucible (porcelain or platinum), ignite it in the Bunsen flame, cool it until it radiates heat gently, place it in the desiccator, and, after it has been thoroughly *cooled to the temperature of the air* (at least ten to fifteen minutes) place it upon the left-hand pan of the balance, and weigh carefully. Put into the crucible, with the aid of a spatula, about 1 grm. of barium chloride, $BaCl_2 \cdot 2\,H_2O$, previously prepared by powdering in a mortar the pure air-dried crystals. Weigh again carefully. The difference between the two weights will be the *weight of the substance taken.* Now, place the crucible in an air-bath heated at 115° to 120°, and let it stay there for half an hour.* Then remove the crucible to the desiccator, let it cool for fifteen minutes, and weigh. Repeat the process of exposure in the air-bath and weigh until a *constant weight,* within reasonable limits of variation in weighing (0.0003 grm.), is obtained.

Calculate: (*a*) the percentage weight of water found in the salt, (*b*) the theoretical percentage of water in $BaCl_2 \cdot 2\,H_2O$, (*c*) the amount of water which should theoretically be lost from the actual weight of the substance taken, and (*d*) the error (which may be due either to the manipulation or to imperfection of the substance) in grams and per cent.

State the results in the following form:

Weight of $BaCl_2 \cdot 2\,H_2O$ taken.	Weight of water found by loss.		Theory for water in $BaCl_2 \cdot 2\,H_2O$ taken.		Error.	
Grm.	Grm.	Per cent	Grm.	Per cent	Grm.	Per cent

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* In the case of barium chloride further reaction takes place if the temperature is too high and the heating too rapid, hydrochloric acid being formed and eliminated while oxygen replaces chlorine in the residue.

Determination of Water by Loss on Heating with a Flux. — Instead of dehydrating crystallized copper sulphate, $CuSO_4 \cdot 5\,H_2O$, by carefully adjusting the conditions so that the salt shall be heated for a considerable time in a current of dry air at a temperature gradually raised and not much exceeding 200 degrees, the operation may be completed speedily and safely if a suitable amount of the easily fusible sodium tungstate * is mixed with the copper sulphate and the mixture heated gradually to the fusing point. The following expression may serve as a typical representation of this reaction:

$$CuSO_4 \cdot 5\,H_2O + nNa_2WO_4 = Na_2SO_4 + CuO + WO_3 + (n-1)\,Na_2WO_4 + 5\,H_2O.$$

Other sulphates may be similarly dehydrated without losing sulphur trioxide.†

Experimental Process: Determination of Water in Copper Sulphate.— Weigh exactly in a porcelain crucible about 0.5 grm. of copper sulphate, $CuSO_4 \cdot 5\,H_2O$, mix the sulphate well with 2.5 grm. of anhydrous sodium tungstate, Na_2WO_4, and cover the mixture with 0.5 grm. of the tungstate. Weigh the crucible and mixture, warm very gently at first, and finally increase the heat gradually until the fusion is complete. Cool and weigh. Arrange the results in the following form:

Copper sulphate taken.	Loss on heating.		Theory for water in $CuSO_4 \cdot 5\,H_2O$ taken.		Error.	
Grm.	Grm.	Per cent	Grm.	Per cent.	Grm.	Per cent

Determination of Water by Direct Weighing. — When substances lose water upon application of heat or upon fusion with a flux and the loss is accompanied by indefinite change in the

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* To prepare the anhydrous tungstate, the commercial material, Na_2WO_4, which is ordinarily contaminated with sodium carbonate, is fused in a platinum crucible (or dish) and tungstic oxide, WO_3 (thoroughly ignited to insure the absence of ammonia and the oxidation of the product) is added until bubbles of carbon dioxide cease to form.

† Kuzirian: Am. Jour. Sci., [4] **36**, 401 (1913).

residue due to atmospheric action, or by loss of other volatile material, the water evolved may be carried in a current of air to a suitable absorption apparatus and weighed directly, provided that the other volatile products (if any) are held back or intercepted before they reach the water retainer, or else pass through the retainer and escape retention with the water.

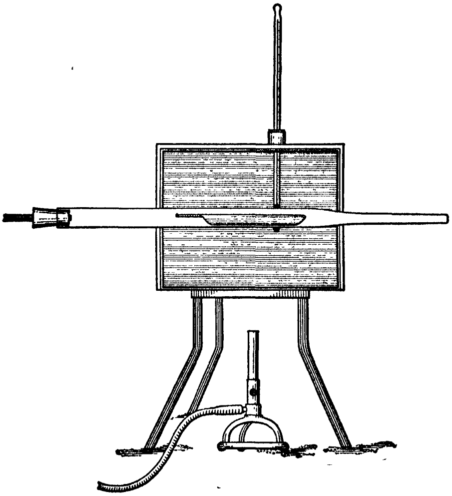

FIG. 9.

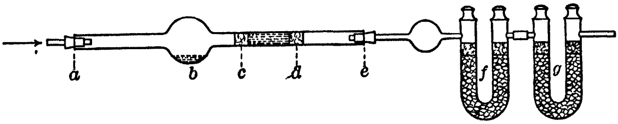

FIG. 10.

Ignition tube (Jannasch): inside diameter, 1.2 cm.; length (*a* to *e*), 26 cm.; volume of ignition-bulb *b*, 25 cm.^{3}; lead oxide between plugs of glass wool, *c* to *d*; absorption tube, *f*; protective tube, *g*.

A common method for the direct determination of water of composition is to place the substance in a horizontal combustion tube of glass (with or without a flux, and best in a boat of porcelain or platinum), and to heat the tube to a suitable temperature (in a tubulated air-bath (Fig. 9), by the direct flame of burner or blast-lamp (Fig. 10), or in an electric furnace) while a current of specially dried air passes over the substance and carries the evolved water to an absorption tube charged with the same kind of material (e.g., sulphuric acid), which is used to dry the air before it is admitted to the tube.*

The Determination of Carbon Dioxide

The carbon dioxide of carbonates may be determined, according to circumstances, by loss on heating simply, by loss on heating with a flux, by loss of the gas liberated by the action of a suitable acid, or by direct weighing of the gas evolved and absorbed in any suitable way.

Determination of Carbon Dioxide in Carbonates by Loss on Heating. — Excepting the carbonates of the alkali elements, barium, and strontium, the carbon dioxide of fixed carbonates may be expelled by heating (ignition) to temperatures easily attainable in analytical processes, and when the residual substance suffers no change of weight other than that consequent upon the loss of carbon dioxide the amount of the carbon dioxide may be determined by finding the difference between the weight before ignition and the weight after ignition.

From the carbonates of magnesium, zinc, cadmium, and lead, the carbon dioxide may be expelled by simple ignition at the temperature of the Bunsen burner:

$$\begin{aligned} MgCO_3 &= MgO + CO_2, \\ ZnCO_3 &= ZnO + CO_2, \\ CdCO_3 &= CdO + CO_2, \\ PbCO_3 &= PbO + CO_2. \end{aligned}$$

In the case of calcium carbonate the process of decomposition in the reversible reaction

$$CaCO_3 \rightleftarrows CaO + CO_2$$

is practically complete only at the high heat of the blast-lamp and when the resulting carbon dioxide is removed.

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* For details in respect to apparatus used in the determination of water in minerals and rocks, see Hillebrand: Bulletin No. 422 of the U. S. Geological Survey.

Experimental Process: Determination of Carbon Dioxide in Calcite by Ignition. — Weigh out exactly in a weighed platinum crucible about 0.5 grm. of powdered calcite. Heat the crucible and contents for five minutes well above the Bunsen flame turned low. Cool and weigh again. The loss of weight should represent hygroscopic moisture. Take the difference between the weight of the crucible and the weight obtained after the gentle ignition as the weight of dry calcite. Now ignite fully for half an hour in a strong Bunsen flame (keeping the crucible above the blue cone of the flame, to avoid unfavorable action of the unburned gas upon the platinum) and finally over the blast-lamp for five minutes. Cool in the desiccator and weigh. Repeat the five-minute ignition over the blast-lamp as many times as may be necessary to secure a practically constant weight (i.e., a weight which does not differ from the preceding weight by more than 0.0003 grm.). Note the loss found in igniting the dried calcite to constant weight, and calculate the percentage loss. Compare the results obtained with those which should have been obtained if the calcite were pure $CaCO_3$ and the analytical process perfect. State the results in the following form:

Weight of calcite taken.	Loss on drying.	Loss on ignition.		Theory for loss in ignition of pure dried calcite.		Error.	
Grm.	Grm.	Grm.	Per cent.	Grm.	Per cent.	Grm.	Per cent.

Determination of Carbon Dioxide in Carbonates by Fusion with a Flux. — Some carbonates — strontium carbonate, barium carbonate, and the carbonates of the alkali elements — do not yield their content of carbon dioxide in a simple ignition under conditions ordinarily available. Such carbonates, as well as the less refractory carbonates, may be satisfactorily decomposed by the aid of a suitable flux to combine with the residual oxide in a non-reversible reaction and thus to assist in the expulsion of volatile carbon dioxide. Sodium paratungstate, $Na_{10}W_{12}O_{41}$, makes a very good and easily fusible flux for the treatment of the refractory carbonates.* Approximately

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* This material may be prepared by heating to fusion over the blast-lamp a known weight of sodium tungstate, $Na_2WO_4 \cdot 2\,H_2O$, adding an equal weight of previously ignited tungsten trioxide, WO_3, heating to the clear fusion, cooling, and grinding in a mortar.

half the weight of the paratungstate is tungsten trioxide (equivalent weight, 232) and this should be capable of expelling carbon dioxide (molecular weight, 44) to the amount of a fifth of its own weight. The weight of paratungstate employed in the analytical determination should, therefore, be somewhat in excess of ten times the weight of carbon dioxide to be expelled.

Experimental Process: Carbon Dioxide in Calcite. — Put in a weighed crucible (platinum or porcelain) about 0.5 grm. of powdered calcite. Heat the crucible and contents for five minutes well above the Bunsen flame turned low. Cool and weigh. Take the difference between the weight of the crucible alone and the crucible with contents after drying as the weight of the dried calcite. Now add about 2.5 grm. of previously dried sodium paratungstate, $Na_{10}W_{12}O_{41}$. Stir carefully with a platinum wire taking care to avoid mechanical loss, and weigh again. Heat the crucible over a Bunsen flame, first at very low heat and then to fusion of the mixture for five minutes. Cool in a desiccator and weigh. Repeat the ignition to constancy of weight, which, however, is usually obtained in the first fusion. Note the weight of carbon dioxide lost from the dry calcite, calculate the percentage loss, and compare the results obtained with those which should have been obtained if the material were pure and the process perfect. State the results in the form given on p. 39.

FIG. 11.

Determination of Carbon Dioxide Evolved by the Action of an Acid upon Carbonates. — The carbon dioxide of a carbonate may be liberated by the action of a suitable acid, and in absence of other volatile substances it may be determined by the loss in weight of a suitably designed apparatus.

Various forms of apparatus, some of them very elaborate, have been devised to determine, by loss of weight, carbon dioxide and other volatile products of reaction. A convenient and effective device for such purposes is the Kreider apparatus, made very simply from three test-tubes, modified and fitted as shown in the accompanying figure. The test-tube *A* serves as the reaction chamber; *B*, the drying chamber, is perforated with a hole about 1 cm. in diameter and fits tightly within *A*; and the reagent chamber *C*, so selected that it fits loosely within *B*, is drawn out to a small capillary tube. To *C* is fitted a one-holed stopper, through which passes a short glass tube which is provided with a rubber cap and plug or with a stop-cock. Upon removing the plug or opening the stop-cock and applying suction to the short tube, the reagent employed to liberate the volatile product may be drawn up through this capillary until *C* is sufficiently filled with acid and the lower end of the capillary with air.

When the apparatus is to be used, the capillary of *C*, which has been fitted as described, is pushed through the hole of *B*, packed loosely with cotton; *B* is filled to the depth of from 6 cm. to 8 cm. (about two-thirds of its contents), with granular calcium chloride; and *B* and *C* are adjusted as shown. The substance to be analyzed is weighed and put in *A*. The reagent to be employed (10 cm.^{3} to 15 cm.^{3}) is drawn into *C*, and held there in the manner described above. The test-tube *A* is slipped over *B*, and a ring of paraffin is melted into the mouth of *A*, about *B*, by means of a hot iron or wire, to seal the joint securely. The apparatus is wiped, hung in the balance, and, after a suitable interval, weighed. A very convenient way to attach the paraffin is to melt it between *A* and another tube, which fits *A* just as *B* does, and which may be removed by a turning motion, leaving the ring into which *B* will fit. Very little heating is then required to make a tight joint. If care be used in taking apart *A* and *B*, at the close of an experiment, such a ring of paraffin remains in place and may be used many times without replacement, being remelted by a touch of the hot wire before every new experiment.

Experimental Process: Carbon Dioxide in Calcite. — Weigh out exactly upon a balanced watch-glass about 0.5 grm. of powdered calcite. Place in the mouth of the upright reaction chamber *A* of the Kreider apparatus, just described, a funnel having the stem cut off close to the cone. Transfer nearly all of the weighed calcite to the funnel by inclining the watch-glass and tapping it on the edge with the quill of a camel's-hair brush and complete the transfer by touching the glass lightly with the tip of the brush, taking care to remove to the funnel any adherent particles of the powder by bringing the brush lightly upon the edge of the watch-glass.

Fill the reagent chamber *C*, in the manner described, with 10 cm.^{3} to 15 cm.^{3} of dilute hydrochloric acid (1 : 3). Put the apparatus together, sealing the paraffin joint, and hang it upon the balance. Weigh after an interval of twenty minutes.

Remove the cap from the small tube in the stopper of the reagent chamber *C* or open the stop-cock and allow the acid to run from *C* into *A*. The carbon dioxide liberated is forced upward through the drying chamber *B* and escapes through the annular space between *B* and *C*. When the visible action has ceased, force a gentle current of air, dried by passing it through calcium chloride, through *C* to remove the carbon dioxide from the apparatus. Replace the cap, hang the apparatus on the balance, and weigh after twenty minutes. The loss of weight represents the carbon dioxide.

Calculate the weight of carbon dioxide in the weight of calcite taken, and the percentage of carbon dioxide, and compare the results with those which should be obtained upon the theory that the calcite is pure and the analytical process free from error. State the details of the analysis in the following form:

Weight of calcite taken.	Loss in weight of apparatus.	Theory for loss of CO_2.		Error.	
Grm.	Grm.	Grm.	Per cent.	Grm.	Per cent.

Determination of Carbon Dioxide by Direct Weighing. — Carbon dioxide evolved from carbonates by heating either with or without a flux, or liberated by the action of an acid, may be dried by passing it through some drying material which is incapable of retaining it and may then be absorbed in some suitable retainer like potassium hydroxide or soda-lime. Usually when carbon dioxide is to be weighed directly it is evolved by the action of an acid.

A convenient apparatus for the evolution of carbon dioxide from carbonates by the action of an acid and the absorption of that gas in a suitable retainer for weighing is shown in Fig. 12.* This apparatus consists of an evolution flask, a cooler to return condensed steam to the flask, a U-tube *A* filled with calcium chloride, a double U-tube *B* charged in the central section with anhydrous copper sulphate (to intercept traces of hydrochloric acid which may escape previous condensation) with calcium chloride to dry the gas, two absorption tubes *C* and *D* filled with soda-lime (followed by calcium chloride) to retain the carbonic acid, and gas observation bulbs *E* filled with sulphuric acid to show the rate of gas flow. Through the rubber stopper of the flask is passed the tube of a separating funnel, the end of the condensing tube, and a tube (which connects the interior of the flask

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* Hillebrand: Bulletin 422 of the U. S. Geological Survey, p. 179.

with the system of bottles and the purifying tower) to supply under slight pressure, air free from carbon dioxide.

In carrying out the determination of carbon dioxide, the powdered carbonate is introduced into the flask and covered with hot, boiled water. A current of air, freed from carbon dioxide by passing through the purifier charged with soda-lime, is forced through that part of the system which precedes the weighed absorption bulbs and tube, to displace the unpurified air. The stop-cock in the separating funnel is closed and the funnel is charged with hydrochloric acid (1 : 1). The connection is made between the weighed absorption apparatus and the rest of the system. The liquid in the flask is brought to the boiling point and the acid is allowed to flow into the flask and purified air is sent slowly through the boiling liquid into which the end of the aspirating tube and the end of the funnel tube dip. At the end of half an hour the burner is removed from under the flask and the apparatus is permitted to cool for another half hour in the current of purified air. The difference between the

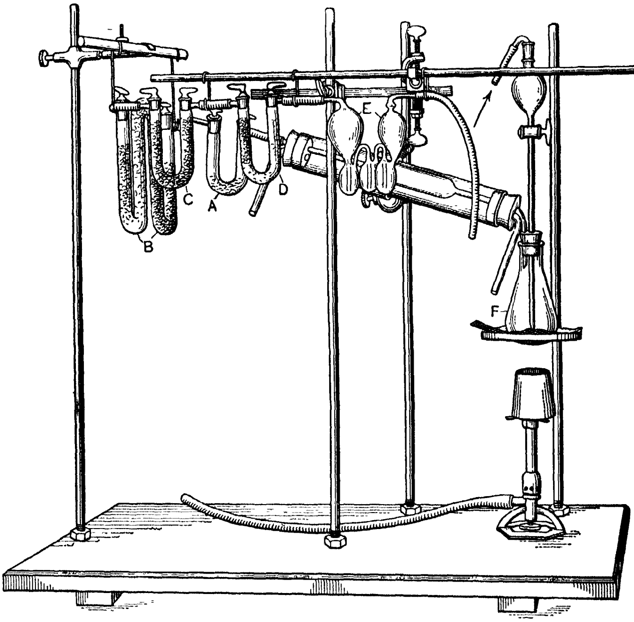

FIG. 12.

weights of the potash bulbs, and the accompanying drying tube before and after the operation is the weight of carbon dioxide absorbed.

Determination of Carbon as Carbon Dioxide and Hydrogen as Water: by the Combustion Process. — Organic compounds containing carbon and hydrogen may be decomposed by ignition with copper oxide in oxygen. The hydrogen forms water which is absorbed by granulated calcium chloride. The carbon forms carbon dioxide which passes through the calcium chloride (free from oxide) and is absorbed by an alkali hydroxide. In estimating the carbon dioxide formed in the process of combustion the apparatus is arranged so that combustion shall be complete, the water taken up by weighed calcium chloride, and the residual carbon dioxide passed on to an absorption tube containing a weighed amount of potassium hydroxide.*

The Determination of Boric Acid

Free boric acid reacts with an excess of methyl alcohol to form methyl orthoborate which boils at 65 degrees.

$$3\,CH_3OH + H_3O_3B \rightleftarrows (CH_3)O_3B + 3\,H_2O.$$

When methyl borate meets calcium hydroxide moistened with water calcium borate is formed and methyl alcohol is set free.

$$\begin{aligned} n\,CaO_2H_2 + 2\,(CH_3)_3O_3B + 2\,H_2O &= CaO_2(BO)_2 \\ &+ 6\,CH_3OH + (n-1)CaO_2H_2. \end{aligned}$$

Similarly when methyl borate and sodium tungstate react in solution a sodium borate and methyl alcohol result in the sense of the following representative equation:

$$\begin{aligned} n\,Na_2WO_4 + 2\,(CH_3)_3O_3B + 3\,H_2O &= 2\,NaOBO \\ &+ 6\,CH_3OH + (n-1)Na_2WO_4 + WO_3.\dagger \end{aligned}$$

Upon treating boric acid or borates of the alkali elements with absolute methyl alcohol (free from acetone) and acetic acid the

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* For a description of apparatus and procedures in the determination of carbon, hydrogen, and nitrogen by the combustion process, see Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, pp. 414 to 426.

† In combination.

volatile methyl borate is formed which upon treatment with calcium hydroxide formed from a weighed amount of calcium oxide, or with a known weight of sodium tungstate, is decomposed with the elimination of alcohol and the formation of a residue, the weight of which after ignition differs from that of the original calcium oxide, or sodium tungstate, by the amount of the weight of boron trioxide absorbed. These reactions have been made the basis of analytical processes for the determination of boron trioxide in boric acid or borates.*

The Apparatus. — The distillation apparatus, which is shown in the accompanying cut, Fig. 13, consists essentially of a retort, condenser, and a paraffin bath for heating. The condenser is set vertically, to facilitate changing the level of the retort within the bath, and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made from a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former is fitted or sealed a glass funnel-tube provided with a stop-cock. The end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. A small Erlenmeyer flask which is joined to the condenser, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air, receives the distillate. In carrying

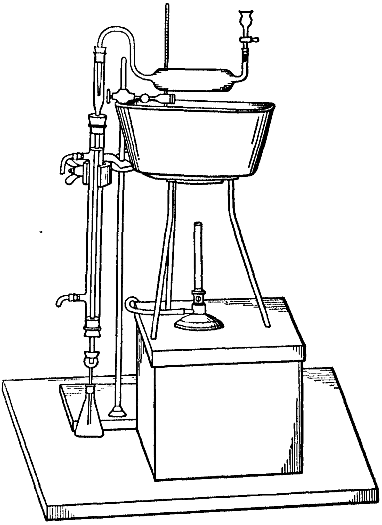

FIG. 13.

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* Rosenbladt: Zeit. Anal. Chem., **27,** 18.
Gooch: Proc. Am. Acad., **22,** 167 (1886); Am. Chem. Jour., **9,** 23 (1887).
Gooch and Jones: Am. Jour. Sci., [4], **7,** 34.

out a distillation, the liquid to be distilled is introduced into the retort by the funnel-tube, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffin, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200-cm.^{3} pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 cm.^{3} of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0.7 cm. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils, — something between 130° and 140° does very well for water, and is not too high for methyl alcohol, — and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0.2 grm. of boric anhydride completely to the distillate, six charges of methyl alcohol of 10 cm.^{3} should be ample.

In treating borates soluble in water, the solution, made barely acid to litmus (added to the solution) by means of hydrochloric acid, then just alkaline by sodium hydroxide, and again faintly acid by acetic acid, is put in the retort through the funnel tube which is washed down by two or three cubic centimeters of water used in three portions, successively.

Use of Calcium Oxide as the Retainer. — When calcium oxide is to be used to retain the boric acid in the distillate it is first ignited in the crucible in which the evaporation of the distillate is to be made subsequently, and then transferred to the receiving flask which is attached to the condenser. To prevent the caking of the lime by the action of the alcohol, it is slaked with a little water before the distillation.

The retort is connected with the condenser and submerged in the paraffin at a temperature not exceeding 140 degrees. When all of the liquid has passed to the distillate the retort is raised from the bath, allowed to cool, and the dry residue is drenched with 10 cm.^{3} of methyl alcohol (free from acetone), the retort is again submerged in the paraffin, and the methyl alcohol is distilled to the receiver. After three such treatments with methyl alcohol, the residue in the retort is moistened with a very little water (2 cm.^{3}) and the blue color of the litmus (due to the hydrolytic decomposition of the acetate present) is changed to red by the addition of a drop or two of acetic acid. Thereafter the treatment with methyl alcohol, applied in 10-cm.^{3} portions, is repeated three times, and the receiver is then detached from the condenser, stoppered, shaken thoroughly, and allowed to stand fifteen minutes. The contents of the receiver are poured and washed out as completely as may be into a large platinum dish and the alcoholic liquid is slowly evaporated to dryness at a temperature below that at which it will boil. The residue is transferred by means of a little water to the crucible in which the calcium oxide was originally ignited. Any material adhering to the walls of the receiver and of the dish is dissolved in a very few drops of dilute nitric acid and added to the contents of the crucible which are evaporated to dryness on the water-bath, ignited, gently at first and finally to constant weight.

Use of Sodium Tungstate as the Retainer. — Sodium tungstate, fused with a slight excess of tungstic acid over that contained in the normal tungstate (to insure its freedom from carbonate), may be used with good results as an absorbent for boric acid. This substance is definite in weight, not hygroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition.

In this procedure use is made of the apparatus described above and shown in Fig. 13, modified in the single point that the Erlenmeyer flask used as a receiver is fitted tightly to the condenser and provided with a water trap. Special care should be taken to give the tungstate ample time for contact with the distillate before exposing the latter to atmospheric evaporation. The distillate is received, therefore, in a dilute solution of sodium tungstate which is placed in the receiver, cooled by ice, and trapped with water. The mixture is well stirred, allowed to stand half an hour after the distillation is complete, evaporated to small volume in a large dish, and transferred to the crucible in which the tungstate was originally weighed. After thorough drying the residue is ignited to fusion and weighed. When acetic acid is employed in the retort, care must be taken in the ignition to expose the fused mass freely to the air (by causing it to flow upon the sides of the crucible) until the color of the cooled tungstate is white, in order that the reducing effect of the acetate may be eliminated.

In determining boron trioxide in insoluble substances, such as silicates, the material is fused with four times its weight of sodium carbonate and the melt is extracted with water. The solution is evaporated to small volume, hydrochloric acid is added to faint acidity, a drop or two of a solution of sodium hydroxide to alkalinity, and acetic acid to acid reaction to litmus. The solution thus prepared may be introduced into the retort and treated in the manner described above for the determination of boron trioxide in soluble borates.

The Determination of the Fixed Product of Action of a Volatile Reagent

The determination of the fixed product of the action of a volatile reagent upon a substance may be the object of analysis, and it is frequently desirable to make use of a reagent, by itself volatile, which will enter into definite reaction with the substance to form a definite and weighable product.

Determination of Magnesium and Manganese as Anhydrous Sulphates. — Examples of such processes are the determination of magnesium and the determination of manganese, each in the form of the anhydrous sulphate derived by the action of sulphuric acid in excess upon salts of these elements, the excess of the sulphuric acid, as well as the volatile product liberated in the action, being expelled.

Experimental Process: Conversion of Magnesium Chloride to Magnesium Sulphate. — Draw from a burette into a roomy crucible a definite volume (50 cm.^{3}) of a solution of magnesium chloride (about N/10 in respect to the anhydrous salt), add sulphuric acid (about 1 cm.^{3} of the concentrated acid, or its equivalent), evaporate the solution on the water-bath, suspend the crucible in another crucible (to be used as a radiator) with the walls about 1 cm. apart, heat the outer crucible with gradually rising temperature until the free sulphuric acid has been removed and then to incipient redness, and weigh the residue as magnesium sulphate, $MgSO_4$.

Calculate and state the magnesium content per cm.^{3} of the solution.

Volume of solution taken.	Weight of $MgSO_4$ found.	Weight of magnesium calculated.	Magnesium content per cm.^{3}
Cm.^{3}	Grm.	Grm.	Grm.

Experimental Process: Determination of Manganese in the Hydrous Sulphate. — Weigh out exactly in a crucible about 1 grm. of hydrous manganous sulphate ($MnSO_4 \cdot nH_2O$). Place the crucible upon a triangle within a larger porcelain crucible in such manner that the walls of the inner crucible shall be distant from that of the outer crucible by about 1 cm. Heat the outer crucible gradually until the bottom is at red heat. Continue the heating (at a temperature of 400 to 450 degrees) weighing at intervals, until the weight is constant. State the results in the form given below, finding by calculation the numerical symbol which best represents the indefinite symbol $MnSO_4 \cdot nH_2O$.

Weight of $MnSO_4 \cdot nH_2O$ taken.	Weight of $MnSO_4$ found.	Weight of H_2O in $MnSO_4 \cdot nH_2O$ found.	Numerical symbol of $MnSO_4 \cdot nH_2O$.
Grm.	Grm.	Grm.	

ELECTROLYTIC PROCESSES

Many valuable methods of electro-analysis, chiefly determinations of the metals, are based upon the decomposition of electrolytes in solution. Solutions of such substances carry the electric current and the dissolved electrolytes are decomposed at the electrodes, with the separation of an *anion* at the anode (positive pole) and a cation at the cathode (negative pole). The current necessary for the *electrolysis* may be derived from primary cells, storage cells, or the electric-lighting circuit, as may be convenient.

The Conditions of Electrolysis

According to the prevailing theory of electrolysis, all the ions of a solution, of whatever nature, are acted upon by the electric force and all carry the current by moving through the solution. If more than one kind of ion of the same sign is present that kind which has the lower decomposition voltage is first deposited at the corresponding electrode.

In the decomposition of a metallic salt in a water solution from which the metal can be deposited by action of the current, the metal ion is deposited at the cathode, while the acid ion is liberated at the anode. If the concentration of the electrolyte near the cathode falls to a point at which the solution is deficient in metal ions to deliver the current to the cathode, hydrogen ions of the water or acid may be discharged simultaneously with the metal and the continuity of the metallic deposit affected. In order that smooth and adherent deposits may be obtained it is generally necessary to regulate the rate of deposition of the metal by keeping the current within defined limits of surface-density — that is, within certain limits which may be expressed in terms of amperes per 100 cm.^{2} of electrode surface, or *normal density* (ND_{100}).

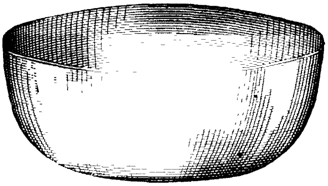
$$ND_{100} = \frac{amperes \times 100}{cm.^2 \ of \ electrode \ surface}.$$

With stationary electrodes the surface density must be low and the deposition of the metal consequently slow, in order that the deposits may be smooth and adherent.

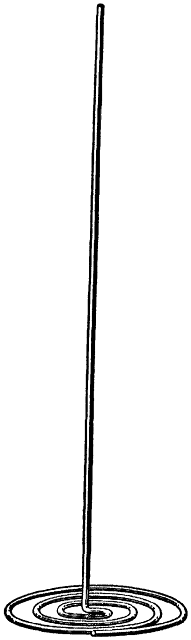
In certain electrolytic processes which involve separations of cations from one another, or anions from one another, careful attention must also be given to the current pressure (voltage), since, at normal concentrations, every electrolyte has a definite *decomposition pressure.*

Stationary Electrodes. — A platinum dish of 200 cm.^{3} capacity is very serviceable, both as the container and as the electrode to receive the deposit, in processes conducted with stationary electrodes; and for the second electrode, generally the anode, a stiff platinum wire bent at one end to a flat spiral is convenient (Fig. 14*ab*). Many forms of cathodes and anodes have been described for special purposes, or as possessing special advantages for general purposes. Electrodes of platinum gauze possess the advantage of being permeable to the solution and of receiving the deposit on the entire surface of each separate wire, so that the electrode surface is very large in comparison with that of a dish electrode or foil electrode of similar weight.

Experimental Process: Copper in Copper Sulphate.— Dissolve in 100 cm.^{3} of water, in a platinum dish, about 0.5 grm. of copper sulphate, $CuSO_4 \cdot 5\,H_2O$, weighed exactly, and add 5 cm.^{3} of concentrated nitric acid. Set the dish, which is to be used as the cathode, upon a metal triangle connected with the negative pole of a storage battery. Connect the platinum anode (e.g., the spiral of Fig. 14*b*) with the positive pole of the battery and immerse it in the solution. Cover the dish with a split watch-glass. The battery should be arranged to deliver the current at a potential of 2 volts at the electrodes. Under the conditions described, the electrolysis may be completed in the cold over night, or in a few hours if the solution is kept at 70 to 80 degrees by means of a heated disk of wire gauze or asbestos placed about a centimeter below the dish. Determine the end of the decomposition by diluting the solution slightly with water and noting whether copper is deposited in the course of ten minutes upon the newly covered cathode surface. To avoid the action of the strong free acid upon the deposited copper, either siphon off the liquid while introducing distilled water, until the current ceases, or else add a solution of ammonium acetate, made by neutralizing with acetic acid at least as much ammonia as is equivalent to the nitric acid taken and the sulphuric acid set free. Remove the dish, wash the deposit with water and then rinse with alcohol. Dry the dish, with the deposit, by heating it in an air-bath at a temperature below 100 degrees, or by passing it back and forth over and well above a



a



b

Fig. 14.

flame until the film of moisture vanishes. Cool in a desiccator and weigh.

Compare the amount of copper found with that which should be present theoretically in the amount of copper sulphate taken. State the results in the following form:

Copper sulphate taken.	Copper found.	Theory for copper in copper sulphate.		Error.	
Grm.	Grm.	Grm.	Per cent.	Grm.	Per cent.

The Rotating Electrode. — If the liquid be stirred by rotation of either electrode (or otherwise) the available range of current density may be much increased.

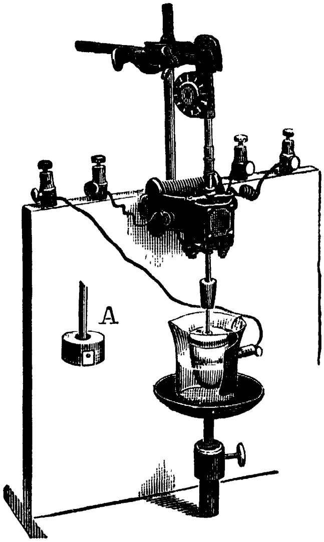


Fig. 15.

Satisfactory and very rapid depositions of metals may be made without the use of special or expensive electrodes by utilizing the common platinum crucible as a rotating cathode. An ordinary (20-cm.^{3}) platinum crucible may be rotated at a speed as high as 800 revolutions per minute by means of a small, inexpensive electric motor fastened so that its shaft is vertical (Fig. 15). Upon this shaft the crucible is fixed by pressing it over a rubber stopper bored centrally and fitted tightly on the end of the shaft (Fig. 15A). To secure electrical connection between crucible and shaft, a narrow strip of sheet platinum is soldered to the shaft and then bent upward along the sides of the stopper, thus putting the shaft in contact with the inside of the crucible when the latter is pressed over the stopper. As a matter of convenience in removing the crucible, the shaft is made in two parts which are joined, with care to make a good contact between the two pieces of shafting, by a rubber connector of sufficient thickness to prevent the crucible from wabbling when rotated.

The solution to be electrolyzed is placed in a beaker upon a small adjustable stand, so that the crucible may be dipped into the liquid to any desired depth. A platinum plate is employed as an anode and connected to the positive pole of a series of storage batteries, while the negative pole of the series is connected to the bearing in which the shaft rotates, thus allowing the current to go from the platinum plate through the solution to the crucible, up the shaft of the motor, and back to the batteries. The power to run the motor may be conveniently taken from the incandescent light circuit.

Experimental Process: Copper and Nickel. — Dissolve a weighed nickel five-cent piece in a mixture of 10 cm.^{3} of sulphuric acid, 10 cm.^{3} of nitric acid, and 30 cm.^{3} of water. Evaporate on the water-bath or steam-bath to remove all nitric acid. Dissolve the residue and evaporate again until the escaping vapor contains no nitric acid as shown by testing with litmus paper. Transfer the solution to a 500-cm.^{3} flask and fill to the mark with water, mixing carefully. Draw off 50 cm.^{3} of the solution into a 150-cm.^{3} beaker, add three grams of ammonium sulphate, dilute to about 100 cm.^{3}, in readiness to electrolyze with the crucible used as a rotating cathode. To make the electrolysis attach to the shaft of the motor a weighed platinum crucible, to be used as the cathode, in the manner described on p. 52 and shown in Fig. 15. Adjust the levels so that about two-thirds of the crucible shall be immersed in the liquid, exposing a cathode surface of about 30 cm.^{2}. Introduce the anode, run the motor rapidly (at the rate of about 600 revolutions per minute). Connect the crucible with the negative pole of the battery and the anode with the positive pole. Electrolyze the solution with a current of about 1.5 amp. to 3 amp. (corresponding to about ND_{100} = 5 amp. or 10 amp.). When the deposition is nearly complete stop the rotation; wash down the sides of the beaker, the anode, and the crucible, with a fine jet of water; again start the motor, and note whether copper is deposited on the newly covered cathode surface. If the deposition is complete, stop the motor, remove the crucible from the liquid, and wash it with water, saving carefully the solution and the washings. Then wash the deposit with alcohol, hang the crucible over the end of a nearly vertical glass rod and dry the deposit well above a flame. Cool and weigh. Calculate the percentage of copper in the coin.

Evaporate the solution and washings to a volume of about 20 cm.^{3}, neutralize the solution with ammonium hydroxide, add 30 cm.^{3} of concentrated ammonium hydroxide, filter if necessary and electrolyze the solution with a current of 1.5 amp. to 3 amp. (corresponding to about ND_{100} = 5 amp., or 10 amp.), depositing the nickel upon the crucible used as the cathode and rotated at the rate of about 600 revolutions per minute. When the deposition is completed, stop the motor, remove the crucible from the liquid, wash with water and with alcohol, dry carefully well above a flame, cool, and weigh. Remove the nickel from the crucible by heating, for at least fifteen minutes, in nitric acid (1 : 1). State the results in the following form.

Weight of coin.	Copper found.		Nickel found.	
Grm.	Grm.	Per cent.	Grm.	Per cent.

Small Electrodes with Weighable Cell. — Very small electrodes may be used in electrolytic analysis, even with high currents, provided means be taken to retain and gather that portion of the deposit which under such conditions is generally detached from the electrode. The device shown in Fig. 16 is designed to accomplish this purpose.* It consists of a 35-cm.^{3} cell *C* made from a thistle-tube. The anode *a* is a small piece of thin platinum foil, about a centimeter square, welded to a platinum wire *w′* which is sealed into the thistle, as shown. The cathode *c* consists of a disk of gauze or foil, about a centimeter in diameter, carried by a rod of lead glass which is fused into the meshes of the gauze or into a central hole in the foil, an arrangement which gives great rigidity without the use of much platinum. The electrical connection between the disk cathode and the shaft which carries the current is made by a platinum wire *w*. A stand *s* of spring brass holds the cell during the process of electrolysis, and a similar lighter stand (best made of sheet aluminium) serves to support the cell and contents upon the balance pan. In order to show details clearly, the cell is represented in the figure as resting lightly upon this frame. In actual use, the cell is pushed downward as far as possible, and is held rigidly.

In using this apparatus, the cathode cell is washed, dried,

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* Gooch and Burdick: Am. Jour. Sci., **34**, 107 (1912).

and weighed. The material for analysis, dissolved in about 15 cm.^{3} of liquid, is placed in the cell. To prevent possible loss of liquid by spattering, a collar (conical) cut from a funnel or (concave) made from a perforated and split watch-glass, is set upon the rim of the thistle. The glass rod of the cathode is fixed to the motor shaft. The electrical connections are made as shown. The cathode is rotated at about 300 revolutions per minute.

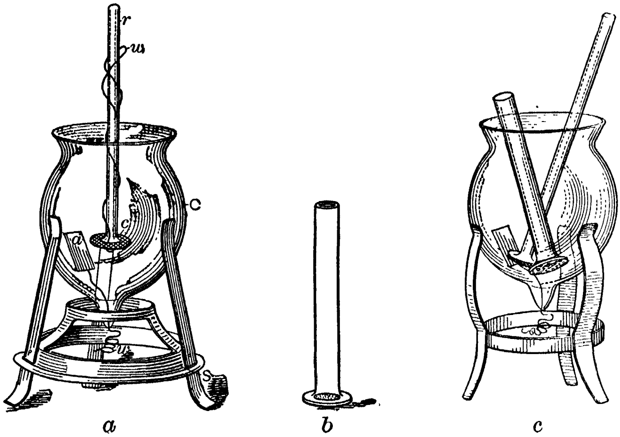

FIG. 16.

At the end of the electrolysis the cathode is disconnected from the shaft and washed in the cell. Loose particles of the deposit may be allowed to settle, the supernatant liquid decanted, and after washing by decantation with water, and finally with alcohol, the cell and cathode may be dried in the air-bath, and weighed. The difficulty of washing thoroughly by decantation without loss of any loose particles, and with complete removal of the washing liquid so that the drying process need not be prolonged unduly, is, however, considerable. To meet this difficulty use is made of the little filter tube shown in Fig. 16*b*. This is made by fusing the end of a lead glass tube, flared slightly, to a little disk of platinum foil perforated by a sharp point, the rough edges of the perforations being turned outward. By applying the suction of the filter pump to the open end of the tube, and dipping the disk end into an emulsion of asbestos, a felt of asbestos is deposited upon the perforated disk. The tube and felt may be dried, and even ignited, without difficulty.

This little reverse filter is dried and weighed with the cell and cathode ready for use. The electrolysis is made in the manner previously described. The liquid of the cell and the washings of the cathode and cell are drawn off through the reverse filter. The stand, cell, cathode, and reverse filter, shown in Fig. 16*c*, are dried and weighed together.

In experimental determinations made with this apparatus it has been found that as much as 2 amp. of current may be applied successfully to 2 $cm.^2$ of cathode surface, an amount of current which corresponds to a normal density of 100 amperes (ND_{100} = 100 amp.). Moreover, fair results may be obtained without rotation of the cathode, but in this case the deposit is more bulky, rather slow in drying, and perhaps more sensitive to oxidation.

PROCESSES DEPENDENT UPON DIFFERENCES IN RESPECT TO SOLUBILITY

Processes of analysis frequently depend upon differences in solubility of a substance in respect to different liquid solvents, and upon differences between different substances in respect to solubility in the same liquid solvent.

The Distribution of a Solute between Two Non-Miscible Solvents. — *A dissolved substance may sometimes be withdrawn from solution by agitation of the solution with a more efficient solvent which is not miscible with the former solvent.* The common mode of identifying iodine in dilute aqueous solution by concentrating it in chloroform or carbon disulphide shaken up with the solution is a case in point. In applying such processes of extraction quantitatively it is well to bear in mind that, in accordance with the general principle which governs the division of a solute between two non-miscible solvents, the efficiency of the operation increases rapidly with the number of successive shakings with fresh portions of the more efficient solvent.

When an amount of solute (x_0), in the known volume (V) of the water solution, is shaken (in a separating funnel) with a known volume (v) of the non-miscible absorbent, the relations of concentration of the solute in water x_1 and that of the solute in the absorbent $(x_0 - x_1)$ are given by the expressions $\frac{x_1}{V}$ and $\frac{x_0 - x_1}{v}$ respectively. If the ratio of the concentration of the solute in a cubic centimeter of water to its concentration in a cubic centimeter of the absorbent — always a constant ratio — be represented by the distribution coefficient k, then

$$\frac{x_1}{V} = \frac{x_0 - x_1}{v}\,k, \quad \text{and} \quad x_1 = x_0\left(\frac{kV}{v + kV}\right).$$

The amount of the solute (x_2) which remains in the water solution (V) after shaking it with another similar portion of the absorbent (v) will be given by the equation

$$x_2 = x_0\left(\frac{kV}{v + kV}\right)^2,$$

and for n shakings with similar portions of the absorbent the expression becomes

$$x_n = x_0\left(\frac{kV}{v + kV}\right)^n.$$

Theoretically, the absorption of the solute by the more efficient solvent must be always approximate; but, practically, it is often possible to arrange the conditions so that the amount of solute which escapes absorption will be insignificant.

The extraction of iodine from a water solution by shaking with carbon disulphide * (or chloroform) and the separation of iron and molybdenum from nickel, vanadium, and chromium by the ether extraction of the aqueous solution of the chlorides † illustrate the application of this principle.

Precipitates and Conditions Affecting Precipitation

The exactness of processes dependent upon differences between substances in respect to solubility is determined by the attainment of conditions conducive to the highest degree of insolubility, purity, and definiteness of precipitates. With these conditions assured to a reasonable degree, *the practical separation of the precipitate from the medium in which it is formed also requires consideration.*

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* See p. 185.

† Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 313.

Conditions Affecting the Insolubility of Precipitates.—As has been previously shown * the velocity (if measurable) with which a non-reversible reaction is completed and the degree to which a reversible reaction approaches completion depend upon the adjustment of the concentrations of the reagents which enter into action. In precipitation processes it is important, therefore, to give due attention to the concentrations of the reagents, but other conditions affecting the insolubility of the precipitates must likewise be taken into account, such as the amount and nature of the medium from which the precipitate separates and the state of subdivision in which it exists in the medium.

The Nature of the Medium. — Media in which precipitation may take place may differ in respect to the solvent-effects which they are able to exert upon the precipitate. The insolubility of a precipitate may sometimes be increased advantageously by adding to the medium in which precipitation is effected some miscible liquid in which the precipitate is more insoluble than it is in the original medium. For example, the precipitation of substances which are more insoluble in alcohol than in water may be made more complete by adding alcohol to the water solution. For this reason, potassium fluosilicate and calcium sulphate being more insoluble in the alcoholic mixture than in pure water, it is customary to mix alcohol with the water solution of potassium chloride from which potassium fluosilicate is to be precipitated by fluosilicic acid and with solutions of calcium chloride from which calcium sulphate is to be precipitated by sulphuric acid. In such cases the volume of the alcoholic liquid must not be made too great, because the precipitates are not absolutely insoluble even in that medium and the concentration of the alcohol should not be great enough to induce the precipitation of substances which should remain in solution.

The State of Subdivision. — A very finely divided crystalline substance tends to exhibit greater solubility than does the same substance when it exists in coarser particles under other-

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* See p. 5.

wise similar conditions. For example, it is known that calcium sulphate has a definite solubility of 2.085 grm. in 1 liter of water at 25 degrees (approximately, 1 : 480), provided the saturated solution is in contact with particles of diameter greater than 0.002 mm., while the same substance in particles averaging 0.0003 mm. (and not less than 0.0002 mm. in diameter) goes into solution to the extent of 2.476 grm. to 1 liter (approximately 1 : 400) at 25 degrees. Similarly, barium sulphate dissolves in the proportion of 0.00229 grm. to 1 liter of water (1 : 400,000) when the diameter of the particles approximates 0.018 mm. and in the proportion of 0.00415 grm. to 1 liter (1 : 250,000) when the diameter of the particles is less than 0.00001 mm. If larger particles of a substance are placed in the solution saturated in contact with finer particles, the equilibrium between the solid and the solution is disturbed and the substance in solution is deposited upon the larger grains, while the smaller grains dissolve to keep up the saturation corresponding to the solubility of the finer particles until they finally disappear. Thus, very minutely crystalline precipitates tend to become more coarsely crystalline upon long digestion in the solutions from which they separate, the solubility diminishing at the same time. A substance formed in solution in a state of subdivision corresponding to a certain degree of solubility may, however, remain dissolved to a degree which would correspond to supersaturation with respect to the same substance in coarser and more insoluble state of subdivision until a change of condition, such as change of temperature or surface evaporation on standing, causes the incipient formation of larger particles, which once started, will proceed until an equilibrium is established between the substance in solution and the substance in larger particles. Such is probably the state of affairs when precipitates, like calcium sulphate, or even the ordinarily very insoluble barium sulphate, are deposited tardily from dilute solutions. The variation of solubility with the degree of subdivision of crystalline substances, with the consequent growth of larger particles at the expense of smaller ones, appears to be a result of struggle toward equilibrium between the forces of cohesion and tension acting at the surface of contact between the solid and the liquid.

Colloidal Suspensions. — In colloidal suspension, certain substances, like the acidic hydroxides of silicon, titanium, and tungsten, or the basic hydroxides of iron, aluminium, and chromium, or the sulphides of arsenic and tin, appear to consist of particles in a much finer state of subdivision than that of the finest crystalline precipitates. While the diameters of the finest crystalline particles are of the order of thousandths of a millimeter, those of the colloidal suspensions — invisible with the ordinary arrangement of the microscope and only visible when, like motes in a sunbeam, they are observed by the microscope placed perpendicular to a strong beam of light illuminating them — appear to possess diameters of the order of millionths of a millimeter. It seems probable that, like variations in the solubility of crystalline salts with degree of subdivision, the peculiar properties of colloidal substances have relation to fineness of subdivision, or to extent of contact surface in comparison with mass.

In presence of electrolytes, some colloidal substances may appear as coagulated hydrogels, while in water sufficiently devoid of such coagulating agents they may take the form of hydrosols in suspension or pseudosolution. The proportion of the electrolyte required to produce coagulation may be exceedingly small but it must exceed a certain limit, and free acids and salts of polyvalent elements (easily susceptible to hydrolytic action) are most effective, the coagulating power of these electrolytes at similar concentration increasing very markedly with the valence of the cation. In the process of coagulation, however, the precipitate takes up contaminating material derived from the coagulant, and in analytical operations it is therefore usual to employ volatile acids or ammonium salts of volatile acids as coagulants, in order that the contamination of the colloidal precipitates may be subsequently removed by volatilization. When, however, fixed contaminating material has been introduced into a colloidal precipitate it may be replaced, more or less completely, by the action of another salt, and may often be removed from the colloidal precipitate by digestion and washing with ammonium salts.

In analytical practice it is not uncommon to note that a colloidal precipitate which is insoluble in the presence of suitable coagulating agents will when washed with pure water pass through the filter in clear solution or in turbid pseudosolution; and that from such pseudosolutions or suspensions the hydrogel is again precipitated by the action of the coagulating agents in the filtrate.

It is to be noted also that the colloidal nature of a precipitate may often be modified by evaporating the suspending liquid and drying the residue (e.g., silica), and in some cases by simply digesting the precipitate (e.g., alumina) in the heated liquid.

Purity of Precipitates. — All precipitates tend, more or less according to their nature, to carry down with them other substances from the solution. This tendency is least in the case of coarsely granular substances, greater on the part of minutely granular substances, and greatest in the case of colloidal precipitates. Whenever it is a possibility, processes should be employed which produce precipitates of crystalline habit and care should be taken to secure a proper coarseness of grain by the choice of suitable conditions as regards the medium, the concentrations of reagents, the temperature, and, if necessary, suitable digestion. When colloidal precipitates are necessarily put to use in analytical processes they should be modified as much as may be by digestion at a suitable temperature or by drying and, if they are to be weighed, they should be washed, if possible, with suitable reagents which may later be volatilized, such as ammonium salts of volatile acids to replace adsorbed material. In some cases they must be redissolved and further purified by reprecipitating and finally washing with suitable reagents which, though adsorbed, may be later volatilized. In all processes in which the addition of the precipitant brings about immediate precipitation the precipitating reagent should be added slowly to diminish the chances of mechanical inclusion of foreign matter in the precipitate.

Definiteness in Composition of Precipitates. — Wholly apart from the effects of contamination by the adsorption of impurities taken from the solution, precipitates sometimes exhibit variations from an ideal chemical composition in consequence of secondary reactions with other substances than those concerned in the reaction upon which the analytical process is based or because changes in the concentrations of factors in the reaction make changes in the composition of products. For example, care must be taken in precipitating ammonium magnesium phosphate or ammonium manganese phosphate to control the excess of ammonium salt also present in order that the precipitate may have the ideal composition, and yield on ignition the ideal pyrophosphate.*

The Practical Separation of Precipitates. — *Filtering and Washing of Precipitates.* In separating precipitates by decantation of the liquid in which they are formed, or by filtration of the liquid through paper, asbestos, platinum sponge, or other suitable material, it is necessary to overcome the viscosity of the liquid and the attraction between the insoluble solid and the liquid. In this process, the residual or adherent solution must be removed from the precipitate by washing with another miscible liquid inactive toward the precipitate and separable from it by volatilization at a temperature which does not endanger its stability and definiteness.

Upon the presumption that the residual solution and the washing liquid mix homogeneously in every filtration or decantation, the washing is effective in proportion to the relation between the total volume (V) of the liquid before decanting or filtering and the residual volume (v) left after decanting or filtering. After a single washing, the material remaining is then a definite fraction $\frac{v}{V}$ of the material contained in the residual solution before the washing; and the effect of (n) successive similar washings will be given by the corresponding power of the fraction — viz., $\left(\frac{v}{V}\right)^n$. Thus, if the ratio of the residual liquid to the total liquid is uniformly $\frac{1}{2}$, a single wash-

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* See p. 81.

ing reduces the material in solution to $\frac{1}{2}$, two washings to $\frac{1}{4}$, and four washings to $\left(\frac{1}{2}\right)^4 = \frac{1}{16}$ of the original amount. When the total volume is ten times as large as the volume of the residual liquid, the same number of washings reduces the material to $\left(\frac{1}{10}\right)^4 = \frac{1}{10000}$ of the original amount.

It is advantageous to make the volume of the liquid decanted or drained from a filter large in comparison with the volume of the residual liquid; and similarly, it is best to drain off in the decantation or filtration as much liquid as possible before adding a new portion of the washing liquid. In practice, however, washing is not usually effected with the rapidity and thoroughness which might be indicated by a consideration of the amount and number of the portions of washing liquid used; for when porous solids include solutions homogeneous mixing of the solutions with an external washing liquid takes place only by the slow process of diffusion, and many precipitates show a very marked tendency to hold by *adsorption* matter which is dissolved in liquids in contact with them. The efficiency of the washing process is, therefore, best determined by chemical tests applied to the filtrate. In practical work the conditions of precipitation must be regulated intelligently for each individual case to insure insolubility or the nearest approach to insolubility, the highest degree of freedom from adsorbed or mechanically included foreign matter, and favorable conditions for washing.

Filtration by Paper. — The paper filter used in the separation of precipitates intended for weighing should be "ashless" — that is, of the (purchaseable) sort which has been washed with hydrochloric acid and with hydrofluoric acid, and which leaves on ignition a very small known weight or an inappreciable weight. The disk of paper is folded to a quadrant and opened to a cone of an angle a trifle larger than that of the funnel which it is to fit. The funnel should have an angle of 60 degrees and a long thin stem. The paper, held within the funnel by a finger, is filled with water, and patted into close contact with a glass, with special care to have the fitting perfect on the upper rim. Whenever it is possible, it is very desirable to settle the precipitate carefully and to decant upon the filter the clear supernatant liquid to the lowest possible limit; and it is frequently desirable to repeat the washing by dilution and decantation. The precipitate, transferred from the container to the filter (with care to leave margin of paper half a centimeter broad above the level of the liquid) by means of a fine jet of water directed from a wash-bottle, and with the aid of a rubber-tipped glass rod (the "policeman") to remove any of the precipitate which may adhere to the walls of the container, is washed down into the point of the filter with a rotary motion of the water jet. The washing should be continued until suitable tests show that the precipitate is not yielding foreign material to a fresh washing. The filter, with the precipitate, is usually dried, at least partially, and folded compactly, with the precipitate inside, in readiness to be ignited in a weighed crucible. Sometimes, after drying, the precipitate and paper are separated so far as is possible and ignited apart.

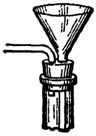
FIG. 17.

If the precipitate is not colloidal, and not susceptible to the compacting action of pressure, a vacuum flask or bell-jar, evacuated by a filter pump (Fig. 17), may be advantageously used to receive the filtrate; but in this case it is necessary to strengthen the point of the filter by placing between it and the funnel a cone of perforated platinum or of parchment paper, so that it will withstand the atmospheric pressure from above.

Filtration by Asbestos. — In many processes, such as those in which the precipitate is affected in ignition by the presence of carbonaceous matter or in which the precipitate must be dried rather than ignited, asbestos used in the filtering crucible * may be advantageously substituted for the paper filter. White, silky, flexible, anhydrous, asbestos fiber † is disintegrated, best by scraping longitudinally to a fine soft down, and prepared

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* Gooch: Proc. Amer. Acad., **13**, 342 (1878); Am. Chem. Jour., **1**, 317.

† The serpentine variety is hydrous and useless for this purpose.

for use by boiling with hydrochloric acid and washing with water. In the first stage of the washing it is best to stir the asbestos into a large volume of water and to allow the coarser pieces, unsuitable for making the pulp, to settle out. Then the main portion of the suspended asbestos is allowed to settle, the supernatant very finest particles are poured off into another receptacle, and the washing may be completed, with the aid of the filter pump, on a perforated cone or in a draining funnel lined with a paper disk. If the fine material is left with the rest, the filter made from the mixture is likely to be too close and compact for the rapid filtration which is desirable and perfectly feasible in ordinary work; but, if preserved by itself it may be used to supplement the more porous material when a very compact filter is required.

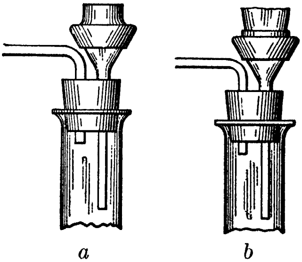

FIG. 18.

The filter is made in a crucible (platinum or porcelain) the bottom of which is perforated with fine holes, the more the better. The crucible is held by a rubber setting made by stretching soft rubber tubing over a funnel, or thistle tube, as shown in Fig. 18*a*, and the funnel is fitted tightly in one of the perforations of the stopper which closes the vacuum flask. A little of the asbestos is suspended in water, poured into the crucible, while the vacuum pump is in action, takes the form of a compact felt, which is easily washed, dried, ignited, and weighed with the crucible. When a precipitate is to be filtered off and weighed upon a felt thus prepared, the crucible, with the felt in place, is placed in the rubber setting, the asbestos is moistened with a drop or two of water, the pump is started, and, after the crucible has settled into place (see Fig. 18*b*), the filtration and washing are carried on in the usual manner.

The Filter of Spongy Platinum. — Instead of asbestos spongy platinum may sometimes be used with advantage, in the perforated crucible, as the filtering medium.* The felt may be made by placing the perforated platinum crucible upon absorbent paper, pouring into the crucible a thick emulsion of ammonium chloroplatinate, and igniting while the layer of the resulting spongy platinum is shaped by pressure with a rounded glass rod; or platinum crucibles with porous bottoms (Neubauer) may now be procured from the manufacturers.

The Anthracene Filter. — In some processes of analysis the necessity arises for the separation of a precipitate from the filter upon which it has been collected or of mixed precipitates from one another. When a precipitate yields easily to a solvent which does not affect paper the use of the paper filter to collect the precipitate to be subsequently dissolved is feasible. When the solvent for the precipitate attacks paper also, as is the case with the stronger acids and alkali hydroxides in concentrated solution, so that the separation of the solution from the disintegrated paper makes trouble, the asbestos filter may be a serviceable substitute for the paper filter. If, however, the separation of a refractory precipitate from the filter upon which it has been collected is required, the problem may sometimes be solved satisfactorily by the use of the anthracene filter † insoluble in water and aqueous solutions of ordinary salts, alkalies, and acids (excepting strong sulphuric, strong nitric, and glacial acetic acid), but easily soluble in naphtha, benzene, carbon disulphide, and in boiling alcohol.

The mode of preparing and using the filter is simple. Anthracene is slightly moistened with alcohol so that water will wet it. An emulsion in water is then made and this is used in the same way as is the emulsion of asbestos employed in making asbestos felts. That is to say, enough of the emulsion to form a layer of the proper thickness is poured into a perforated crucible which is held tightly in the rubber packing of a funnel fitted in the usual manner to a vacuum-flask. If the felt happens to be too coarse for a special use, it may be made as close as need be by coating the layer first deposited with a finer emulsion, made by dissolving anthracene in hot alcohol and precipitating with water. As a protection against disintegration of the felt of anthracene in the subsequent processes of filtration and washing a perforated disk of platinum foil of diameter a little less than that of the crucible may be placed upon the felt. After washing with water the filter is ready for use.

To separate a precipitate from the anthracene filter it is only necessary to act with a solvent for anthracene. It is usually convenient to stand the crucible containing precipitate and filter in a small beaker, add enough of the solvent for anthracene and gently warm until the anthracene dis-

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* Munroe: J. Anal. Chem., **2,** 241; Chem. News, **58,** 101.

† Gooch: Proc. Amer. Acad., **20,** 390 (1885).

solves. On the addition of a water solution of the reagent to act upon the precipitate the solution of anthracene floats to the surface of the water solution. If the precipitate dissolves entirely, the solution of anthracene may be separated from the water solution by simply pouring the liquids upon a filter previously moistened with water, when the solution in water will run through, and the anthracene and its solvent will remain and may be washed indefinitely with water. In case a constituent of a mixture of precipitates dissolves, and it is desired to collect another which is insoluble, the anthracene and its solvent may be made to pass the filter, after the water has run through, by adding a little alcohol to overcome the repulsion between the solution and the water which fills the pores of the filter. The precipitate which stays behind may then be washed first with a solvent of anthracene, and then, if necessary, with alcohol followed by water. If the vacuum filter is used (with either paper or asbestos) both liquids, the aqueous solution and the immiscible solution of anthracene, will leave the precipitate and traverse the filter together.

In general, benzol is to be preferred as the solvent for anthracene, but some advantage may be gained in special cases by a proper choice of solvents. Thus, in removing intermixed sulphur from precipitated sulphides collected upon an anthracene filter both the anthracene and the sulphur may be dissolved in carbon disulphide in a single operation.

Representative Precipitation Processes. — Certain procedures involving the formation of chlorides, sulphates, carbonates, oxalates, phosphates, hydroxides, and sulphides for the purpose of determining either acidic ions or basic ions of reaction may be taken as fairly typical in respect to the phenomena and the treatment incidental to precipitation processes.

The Precipitation of Chlorides

The Determination of the Chloride Ion. — When silver nitrate is added to a dilute solution containing hydrochloric acid or a chloride, silver chloride is formed and nearly all of it is precipitated.

$$AgNO_3 + HCl \rightleftarrows AgCl + HNO_3.$$
$$AgNO_3 + NaCl \rightleftarrows AgCl + NaNO_3.$$

The freshly precipitated, finely divided, and somewhat colloidal silver chloride becomes more compact and somewhat less soluble upon heating or upon long standing in the solution, and the presence of even a slight excess of silver nitrate reduces the solubility to an amount practically negligible in the volumes used in ordinary analytical processes. Sodium nitrate and, to a less extent, nitric acid, though useful in promoting the coagulation of the precipitate, may, if present in considerable amounts, appreciably increase the solubility of the precipitate. In a liter of water containing 8.5 grm. ($\frac{1}{10}$ gram-molecule) of sodium nitrate as much as 0.0030 grm. of silver chloride may be dissolved. Other nitrates, notably mercuric nitrate, have similar effects. Silver chloride possesses in considerable degree the tendency to occlude substances present in solution during its formation, and, as is natural, this tendency increases with increase in the concentrations of the dissolved substances. From the freshly formed, curdy, and flocculent precipitate the occluded material may be easily removed by washing, but it is much more difficult to thus purify the precipitate which has been compacted by long standing in presence of the mother liquor. In precipitating silver chloride in the analytical process the precipitate is subject to contamination with silver nitrate when this reagent is in excess, but if the precipitations are made in solutions containing no more than $\frac{1}{5}$ gram-molecule of the soluble chloride, by the addition of silver nitrate of similar concentration, the material left after washing proves to be insignificant when the washing quickly follows the precipitation. If, however, the precipitate is to be made compact by standing for a long time in contact with the solution both the solution and the reagent should be of concentrations not exceeding $\frac{1}{10}$ gram-molecule in the liter. For example, in the reaction between sodium chloride and silver nitrate the reagents should react in solutions containing not more than 0.58 and 1.7 grm. of these substances, respectively, in every 100 cm.^{3} of solution, if the precipitate is to stand long in contact with the solution.

The precipitate is best collected on asbestos in the perforated crucible, carefully washed, dried at 130 to 140 degrees and weighed.

It is also possible to collect the precipitate upon ashless paper. In this case the paper and precipitate are dried, and the precipitate is separated as completely as possible from the paper and reserved. The paper is carefully rolled up and burned in a spiral of platinum wire over a weighed crucible into which the ash is allowed to fall. The ash is treated with a drop or two of nitric acid (to dissolve reduced silver) and then with a drop or two of hydrochloric acid (to form silver chloride again), the main portion of the precipitate, previously separated, is added and the entire amount of silver chloride is heated to incipient fusion, and weighed.

Experimental Process: the Chloride Ion in Barium Chloride.—Weigh out carefully about 0.5 grm. of barium chloride, $BaCl_2 \cdot 2\,H_2O$. Dissolve the weighed material in about 300 cm.^{3} of water. Add a few drops of nitric acid and then a solution of silver nitrate, gradually and with constant stirring to curd the precipitate, until no further precipitation takes place. Heat the liquid to boiling and set the whole aside in the dark to cool. When the precipitate has settled completely filter it off on asbestos in a perforated crucible previously weighed, wash thoroughly with water containing a few drops of nitric acid to the liter (to keep the precipitate from passing into the colloidal condition) and then with a little pure water. Dry to constant weight, first at 100 degrees and then in an air-bath heated to at least 130 degrees or over a low flame at a temperature well below that of the fusing point of silver chloride (450 degrees). Calculate the weight of chlorine in the silver chloride weighed and compare it with the weight which should be contained in the amount of barium chloride taken. Tabulate the results of analysis.

$BaCl_2 \cdot 2\,H_2O$ taken.	AgCl formed.	Cl in AgCl formed.	Cl present in $BaCl_2 \cdot 2\,H_2O$ taken.		Error in terms of Cl.	
Grm.	Grm.	Grm.	Grm.	Per cent.	Grm.	Per cent.

Bromide Ion and Iodide Ion.—The bromide ion and the iodide ion of soluble salts may be determined similarly, by precipitating with silver nitrate and weighing the insoluble silver salt collected on asbestos.

The Determination of the Silver Ion. — The gravimetric determination of silver may be accomplished by taking advantage of the reaction between a soluble silver salt and a soluble chloride, hydrochloric acid, which is easily removed by washing and is volatile in the process of drying, being the best precipitant.

$$HCl + AgNO_3 \rightleftarrows AgCl + HNO_3.$$

The solubility of the silver chloride is less at low temperatures and is diminished by the presence of hydrochloric acid in moderate excess, although considerably increased by the action of very large amounts of that acid, or of its soluble salts. While 100 $cm.^3$ of pure water will dissolve 0.000154 grm. of silver chloride at 20 degrees (and 0.00217 at 100 degrees), the solubility of the silver chloride amounts at 21 degrees to 0.00002 grm., 0.00003 grm., and 0.00555 grm. in 100 $cm.^3$ of hydrochloric acid of 1, 5, and 10 per cent, respectively.

Experimental Process: Determination of Silver as Silver Chloride. — Make a nearly N/10 solution of silver nitrate by dissolving 17 grm. of silver nitrate in a liter of water. Of this solution, draw from a burette an exactly measured portion (50 $cm.^3$). Add a few drops of nitric acid (for its favorable influence upon the condition of the precipitate), dilute the solution to a volume of about 200 $cm.^3$ with boiling water (so that the temperature may be at least 70 degrees), add hydrochloric acid slowly, with vigorous stirring (to curd the precipitate) until the precipitation appears to be complete. Set the mixture aside to cool and, after the precipitate has settled leaving the supernatant liquid clear, test with a drop or two of hydrochloric acid to make sure that the reaction has been completed. Filter (preferably) on asbestos in the perforated crucible (previously ignited and weighed) and wash with cold water. Dry the precipitate upon the filter to constant weight at 140 degrees, or (cautiously) over a very low flame at a temperature below the fusing point of silver chloride (450 degrees).

Or the precipitate may be collected on paper and treated subsequently as described in the process for the determination of the chlorine ion by precipitation as silver chloride (p. 69).

Calculate the silver content of the solution per $cm.^3$.

Determination of Mercury as Mercurous Chloride. — The determination of mercury in the mercurous form by precipitation as mercurous chloride, Hg_2Cl_2, may be made by treating the solution of mercurous nitrate with hydrochloric acid, filtering and washing on asbestos in the perforated crucible, after standing for twelve hours, and drying at 105 degrees:

$$Hg_2(NO_3)_2 + 2\,HCl \rightleftarrows Hg_2Cl_2 + 2\,HNO_3.$$

The same process may be applied to the analysis of mercuric nitrate if phosphorous acid be also added to effect a preliminary reduction:

$$2\,Hg(NO_3)_2 + H_3PO_3 + H_2O = Hg_2(NO_3)_2 + H_3PO_4 + 2\,HNO_3.$$

Determination of Barium as Chloride. — Water which dissolves barium chloride very easily becomes so modified in solvent power by hydrogen chloride dissolved in it to saturation that barium chloride will dissolve in the solution only in the ratio of 1 to about 20,000 parts. The addition of ethyl ether to the concentrated aqueous hydrochloric acid thus produced further diminishes the solvent action of the mixture, so that in a mixture of concentrated aqueous hydrochloric acid with 20 per cent of its volume of absolute ether the salt dissolves in the solvent mixture in the proportion of 1 : 120,000 parts. Advantage may be taken of this fact to precipitate barium chloride and separate it from calcium chloride and magnesium chloride which remain soluble in high degree. The chlorides of these elements are dissolved in the least possible amount of hot water and, after cooling, the mixture of concentrated hydrochloric acid and ether (5 : 1) is added drop by drop at the outset, to induce the formation of the precipitate in coarsely crystalline condition. After standing a few minutes, the precipitated hydrous chloride, $BaCl_2 \cdot 2\,H_2O$, is collected upon asbestos in the perforated crucible, washed with the hydrochloric acid-ether mixture, dried at 150 to 200 degrees, and weighed as the anhydrous chloride $BaCl_2$.*

Instead of charging the water solution with gaseous hydrochloric acid, that reagent may be produced by the action of acetyl chloride upon the water, inconvenient violence of reaction being moderated by the addition of acetone which mixes in all proportions with both acetyl chloride and water:

$$CH_3COCl + H_2O = CH_3COOH + HCl.$$

When a mixture of acetone and acetyl chloride, preferably 4 : 1, is added slowly to a very concentrated solution of barium chloride in water, the water is attacked at once, hydrogen chloride is liberated, and precipitation begins immediately. If the temperature is kept down during the process by immersing in cool running water the vessel in which reaction takes place, no more than a mere trace of barium can be detected by testing with sulphuric acid the residue after evaporating the liquid separated from the precipitate by filtration through

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* Mar: Methods in Chemical Analysis, Gooch, p. 174.

asbestos. When, however, the temperature is allowed to rise, in consequence of the heat liberated in the reaction, an appreciable amount of barium may be found by sulphuric acid in the filtrate. It appears that when the acetone-acetyl chloride mixture (4 : 1) acts upon the cooled concentrated water solution of barium chloride the precipitate is the hydrous chloride, $BaCl_2 \cdot 2\,H_2O$, while the water in excess of that needed to form the hydrous salt is immediately attacked; that acetyl chloride by itself produces only slight dehydration of this salt without marked solubility; and that prolonged action of an acetone-acetyl chloride mixture (2 : 1) results in an appreciable dehydration and considerably increased solubility of the salt. When the acetone-acetyl chloride mixture is added without cooling to the water solution of barium chloride the heat of reaction favors dehydration of the hydrous salt, and the anhydrous salt may go into solution to the amount of several milligrams in 10 $cm.^3$ of the precipitating mixture. Upon filtering the mixture and treating the filtrate with acetone, with acetyl chloride, or with the acetone-acetyl chloride mixture, the dissolved anhydrous salt is not thrown out of solution, but the addition of a drop of water is sufficient to induce immediate precipitation in the form of the hydrous salt.

The best conditions for the quantitative precipitation of barium chloride by the acetone-acetyl chloride mixture are found in the use of minimum amounts of water, the preservation of ordinarily low temperature, a liberal proportion of acetone, and not too prolonged digestion of the precipitate in the excess of the precipitant. The salt to be analyzed is weighed out into a small beaker and dissolved in 1 $cm.^3$ of water. The beaker is cooled by immersion in a water-bath, preferably supplied with running water, at a temperature of about 15 degrees. To the cooled solution, constantly shaken, the acetone-acetyl chloride mixture is added from a dropping funnel at the rate of five drops to the second. The precipitate is filtered off upon asbestos in a perforated crucible, dried, or ignited, and weighed as the anhydrous chloride, $BaCl_2$. The best conditions studied for the handling of 0.1 grm. of hydrous barium chloride are the solution of the salt in 1 $cm.^3$ of water, treatment with 30 $cm.^3$ of the 4 : 1 mixture of acetone and acetyl chloride, washing with acetone, and drying in the air-bath at 135 degrees or at low redness.*

Precipitation of Aluminium Chloride. — Aluminium chloride may be precipitated similarly by thoroughly saturating the cold aqueous solution of the chloride with hydrogen chloride after

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* Gooch and Boynton: Methods in Chemical Analysis, Gooch, p. 175.

adding an equal volume of ether. The precipitated hydrous chloride, $AlCl_3 \cdot 6\,H_2O$, undergoes hydrolysis when carefully dried and ignited, leaving aluminium oxide. Any slight danger of mechanical loss during the ignition may be counteracted by covering the precipitate in the filtering crucible with a layer of mercuric oxide which, after acting as a sieve to prevent the escape of solid particles during the decomposition of the hydrous chloride, will finally be entirely volatilized. By this process aluminium may be separated from iron,* and from glucinum, mercury, zinc, copper, and bismuth.†

In the practical execution of the process the concentrated aqueous solution of the salts is mixed with a suitable volume of strongest aqueous hydrochloric acid — enough to make the entire volume approximately 15 cm.^{3} to 25 cm.^{3}. This mixture is saturated with gaseous hydrochloric acid while cooled by immersing the container in running water. A volume of ether equal to the volume of the liquid is introduced, and the cooled etherial mixture is treated with gaseous hydrochloric acid to saturation at a temperature not exceeding 15 degrees.‡ The precipitated crystalline chloride is collected upon asbestos in a perforated crucible, washed with a previously prepared mixture of hydrochloric acid and ether carefully saturated at 15 degrees, dried half an hour at 150 degrees, covered with a layer of pure mercury oxide (about 1 grm.), and ignited (under a ventilating flue) gently at first and finally with the blast-lamp.

The Precipitation of Sulphates

The Determination of the Sulphate Ion. — The gravimetric determination of the sulphate ion in free sulphuric acid and in sulphates rests fundamentally upon the reaction which may take place between the free acid, or a metal sulphate, and barium chloride, according to the typical reactions

$$H_2SO_4 + BaCl_2 \rightleftarrows BaSO_4 + 2\,HCl,$$

$$\overset{\text{I}}{M}_2SO_4 + BaCl_2 \rightleftarrows BaSO_4 + 2\,MCl.$$

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* Gooch and Havens: Methods in Chemical Analysis, Gooch, p. 214.

† Havens: Ibid., p. 216.

‡ The gaseous hydrochloric acid is most conveniently produced in regulated current by treating massive ammonium chloride with strong sulphuric acid in the Kipp generator. A platinum dish hung in an inverted bell jar, provided with inlet and outlet tubes through which the current of water for cooling is passed, makes a convenient container for the solution to be saturated with the gas.

In regard to the former of these reactions it has been pointed out * that, while the reaction is reversible, the concentration of the barium sulphate in solution is always very low (0.0023 grm. in 1 liter of pure water) and is only slightly affected by small changes in the concentration of the hydrochloric acid. The second reaction, that between a soluble sulphate and barium chloride, is likewise reversible, and in it the concentration of dissolved barium sulphate is also very low and not very much affected by changes in the concentration of the chloride produced. The determination of the sulphuric acid ion should, therefore, be a comparatively simple matter if the reactions indicated were the only possible reactions between barium chloride and sulphuric acid or a sulphate. The fact is, however, that other reactions intervene.

Contamination of Precipitated Barium Sulphate. — When a solution of barium chloride is added to a dilute solution of sulphuric acid (kept at the boiling temperature in order that the precipitate of barium sulphate may be coarse enough to settle well) very nearly all of the sulphuric acid ion is precipitated, but the barium sulphate includes some barium chloride, not removable by washing; and the inclusion is greater when the barium chloride is added rapidly. Furthermore, it has been found that the precipitate may yield upon ignition sulphuric acid or hydrochloric acid, or both. When barium reacts with a soluble sulphate still other complexities may come to light. The precipitated sulphate may not only include barium chloride but it may contain other sulphates. When, for example, barium chloride and potassium sulphate react in solution the precipitate may contain potassium sulphate amounting to as much as several per cent of the total weight.

To explain the obstinate retention of barium chloride in the precipitated barium sulphate and the evolution of the free acids upon ignition it has been suggested † that combinations, such as $BaCl \cdot HSO_4$ and $BaCl_2 \cdot BaSO_4$, are formed, which may be figured as shown in the following symbols:

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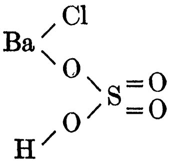
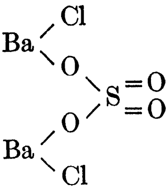
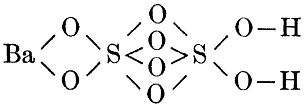
* Page 8.

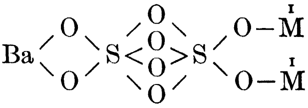
† Hulett and Duschak: Zeit. anorg. Chem., **40**, 196 (1904).





The obstinate retention of an ordinarily soluble sulphate by precipitated barium sulphate may, likewise, be explained by assuming the formation of double sulphates derived from sulphuric acid or a soluble sulphate existing in molecules more complex than those which are represented by the simple equivalent symbols. If, for example, some, at least, of the molecules of sulphuric acid and of the sulphate are present in polymeric form, it is easy to see how complex molecules may result, such as $BaSO_4 \cdot H_2SO_4$ and $BaSO_4 \cdot M_2SO_4$, which may be figured as





The formation of such complex substances must introduce many inaccuracies in determinations based upon the fundamental presumption that barium sulphate, $BaSO_4$, is the final and only product weighed. Thus, the product $BaCl_2 \cdot BaSO_4$ will weigh too much by the amount of $BaCl_2$ in it; $BaCl \cdot HSO_4$ may lose on ignition hydrochloric acid and become normal in composition and weight, or it may lose sulphuric acid and be deficient in weight; $BaSO_4 \cdot H_2SO_4$ will lose sulphuric acid on ignition, weighing too little by the amount of loss; and the weight of $BaSO_4 \cdot \overset{\text{I}}{M}_2SO_4$ will differ from what the weight of the barium sulphate should be by an amount depending upon the difference between the atomic weights of Ba and $\overset{\text{I}}{M}_2$.

Precaution in Precipitations. — In the practical determination of the sulphate ion of free sulphuric acid, and of certain sulphates (e.g., copper sulphate, magnesium sulphate, and alkali sulphates in absence of a large excess of alkali salts) results very near the truth may be obtained by adding, drop by drop, to the hot dilute solution of the acid or sulphate a dilute solution of an equivalent amount of barium chloride, and when the precipitation is practically complete a considerable excess of that reagent to bring about the highest degree of insolubility of the barium sulphate. Under such circumstances the inclusion of barium chloride is at a minimum and the increase of weight, due to such inclusion, is approximately equal to that of the barium sulphate lost in consequence of solubility.

Experimental Process: the Sulphate Ion in Copper Sulphate. — Weigh out carefully about 0.5 grm. of copper sulphate, $CuSO_4 \cdot 5\,H_2O$, transfer it to a beaker, dissolve it in about 400 cm.^{3} of water, heat the solution to boiling, and add 0.5 cm.^{3} of concentrated hydrochloric acid. To the solution, at the boiling temperature, add slowly from a dropping funnel or burette, with constant stirring, 25 cm.^{3} of a solution of barium chloride, $BaCl_2 \cdot 2\,H_2O$, containing 25 grm. of this salt to the liter. This amount of the precipitant is approximately that required to bring about the reaction

$$BaCl_2 + CuSO_4 \rightleftarrows BaSO_4 + CuCl_2$$

Then add 25 cm.^{3} more of the precipitant and let the precipitate settle for half an hour.

A. Filtration on Paper. — Using a rod held vertically to direct the flow, decant upon the filter the clear liquid, above the settled precipitate, to the lowest possible limit, taking care in filling the filter to leave a margin half a centimeter broad above the level of the liquid. Fill the beaker with distilled water to the original level of the liquid, settle the precipitate and decant as before. Finally transfer the precipitate to the filter, washing out the beaker carefully and dislodging any adherent precipitate with the aid of a rubber-tipped glass rod (the "policeman"). Wash the precipitate into the point of the filter with a fine jet of water from the wash-bottle, directing the jet with a rotary motion around the paper from the rim downward, and continue the washing until silver nitrate fails to show the presence of a chloride in a portion of the washings collected separately. Dry the filter in the funnel, at least partially, fold it compactly in a weighed platinum crucible, cover the crucible, and heat very gently until dry. Incline the crucible (Fig. 19), arrange the cover so as to make a draft of hot air from the flame through

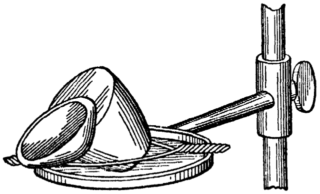


FIG. 19.

it, increase the heat until the paper begins to char, but keeping it low until all volatile matter has escaped. Then move the flame so that it strikes the bottom of the inclined crucible and increase the heat to redness until all carbon has been consumed. It is important not to raise the temperature to too high a point in the early stages of the ignition lest the barium sulphate be reduced and sulphur liberated appreciably, and not to heat finally in the blast lamp lest sulphur trioxide be expelled.

Cool the crucible nearly to the room temperature, place it in the desiccator and keep it there (ten minutes) until thoroughly cool, and weigh. Moisten the residue with sulphuric acid, heat gently within another crucible or in an iron cone, used as a radiator, and ignite to a constant weight. Take the difference between the weight thus found and the weight of the crucible as that of the barium sulphate. Calculate the weight of the SO_4 ion in the barium sulphate and compare it with that which should be obtained from the copper sulphate taken. State the results in a scheme like the following:

$CuSO_4 \cdot 5\ H_2O$ taken.	$BaSO_4$ found.	SO_4 calculated.	Theory for SO_4 in $CuSO_4 \cdot 5\ H_2O$ taken.		Error in the determination of SO_4.	
Grm.	Grm.	Grm.	Grm.	Per cent.	Grm.	Per cent.

B. Filtration on Asbestos. — Place in the rubber holder of a vacuum flask a perforated crucible, fitted with an asbestos felt (as previously described, p. 64), ignited, and weighed. Start the pump, moisten the asbestos with a little water, and, after the crucible has settled into place, decant into it the clear supernatant liquid. Transfer the precipitate to the crucible and wash it, directing the jet from the wash-bottle upon the wall of the crucible, in order to avoid any disturbance of the asbestos. Place the crucible containing the asbestos felt and the precipitate upon a pipe-stem triangle of such size that the cap * which covers the bottom will rest firmly. Heat with a Bunsen burner, very gently at first, so that the felt will not be stirred by escaping steam, then to red heat, cool in the desiccator and weigh. Arrange the results of the analysis in the form given for the preceding process.

General Procedure. — Beside the contamination of the precipitated barium sulphate there is sometimes another difficulty, as when salts of chromium or iron are present, due to the fact that the precipitation of some of the sulphate ion is

* Blair's pattern.

retarded or prevented, probably by the formation of complex ions. Generally, therefore, it is better in determining the sulphate ion of sulphates, and in many cases necessary, to remove the basic element by a preliminary precipitation, before attempting the precipitation of the sulphate ion by the soluble barium salt; although the compounds of certain bivalent elements, like magnesium and copper, when present in small amount, do not interfere seriously.

In practical analysis it is often necessary to determine the sulphuric acid ion in the presence of considerable amounts of alkali salts. For example, in certain processes, such as the determination of sulphur in pyrites, in which it is usual to oxidize the sulphur by fusion with sodium carbonate mixed with sodium peroxide, or other oxidizer (protected from the action of sulphur compounds in the fuel gases *), sodium sulphate is obtained in a mass of sodium carbonate with insoluble oxides or carbonates. Upon treatment with water this mass yields the sulphate in solution with sodium carbonate and, perhaps, sodium silicate. By acidifying the solution with hydrochloric acid and evaporating to dryness, silica is made nearly insoluble † and, upon extracting with water containing hydrochloric acid and filtering, it is nearly completely removed, while the solution holds the sodium sulphate with much sodium chloride. To get the best results the larger part of the sodium chloride should be removed before attempting the precipitation of the sulphate by means of barium chloride; and this may be accomplished by adding to the solution, previously concentrated to the lowest limit, five or six times its volume of concentrated hydrochloric acid, filtering on asbestos in the perforated crucible, and washing the residue of sodium chloride with concentrated hydrochloric acid. The soluble sulphate is thus separated from the greater part of the sodium chloride, insoluble to a very considerable extent in the concentrated hydrochloric acid. After diluting (to

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* The platinum crucible in which the fusion is made may be fitted into a circular hole cut through the middle of an asbestos disk and edged with platinum foil, the heating flame being applied from below.

† See p. 93.

prevent loss during the evaporation) and evaporating (to remove the free hydrochloric acid) the sulphate ion may be determined by precipitation in the form of reasonably pure barium sulphate.*

The Determination of Barium. — In precipitating barium sulphate by the action of an excess of sulphuric acid upon barium chloride in solution the barium is held in the precipitate (excepting the extremely small amount which dissolves as sulphate) but not all in the form of the sulphate. If the precipitate is weighed the result is low upon the hypothesis that barium sulphate is the sole product in which barium appears; moreover, chlorine may be detected in the precipitate. As in the reverse precipitation of sulphuric acid by barium chloride, the precipitate contains barium, the sulphate ion, and chlorine; but in the present case it is possible to make the necessary correction by simply moistening the precipitate with sulphuric acid and volatilizing by gentle ignition the excess with the hydrochloric acid produced in the reaction:

$$BaCl_2 \cdot BaSO_4 + H_2SO_4 = 2\,BaSO_4 + HCl.$$

In the precipitation of barium by sulphuric acid in the presence of alkali salts, as in the process in which barium sulphate is precipitated by the action of barium chloride upon alkali sulphates, the precipitate is in like manner contaminated by alkali sulphates — sometimes as much as 20 mgrm. in 0.5 grm. of precipitate. In this case, however, advantage may be taken of the fact that barium sulphate may be dissolved in concentrated sulphuric acid and, by evaporation of the acid, recovered in crystalline grains from which the alkali sulphates may be washed with water. Fig. 20 shows a simple device† for effecting the purification of barium sulphate from alkali sulphates, by solution in sulphuric acid, recrystallization and evaporation of the acid. The precipitate, filtered upon ashless paper, is ignited with the paper in a weighed platinum crucible and concentrated sulphuric acid (2 cm.^{3} to 5 cm.^{3}) is added. Within the mouth

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* Turner: Am. Jour. Sci., [4], **38,** 41.

† Gooch and Hill: Am. Jour. Sci., **35,** 311 (1913).

of the crucible a weighed cone of fine platinum gauze is fitted to prevent loss by spattering, and the flame of blast-lamp is directed into the point of the cone from above. When the evaporation of the excess of sulphuric acid is completed, the residue is washed with water and that portion of the barium sulphate which is removed from the crucible in this process is collected upon a filter of ashless paper. The filter is dried and ignited in the crucible. The crucible, cone, and the residue of purified barium sulphate are weighed together.

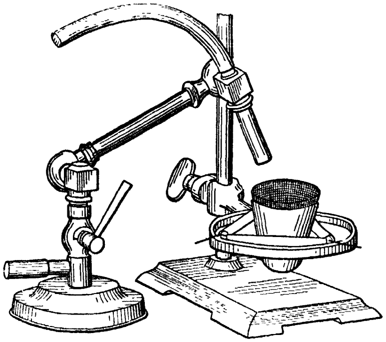


FIG. 20.

Experimental Process: Determination of Barium as Barium Sulphate. — Dissolve in hot water about 0.5 grm. of barium chloride, $BaCl_2 \cdot 2\,H_2O$, weighed exactly, dilute the solution to a volume of about 400 cm.^{3}, heat it to boiling, add dilute [1 : 4] sulphuric acid in excess, boil a few minutes, settle, filter on asbestos in the perforated crucible, wash, dry, ignite, and weigh. Moisten the residue with a drop of dilute sulphuric acid, ignite, and weigh as $BaSO_4$. This process will give good results in presence of large amounts of hydrochloric acid, provided the excess of sulphuric acid is large, e.g., 1 to 2 per cent by volume of the entire solution.

The Determination of Strontium. — Strontium may be precipitated and determined as strontium sulphate provided means be used to properly decrease the solubility of the precipitate — about 1 : 7000 in water at the atmospheric temperature and somewhat more at the boiling temperature, and considerably more in presence of hydrochloric acid, nitric acid, or salts of these acids.

$$SrCl_2 + H_2SO_4 \rightleftarrows SrSO_4 + 2\,HCl.$$

The addition of an equal volume of alcohol to the solution after precipitation by a slight excess of sulphuric acid will render the insolubility sufficient for analytical purposes. The precipitate, after standing twelve hours, is collected upon asbestos in the perforated crucible, washed with 50 per cent alcohol containing a little sulphuric acid, dried, and ignited at low red heat.

The Determination of Calcium. — Calcium may be precipitated as calcium sulphate by adding an excess of sulphuric acid to the solution of the calcium salt and a volume of alcohol equal to four times that of the aqueous solution and allowing the mixture to stand for twelve hours.

$$CaCl_2 + H_2SO_4 \rightleftarrows CaSO_4 + 2\,HCl.$$

The precipitate is collected on asbestos in the perforated crucible, dried, and ignited at low red heat.

The Determination of Lead. — From the water solution of lead chloride, lead nitrate, or lead acetate, the lead may be precipitated as lead sulphate by the addition of an excess of sulphuric acid and a volume of alcohol twice that of the water solution.

$$Pb(NO_3)_2 + H_2SO_4 \rightleftarrows PbSO_4 + 2\,HNO_3.$$

If the addition of alcohol is undesirable on account of subsequent analytical operations the precipitate may be made nearly insoluble by the addition of a large excess of sulphuric acid (e.g., 10 per cent by volume of the entire solution).

Experimental Process: Determination of Lead as Lead Sulphate. — *A.* Weigh out carefully about 0.5 grm. of powdered and dried lead nitrate, dissolve it in water (50 cm.^{3}) with the aid of a drop or two of nitric acid (to dissolve a trace of basic salt), and add dilute sulphuric acid, in excess, with a volume of alcohol twice as great as that of the water solution. Settle the precipitate, filter it off on asbestos in the perforated crucible, wash with alcohol (80 per cent), ignite, and weigh as $PbSO_4$.

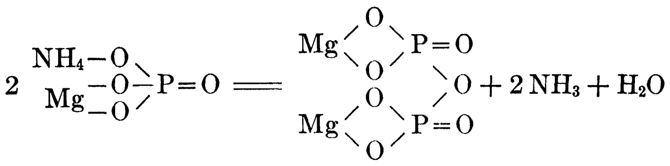
B. Take about 0.5 grm. of powdered and dried lead nitrate weighed exactly. Dissolve it in water (50 cm.^{3}) with the aid of a drop or two of nitric acid. Add a volume of dilute sulphuric acid (1 : 4) equal to that of the water solution. Filter on asbestos in the perforated crucible, wash with dilute sulphuric acid (1 : 4), ignite, and weigh as $PbSO_4$.

The Precipitation of Phosphates

The Determination of the Orthophosphate Ion. — One of the processes by which the acidic ion of free orthophosphoric acid and its salts may be determined depends upon the reaction in which ammonium magnesium phosphate, $NH_4MgPO_4 \cdot 6\,H_2O$, is precipitated from solution by the action of the soluble "magnesia mixture," made up by putting together in solution magnesium chloride, ammonium chloride, and ammonium hydroxide. The ideal reaction proceeds in the sense of the expression

$$\mathrm{MgCl_2 + NH_4OH + HNa_2PO_4} + n\mathrm{NH_4Cl = NH_4MgPO_4} \\ \mathrm{+ 2\,NaCl + H_2O} + n\mathrm{NH_4Cl.}$$

The function of the ammonium chloride is the prevention of the precipitation of magnesium hydroxide so that the composition of the precipitate may be definite and ideal. From the precipitate, submitted to ignition, ammonia and water are eliminated while magnesium pyrophosphate remains in weighable form.



As little as 0.0001 grm. of the orthophosphoric acid ion may be precipitated in 500 cm.^{3} of faintly ammoniacal solution, even in presence of as much as 60 grm. of ammonium chloride, by a sufficient excess of the magnesium chloride; but the ideal ammonium magnesium phosphate, NH_4MgPO_4, which yields upon ignition the pyrophosphate, $Mg_2P_2O_7$, may, according to conditions of precipitation, be contaminated by the trimagnesic phosphate which upon ignition gives the anhydrous phosphate $Mg_3P_2O_8$, or by a double phosphate, $(NH_4)_4Mg(PO_4)_2$ which upon ignition leaves magnesium metaphosphate $Mg(PO_3)_2$. The ammonium salts tend to bring about the contamination of the precipitate which results in the formation of the metaphosphate on ignition, and the use of strongly ammoniacal solutions induces contamination by the trimagnesic phosphate. The results of practical experiments go to show that the constitution of the precipitate is very nearly ideal when the boiling solution of the phosphate, containing a moderate excess of the magnesium salt and not more than 5 to 10 per cent of ammonium chloride is made ammoniacal very gradually, so that the precipitate is formed in crystalline condition. If more ammonium chloride than this proportion, or more magnesium salt than twice the amount theoretically necessary, is present, it is safer to decant the supernatant liquid from the precipitate (through the filter to be used subsequently to hold the phosphate), to dissolve the precipitate in a little hydrochloric acid and then to reprecipitate by dilute ammonia.

The Determination of Magnesium. — As little as 0.0001 grm. of magnesium may be precipitated in 500 $cm.^3$ of a faintly ammoniacal solution, even when the solution contains as much as 60 grm. of ammonium chloride (or 100 $cm.^3$ of a saturated solution of ammonium oxalate). As in the precipitation of ammonium magnesium phosphate in the determination of the orthophosphoric acid ion, much ammonia tends to the formation of the trimagnesium phosphate while a large amount of ammoniun salts tend to introduce too much ammonium into the double phosphate.*

When ammonium salts are present in quantity, as is often the case in the ordinary course of analysis, the precipitate first thrown down by addition of ammonium sodium phosphate and ammonia in distinct excess should be settled and the supernatant liquid poured off through the filter used subsequently in collecting the precipitate. The precipitate is then dissolved in the least possible amount of hydrochloric acid and thrown down again from the diluted solution by ammonia in slight excess. For safety, a little ammonium sodium phosphate may also be added. The precipitate, filtered off and washed with distinctly ammoniacal water, is ignited very gently at first (to avoid reduction of the phosphoric oxide by the ammonia set free) until all ammonia is expelled, when the temperature is raised to redness.

Good results are also obtained (*Gibbs*) by adding to the boiling solution of the magnesium salt a solution of ammonium sodium phosphate until no further precipitation takes place and then (dilute) ammonium hydroxide in excess. Even in presence of considerable amounts of ammonium chloride this

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* See p. 82.

process yields a phosphate of nearly ideal constitution if only the boiling be prolonged from three to five minutes. The greater part of the ammonium magnesium phosphate — about 90 per cent — forms in this process before free ammonia is added, and the ammonium which enters the phosphate thus formed is derived from the ammonium sodium phosphate, which becomes correspondingly acidic. Under these conditions, the tendency to form an insoluble ammonium magnesium phosphate, richer in ammonium and poorer in magnesia than the normal salt, is slight.

Experimental Process: Determination of Magnesium as Magnesium Pyrophosphate. — I. Draw from a burette 50 cm.^{3} of a solution of magnesium chloride (about N/10 in respect to the anhydrous salt) standardized as described in the Experimental Process of page 48. Dilute the solution to a volume of 150 cm.^{3} Add in solution 2.5 grm. of microcosmic salt, $4\,Na(NH_4)PO_4 \cdot 4\,H_2O$, dissolve the precipitate which comes down in flocculent condition in hydrochloric acid and reprecipitate in crystalline condition by the gradual addition of ammonium hydroxide in distinct excess. Settle the precipitate, pour off the supernatant liquid through asbestos weighed in the perforated crucible. Dissolve the precipitate in the least possible amount of hydrochloric acid, dilute the solution to a volume of 100 cm.^{3} or 150 cm.^{3}, reprecipitate by the very gradual addition of ammonium hydroxide in excess, filter on the asbestos previously weighed and used in the decantation, and wash with distinctly ammoniacal water. Heat the precipitate gently at first, until all ammonia has been expelled (to avoid reducing action), and afterward at full red heat. The "glow" which passes over the gently ignited residue when heated to redness, marking a molecular change in the pyrophosphate, is a good indication that the ignition has been sufficiently prolonged. Weigh as $Mg_2P_2O_7$.

II. Draw from a burette 5 cm.^{3} of the standardized solution of magnesium chloride. Add ammonium hydroxide in faint excess and redissolve any precipitated magnesium hydroxide by the cautious addition of hydrochloric acid. To the neutral or very slightly acid solution heated to boiling add gradually a considerable excess of microcosmic salt, $HNa(NH_4)PO_4 \cdot 4\,H_2O$, boil for five minutes, then cool, add an excess of ammonium hydroxide and set aside to allow the precipitate to become crystalline. Filter on asbestos in the perforated crucible, wash with distinctly ammoniacal water, ignite gently at first and then at full red heat. Weigh as $Mg_2P_2O_7$.

The Determination of Manganese. — The manganese phosphate when precipitated in the cold by an excess of an alkali phosphate in the presence of ammonium chloride and ammonia is very largely in the form of the trimanganese phosphate,

$$3\,MnCl_2 + 2\,NH_4OH + 2\,H(NH_4)NaPO_4$$
$$= Mn_3P_2O_8 + 2\,NaCl + 4\,NH_4Cl + 2\,H_2O,$$

but boiling or even subsequent standing may effect a more or less complete conversion of the manganese phosphate to the ammonium manganese phosphate. The success of the analytical process in which manganese is weighed as the pyrophosphate (*Gibbs*) turns, therefore, upon the change of the trimanganese phosphate, $Mn_3P_2O_8$, to the ammonium manganese phosphate, NH_4MnPO_4; and the presence of a large amount of ammonium salt is essential to the formation of the precipitate of ideal constitution.* The proportion of ammonium chloride present to ammonium manganese phosphate formed should be at least 40 : 1, or, speaking approximately, 200 molecules of ammonium chloride must be present in the liquid to every molecule of the phosphate formed; and the ammonium chloride may be increased almost to the point of saturation of the liquid without causing more than a trifling solubility of the ammonium manganese phosphate in the presence of an excess of the precipitant. Furthermore, the precipitate may be washed with perfect safety with pure water as well as with slightly ammoniacal water. The finely granular precipitate which may be obtained by slow action of dilute ammonia added gradually to the hot solution of the manganese salt apparently includes a portion of unconverted phosphate which resists the replacement of the manganese by ammonium. On the other hand, the precipitate of flocky condition thrown down in the cold passes easily to the silky and crystalline condition when heated with the proper amount of ammonium salt, and possesses a constitution approaching the ideal. In the determination of manganese by this method the presence of a large amount of ammonium chloride is therefore necessary. Good results may be obtained most easily and surely by the following procedure: The slightly acid solution, containing in a volume of 200 cm.^{3}

Gooch and Austin: Methods in Chemical Analysis, Gooch, p. 482.

an amount of manganese not more than enough to make 0.4 grm. of the pyrophosphate, 20 grm. of ammonium chloride, and 5 cm.^{3} to 10 cm.^{3} of a cold saturated solution of ammonium sodium phosphate, is precipitated in the cold by the careful addition of dilute ammonia in slight excess only. The mixture is heated until the precipitate becomes silky and crystalline; the whole is allowed to stand and cool half an hour; the precipitate is collected upon asbestos in a perforated platinum crucible, washed (best with slightly ammoniacal water), dried at gentle heat, and ignited as usual, in the presence of large amounts of ammonia.

Experimental Process: Determination of Manganese as Manganous Pyrophosphate, $Mn_2P_2O_7$. — Put into a weighed crucible about 1 grm. of hydrous manganese sulphate, dehydrate over a radiator (according to the process described on p. 49) to constant weight and, noting the weight, dissolve the anhydrous sulphate in water containing hydrochloric acid. Add 20 grm. of purified ammonium chloride,* 5 cm.^{3} to 6 cm.^{3} of a saturated solution of hydrogen sodium ammonium phosphate, $HNa(NH_4)PO_4$, and ammonium hydroxide drop by drop in *slight* excess. Raise the temperature of the solution to the boiling point and keep it there until the precipitate becomes crystalline. Cool, filter on asbestos in the perforated crucible, wash with distinctly ammoniacal water (containing at the end ammonium nitrate). Ignite, gently at first (to avoid reducing action of liberated ammonia), and then at the full heat of the Bunsen burner. Weigh as $Mn_2P_2O_7$.

Cadmium and Zinc. — With proper precautions, zinc† and cadmium‡ may be likewise precipitated from solutions of their soluble salts as double ammonium phosphates which on ignition leave pyrophosphates.

The Precipitation of Oxalates

The Precipitation of Calcium Oxalate. — Calcium oxalate is extremely insoluble in water and in ammoniacal solutions, very slightly soluble in acetic acid or oxalic acid, but readily

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* Prepared by boiling the solution of the C. P. salt of commerce with ammonium hydroxide and filtering.

† Austin: Methods in Analysis, Gooch, p. 185. Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 140.

‡ Austin: Methods in Analysis, Gooch, p. 190.

dissolved by the stronger acids in fairly concentrated solutions. When precipitated from cold solutions calcium oxalate is so finely divided that it will settle only very slowly and on filtration tends to pass through the pores of the filter, but if precipitated from boiling hot solution and allowed to stand the precipitate takes a more coarsely crystalline form and is then easily filterable.

From neutral or slightly ammoniacal solutions containing only alkali salts beside the soluble calcium salt, calcium oxalate may be precipitated in reasonably pure condition by ammonium oxalate:

$$CaCl_2 + 2\,(NH_4)_2O_2C_2O_2 \rightleftarrows CaO_2C_2O_2 + 2\,NH_4Cl.$$

But if a magnesium salt is also present, as is frequently the case in practical analysis, magnesium oxalate, $MgO_2C_2O_2 \cdot 2\,H_2O$, (soluble in boiling water in the ratio of 1 : 1300, but more soluble in presence of ammonium salts) is likely to be included in the precipitated calcium oxalate and in proportion to the concentrations of both the calcium salt and the magnesium salt. An effective procedure suitable in presence of a magnesium salt * depends upon bringing about the precipitation in the dilute and boiling solution of the calcium and magnesium salts, colored with methyl orange and containing a considerable amount of ammonium chloride, by adding dropwise at intervals a solution of oxalic acid (10 per cent), and alternately a very dilute ammonium hydroxide (1 per cent) to neutralization. The mixture is allowed to stand for an hour and the clear liquid is decanted upon an ashless filter. In case the magnesium present is very largely (more than ten-fold) in excess of the calcium, the precipitate should be dissolved in hydrochloric acid, reprecipitated in the manner described, collected upon the filter used in the former decantation, and washed with hot water. The paper and precipitate are ignited in a platinum crucible, cautiously at first to avoid mechanical loss in the evolution of the gaseous product, afterward at the full heat of

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* Blasdale: Analytical Chemistry, Treadwell-Hall, 3rd ed., Vol. II, p. 77.

the burner, and finally to constant weight over the blast-lamp. The residue is weighed as calcium oxide, CaO.

Experimental Process: Determination of Calcium Precipitated as Oxalate. — Weigh out 0.5 grm. of pure dry calcite into a large beaker, add a little water (20 $cm.^3$), cover the beaker with a watch-glass, and add concentrated hydrochloric acid gradually until the evolution of carbon dioxide begins. Warm gently and add the acid until solution is complete, boil to expel carbon dioxide, neutralize carefully with ammonium hydroxide, dilute to a volume of 300 $cm.^3$, color the solution with methyl orange, and heat to boiling. To the boiling solution add dropwise a solution of 1 grm. of oxalic acid with occasional pauses during which neutralization is slowly effected by means of 1 per cent ammonium hydroxide. Let the mixture stand an hour and then filter upon ashless paper, washing with hot water. Ignite carefully, finally at the full heat of the blast-lamp and weigh as calcium oxide, CaO.

The Precipitation of Strontium Oxalate. — The appreciable solubility of strontium oxalate in water is much diminished by the addition of alcohol to the solution. When the alcohol added amounts to a fifth of that of the water solution the precipitation of strontium oxalate by an excess of ammonium oxalate is practically complete. The precipitate thrown down in hot solution and allowed to stand over night may be filtered off on asbestos in the perforated crucible, washed with 20 per cent alcohol, ignited gently in the flame of the Bunsen burner, and weighed as carbonate:

$$SrCl_2 + (NH_4)_2O_2C_2O_2 \rightleftarrows SrO_2C_2O_2 + 2\,NH_4Cl,$$
$$SrO_2C_2O_2 = SrCO_3 + CO_2.$$

The Precipitation of Barium Oxalate. — The addition of alcohol to the amount of a fourth of the water solution brings the insolubility of barium oxalate within the range of solubilities permissible in fairly good analytical operations. An excess of ammonium oxalate added to the alcoholic solution (25 per cent) brings about a practically complete precipitation of barium as the oxalate, and after standing over night the precipitate may be collected on asbestos, washed with 25 per cent alcohol, ignited gently, and weighed as carbonate:

$$BaCl_2 + (NH_4)_2O_2C_2O_2 \rightleftarrows BaO_2C_2O_2 + 2\,NH_4Cl,$$
$$BaO_2C_2O_2 = BaCO_3 + CO_2.$$

The Precipitation of Mercurous Oxalate. — Mercury taken in the form of mercurous nitrate may be estimated as mercurous oxalate precipitated by ammonium oxalate:

$$Hg_2(NO_3)_2 + (NH_4)_2O_2C_2O_2 \rightleftarrows Hg_2O_2C_2O_2 + 2\,NH_4NO_3.$$

It is necessary, however, to control the acidity, dilution, and presence of mercuric salts. It appears that 5 cm.^{3} of dilute nitric acid, sp. gr. 1.15, may be present in a volume of 100 cm.^{3} and that 5 cm.^{3} of the acid will prevent precipitation of small amounts of mercuric salt (0.0100 grm. to 0.0200 grm., calculated as mercury) depending upon the amount of ammonium oxalate present in excess. According to the procedure recommended,* mercurous nitrate dissolved in 100 cm.^{3} of water containing 2 to 5 per cent of dilute nitric acid, sp. gr. 1.15, is precipitated by the addition of ammonium oxalate in slight excess with stirring. It is an easy matter to keep the excess of the precipitant within the limits of 1 cm.^{3} to 2 cm.^{3} of the N/10 solution, because the mercurous oxalate, when properly stirred, settles rapidly. The precipitate is collected on asbestos in a perforated crucible, washed two or three times with cold water, and dried to constant weight over sulphuric acid at the ordinary temperature, since mercurous oxalate is slowly decomposed at temperatures in the vicinity of 100 degrees.

The Precipitation of Copper Oxalate. — Copper oxalate is insoluble in water, is scarcely attacked by moderate amounts of dilute nitric acid, and the precipitation of copper oxalate from solutions of copper salts by saturation with oxalic acid is very nearly complete, provided the amount of the copper salt present exceeds the amount (equivalent to 0.01 grm. of copper in 50 cm.^{3} of liquid) which may remain in supersaturated solution. The addition of a large proportion of acetic acid to the solution tends to prevent supersaturation as well as hydrolytic decomposition, and small amounts as well as the large amounts of copper may be successfully precipitated as the oxalate in 50 per cent acetic acid. The precipitate may be collected on asbestos in the perforated crucible and converted by careful ignition to copper oxide:

$$CuSO_4 + (NH_4)_2O_2C_2O_2 \rightleftarrows CuO_2C_2O_2 + (NH_4)_2SO_4.$$

The Precipitation of Carbonates

In precipitating carbonates, ammonium carbonate is preferable to sodium carbonate or potassium carbonate whenever its use is possible, in order that contamination of the final product by inclusion of a non-volatile precipitant may be obviated; but

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* Peters: Methods in Analysis, Gooch, p. 195.

some carbonates are not quantitatively precipitable by ammonium carbonate.

The Precipitation of Barium Carbonate, $BaCO_3$; Strontium Carbonate, $SrCO_3$; and Calcium Carbonate, $CaCO_3$. — The carbonates of barium, strontium, and calcium may be precipitated almost completely by ammonium carbonate in absence of ammonium salts other than the precipitant and the salts produced in the reaction. Even in presence of ammonium salts the precipitation may be made practically complete by a large excess of ammonium carbonate in a 50 per cent alcoholic solution:

$$\overset{\text{II}}{M}Cl_2 + (NH_4)_2CO_3 \rightleftarrows \overset{\text{II}}{M}CO_3 + 2\,NH_4Cl.$$

Experimental Process: Determination of Barium as Carbonate. — Dissolve 0.5 grm. of barium chloride, $BaCl_2 \cdot 2\,H_2O$ in water (50 cm.^{3}), add ammonium carbonate in excess, heat the liquid to granulate the precipitate, add alcohol until it equals 50 per cent of the solution, settle the precipitate, filter on asbestos in the perforated crucible, wash, ignite to low red heat, and weigh as barium carbonate, $BaCO_3$.

The Precipitation of Magnesium Ammonium Carbonate, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O$. — When the very concentrated solution of the sulphate, nitrate, or chloride of magnesium is treated with a concentrated solution of ammonium carbonate a voluminous precipitate forms which is further acted upon by an excess of the precipitant, sometimes dissolving completely, and is converted to crystalline magnesium ammonium carbonate, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O$.* This precipitate is noticeably soluble in the aqueous solution of the precipitant. By adding to the solution an equal amount of alcohol and making the precipitation with an equal amount of strongly ammoniacal 50 per cent alcohol saturated with ammonium carbonate the precipitation may be made practically complete.† In practice, the solution containing salts of magnesium (and salts of the alkalies besides) is brought to a volume of about 50 cm.^{3}, an equal amount of absolute alcohol is added, precipitation is

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* Schaffgotsch: Ann. Phys., **104,** 482 (1858).

† Gooch and Eddy: Methods in Chemical Analysis, Gooch, p. 154.

made by addition of 50 cm.^{3} of the saturated ammoniacal ammonium carbonate solution containing 50 per cent alcohol, and, after stirring for five minutes, the mixture is allowed to stand some hours, preferably over night. If an alkali salt is present in amount not exceeding 0.1 grm., the precipitate may be collected on asbestos in a perforated crucible, washed with the precipitant, dried, ignited, and weighed as magnesium oxide. When the amount of alkali salt originally present is larger the precipitate may be freed from traces of the alkali salt by pouring off the supernatant liquid through the weighed asbestos filter, dissolving the precipitate, and precipitating ammonium magnesium carbonate as at first. This second precipitate, collected upon the filter originally used, leaves upon ignition practically pure magnesium oxide:

$$MgCl_2 + 2\,(NH_4)_2CO_3 + 4\,H_2O \rightleftarrows MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O + 2\,NH_4Cl.$$

Experimental Process: Determination of Magnesium. — Draw from a burette 50 cm.^{3} of a solution of magnesium chloride (about N/10 in respect to the anhydrous salt) standardized as the sulphate, according to the process previously described. (Page 48.) Add an equal volume of absolute alcohol (50 cm.^{3}), and an equal volume (50 cm.^{3}) of saturated ammoniacal solution of ammonium carbonate in 50 per cent alcohol.* Stir for five minutes, allow the mixture to stand at least twenty minutes, filter on asbestos, wash with the precipitant, ignite, and weigh the residue as magnesium oxide, MgO.

The Precipitation of Zinc Carbonate (Basic) and Cadmium Carbonate. — Zinc carbonate and cadmium carbonate are not completely precipitated by ammonium carbonate nor by sodium or potassium carbonate in presence of ammonium salts. By treating with sodium or potassium carbonate the solution containing ammonium salts and boiling, the ammonium salts may be converted into sodium salts with the expulsion of ammonia. Upon dissolving in hydrochloric acid the precipitated carbonate thus formed, which may include considerable amounts of alkali salt, and carefully reprecipitating with the fixed alkali

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* Best made by adding to a strong aqueous solution of ammonium carbonate, containing ammonium hydroxide, an equal volume of absolute alcohol, and decanting the liquid from the precipitate of ammonium carbonate thus formed.

carbonate the precipitate may be recovered in purer condition. The precipitant is added to the acid solution until a turbidity is produced, the solution is heated to precipitate the greater part of the zinc or cadmium carbonate in granular form, then a few drops of phenolphthalein are added, and enough of the precipitant to bring out a pink color distinctly. The solution is filtered *hot* on asbestos in the perforated crucible, washed with hot water, ignited, and weighed as oxide. In this process some of the precipitate falls as a basic salt other than the carbonate and unless this basic salt is completely decomposed in the ignition the results of the process will be falsified. For this reason the process is at its best when applied to the analysis of nitrates or chlorides:

$$3\,Zn(NO_3)_2 + 3\,Na_2CO_3 + H_2O \rightleftarrows Zn_3(OH)_2(CO_3)_2 + CO_3 + 6\,NaNO_3.$$

The Precipitation of Bismuth Basic Carbonate. — Bismuth is precipitated from the solution of the *nitrate* by addition of ammonium carbonate in slight excess, the composition of the precipitate being variable with the conditions of temperature, dilution, and excess of the precipitant. Ordinarily the precipitate may be regarded as a basic carbonate (hydroxy-oxy-carbonate), approximating the constitution represented by the symbol $Bi_4(OH)_2O_3(CO_3)_2$; but with the basic carbonate is ordinarily included a basic bismuth salt derived from the soluble bismuth salt acted upon. It is for this reason that the bismuth salt taken for analysis by this method should be the nitrate which, upon ignition, is converted to oxide as is the basic carbonate. The precipitate is collected upon asbestos in the perforated crucible,

$$12\,BiCl_3 + 18\,(NH_4)_2CO_3 + 3\,H_2O \rightleftarrows 2\,Bi_2(CO_3)_3 \cdot 3\,Bi_2O_3 \cdot 2\,BiO_3H_3 + 12\,CO_2 + 36\,NH_4Cl,$$

washed with hot water, ignited, and weighed as the oxide, Bi_2O_3.

The Precipitation of Hydroxides

Of hydroxides which are available for determinative purposes, the hydroxides of silicon and tungsten may be taken as types of acidic hydroxides, and the hydroxides of aluminium, chromium, and iron may be taken as representative basic hydroxides. The acidic hydroxides may be formed by the action of suitable acids upon susceptible salts; the basic hydroxides, by the action of soluble hydroxides or by the hydrolytic effect of water upon susceptible salts.

Acidic Hydroxides

The Precipitation of Silicic Acid from Silicates. — When a silicate in solution is treated with acid the silicic acid is found as hydrosol or as hydrogel, the proportions varying according to the condition of action.

$$Na_2SiO_4 + 4\,HCl = H_4SiO_4 + 4\,NaCl.$$

Upon evaporating the liquid the hydrosol is converted to the hydrogel and the hydrogel, losing water, becomes more insoluble. Upon desiccating the residue, further, best at about 110 degrees, the silica becomes still more insoluble, but by no means absolutely so; for upon filtering and evaporating the acidified filtrate appreciable amounts (some milligrams), depending upon the temperature and thoroughness of the desiccation, may be recovered in a second filtration, leaving still smaller amounts which may be separated from solution by another evaporation. Repeated moistenings and evaporations before the first filtration are not (in the presence of soluble salts) as effective in separating the silica as are repeated evaporations with interpolated filtrations. A final ignition at red heat leaves the silicon dioxide (*silica*) in anhydrous form:

$$H_4SiO_4 = SiO_2 + 2\,H_2O.$$

Silica, like colloidal precipitates in general, is known to take up foreign material which is not wholly removed when the colloidal form is modified by desiccation, nor by digestion with acid. Upon treating such a precipitate with hydrofluoric acid and sulphuric acid silicon fluoride volatilizes and a sulphate residue is left. If the contaminating substance is an alkali salt, like the sodium chloride resulting from the action of acid upon the product of fusion of a silicate with sodium carbonate, the residue will remain as sulphate even at high temperatures;

but certain other contaminating sulphates may on strong ignition leave oxides. It is plain, therefore, that in determining silica separated from a silicate by the action of acid the amount of included impurity should always be determined by weighing the residue of the treatment with hydrofluoric acid and sulphuric acid; and, in order that the residue of this treatment may be as nearly as possible identical with the contaminating material in the silica when it is weighed, it is best to treat the silica, before its final ignition for weighing, with a drop or two of strong sulphuric acid and to subject the products of such treatment to a temperature similar to that employed in the ignition of the final residue left after the treatment with hydrofluoric acid and sulphuric acid.

Experimental Process: Determination of Silica. — Weigh out in a platinum crucible about 0.5 grm. of precipitated silica, the purest obtainable.* Ignite it for half an hour over the full heat of a Bunsen burner, cool, and weigh. Take the difference in weights as the weight of the anhydrous silica. Now add 2 grm. of anhydrous sodium carbonate and mix it thoroughly with the silica by means of a stiff platinum wire, brushing off into the crucible, by means of a camel's hair brush, any particles of material adhering to the wire. Cover the crucible, heat the mixture gradually to the highest temperature of the Bunsen burner and then, if necessary to secure complete fusion, over the blast lamp. As soon as the mass is in quiet fusion, evolving no gas bubbles, so that it may be assumed that the reaction between the silica and the sodium carbonate is complete, take the crucible in tongs applied to the upper edge, and give it a gyratory motion by which the liquid melt is spread over the wall of the crucible. Upon cooling, the solid material may be loosened from the crucible by gentle tapping. Put the solid material, thus loosened, in a rather tall beaker, add water and, gradually, hydrochloric acid (sp. gr. 1.1) to dissolve the excess of the carbonate and to break up the silicate, and treat the material which adheres to the crucible similarly. In case the greater part of the material adheres obstinately, place the crucible in the beaker and treat it with the adherent material in the manner described. Place the beaker on a water-bath and when the disintegration of the melt is complete (aided if necessary by pressure with the rounded end of a glass rod) transfer the contents to a dish of porcelain or (better) platinum, evaporate the liquid, and dry the residue at 110 degrees. Drench the

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* The purity of the silica may be tested by the treatment (with hydrofluoric acid and sulphuric acid) described below for the determination of the impurity in the silica obtained in the analytical process.

residue with concentrated hydrochloric acid, add an equal amount of water, cover the dish, and digest for half an hour, with occasional stirring. Add more water, stir (and, if necessary, grind with a pestle to break up lumps), settle the precipitate, pour off the supernatant liquid upon an ashless filter, wash again by decantation, transfer the precipitate to the filter, wash, and dry.

Return the filtrate to the dish, evaporate to dryness, and treat the residue, in the manner described above, for the recovery of the silica (probably several milligrams) which did not separate in the first evaporation. Even after the second treatment, traces of silica escape precipitation; but, if the desiccation at 110 degrees has been thorough, the amount lost should not exceed about 0.0005 grm., in the average. Put the filter containing the silica in a weighed crucible recovered in the second treatment with that containing the main portion of silica and ignite cautiously until the paper is destroyed, and then at the full heat of the Bunsen burner for half an hour. Moisten the residue with a drop or two of sulphuric acid, heat cautiously, ignite to low redness, cool, and weigh. Then ignite again to constant weight. The difference between this weight and that of the crucible is the weight of the silica plus some sodium sulphate.

Moisten the silica in the crucible with water, add 10 cm.^{3} of hydrofluoric acid, which distils without residue, and a drop or two of concentrated sulphuric acid, and evaporate the hydrofluoric acid (on the water-bath under a good draft-hood) repeating the operation if any solid residue is left. Continue the evaporation to remove the sulphuric acid, by placing the crucible upon a triangle suspended within a large porcelain crucible, or cone of iron (the radiator), heating the latter with a Bunsen burner. Finally ignite the crucible and residue to low redness, cool, ignite, and weigh.

Deduct the weight of the crucible plus that of the residual sodium sulphate, which is inevitably present, from the previously found weight of the crucible, silica, and residue to discover the weight of the silica. Compare the weights of the silica found with that of the silica taken, stating the actual results and the percentage result.

Hydrous silica taken.	Anhydrous silica taken.	Silica recovered with impurity.	Silica corrected.	Error in recovery of anhydrous silica.
Grm.	Grm.	Grm.	Grm.	Grm.

The Determination of Tungsten Trioxide in Tungstates. — When the aqueous solution of an alkali tungstate is treated with an excess of hydrochloric acid and submitted to evaporation the tungstic acid is very largely separated. After drying at 120 degrees, moistening with hydrochloric acid, and boiling out with water containing hydrochloric acid (6 per cent) or ammonium nitrate (10 per cent) as coagulants, the precipitate of yellow tungstic acid may be filtered off, ignited, and weighed as tungsten trioxide, WO_3. But as in the determination of silica by similar procedure not all the tungstic acid is recovered in one operation. Several repetitions of the process of desiccation, extraction, and filtration are essential for the complete recovery of the tungstic acid:

$$Na_2WO_4 + 2\,HCl = H_2WO_4 + 2\,NaCl.$$
$$H_2WO_4 = WO_3 + H_2O.$$

Basic Hydroxides

The Precipitation of Aluminium Hydroxide. — Aluminium hydroxide is easily attacked by an excess of the fixed alkali hydroxides, and these reagents are, therefore, not available for its complete precipitation. Ammonium hydroxide in slight excess and in presence of an ammonium salt (to act as the coagulant of the aluminium hydroxide hydrosol) brings about an approximately complete precipitation of the hydroxide from solution of the halogen salts, the nitrate, or the sulphate, and precipitation is made practically complete by boiling the solution.

$$AlCl_3 + 3\,NH_4OH \rightleftarrows AlO_3H_3 + 3\,NH_4Cl.$$

The reaction is reversible and care must be taken to make sure that the solution shall always retain enough of the volatile ammonia to render it distinctly alkaline. The hydroxide precipitated in this manner is, however, not entirely pure, but retains some of the acidic ion of the original aluminium salt now combined in a basic salt, which, if it is chloride, nitrate, or sulphate, undergoes dissociation on heating and leaves the oxide, as does the hydroxide. The presence of certain organic salts — e.g., tartrates and citrates — prevents precipitation.

The precipitate may be obtained in more easily filterable form if the precipitation is first made by a hydrolytic method, and only completed by the direct action of ammonium hydroxide. Thus, the precipitation may be mainly effected by treating the solution of the aluminium salt with sodium thiosulphate (*Chancel*) and boiling out sulphur dioxide:

$$Al_2(SO_4)_3 + 3\,Na_2S_2O_3 + 3\,H_2O = 2\,AlO_3H_3 + 3\,Na_2SO_4 + 3\,SO_2 + 3\,S.$$

But it is to be noted that in this operation some of the sulphur dioxide may become oxidized by the action of air and form sulphuric acid,

$$2\,SO_2 + O_2 + H_2O = 2\,H_2SO_4,$$

so that the precipitation must be completed by addition of ammonium hydroxide in slight excess to the boiling solution.

Or the greater part of the precipitation may be similarly brought about by sodium nitrite (*Wynkoop: Schirm*) and the neutralization is then completed by ammonium hydroxide:

$$\begin{aligned} Al_2(SO_4)_3 + 6\,NH_4NO_2 + 3\,H_2O &= 2\,Al_2O_3H_3 \\ &\quad + 3\,(NH_4)\,2\,SO_4 + 6\,HNO_2, \\ 3\,HNO_2 &= HNO_3 + 2\,NO + H_2O, \\ HNO_3 + NH_4OH &= NH_4NO_3 + H_2O. \end{aligned}$$

Or the aluminium salt, which of itself undergoes incipient hydrolysis in water, may be treated with an iodide-iodate mixture (which at once reacts with the acid set free), liberating iodine and the iodine taken up by sodium thiosulphate (*Stock*). In this process no free acid is formed and the final addition of ammonium hydroxide is not necessary:

$$\begin{aligned} 2\,AlCl_3 + 6\,HOH &\rightleftarrows 2\,AlO_3H_3 + 6\,HCl, \\ KIO_3 + 5\,KI + 6\,HCl &= 6\,KCl + 3\,H_2O + 3\,I_2, \\ I_2 + Na_2S_2O_3 &= 2\,NaI + Na_2S_4O_6. \end{aligned}$$

Experimental Processes: Determination of Aluminium Precipitated as Hydroxide and Weighed as Oxide. — Dissolve in hot water about 1 grm. of alum, $NH_4Al(SO_4)_2 \cdot 12\,H_2O$ or $KAl(SO_4)_2 \cdot 12\,H_2O$, weighed exactly; dilute the solution to a volume of about 300 cm.^{3}; add concentrated nitric acid (about 5 cm.^{3}), to make a considerable amount of ammonium salt in the subsequent neutralization and thus favor the formation of the aluminium hydroxide hydrogel rather than the hydrosol; heat the solution to boiling and add in slight excess ammonium hydroxide freshly made by charging distilled water with ammonia gas, in order that it may be free from contaminating materials taken up by long standing in glass; and set the mixture aside to settle the precipitate. Decant the clear supernatant liquid upon a paper filter protected at the point by a perforated cone of platinum or of parchment paper; dilute the remaining liquid to the original volume with hot water containing ammonium nitrate (1 per cent) and a very little ammonium hydroxide; transfer the liquid to the filter; and wash with slightly ammoniacal hot water containing ammonium nitrate (1 per cent). At the end of the washing, apply the suction of the filter pump to compact the precipitate; dry, ignite cautiously at first, and later at the full heat of the Bunsen burner, until the carbon of the paper has been entirely consumed and any basic aluminium sulphate of the precipitate has been converted to oxide, and weigh the residue as Al_2O_3.

The Precipitation of Chromic Hydroxide. — Chromium in chromic chloride, nitrate or sulphate is precipitated by the methods described above for the precipitation of aluminium hydroxide, and the reactions involved are precisely similar. From a soluble chromate the chromic salt may be formed by the action of hydrochloric acid and alcohol in the boiling solution (with formation of aldehyde),

$$\begin{aligned} K_2Cr_2O_7 + 14\,HCl + 3\,C_2H_5OH \\ &= 2\,KCl + 2\,CrCl_3 + 3\,Cl_2 + 7\,H_2O + 3\,C_2H_5OH \\ &= 2\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,C_2H_4O + 6\,HCl, \end{aligned}$$

or by sulphur dioxide,

$$K_2Cr_2O_7 + 3\,SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O,$$

and the chromic chloride or sulphate may then be precipitated as hydroxide, ignited, and converted to oxide for weighing.

Experimental Process: Determination of Chromium Precipitated as Chromic Hydroxide and Weighed as Chromic Oxide. — Dissolve in a porcelain dish about 0.5 grm. of potassium dichromate (weighed exactly) in 10 cm.^{3} of hot water, add 15 cm.^{3} of alcohol, and 5 cm.^{3} of concentrated hydrochloric acid. Cover with a water-glass (to prevent loss by spattering) and boil until the clear green color of the liquid indicates that the reduction has been completed. Dilute the solution to a suitable volume (250 cm.^{3}) with hot water, add ammonium hydroxide in very slight excess (or make the neutralization nearly complete with ammonium hydroxide and complete the precipitation by means of freshly made ammonium sulphide added in slight excess); heat the mixture to boiling until the liquid above the precipitate, allowed to settle, is colorless. Filter on ashless paper, wash carefully with hot water. Dry precipitate and paper, separate the precipitate as well as possible from the paper, put the precipitate in a platinum crucible, burn the paper held in a spiral of platinum wire over the crucible, and add the ash to the contents of the crucible. Ignite gently at first, then at red heat in a draft of air to constant weight. Weigh the residue as Cr_2O_3.

The Precipitation of Ferric Hydroxide. — Iron in the form of ferric chloride, nitrate, or sulphate is precipitable by ammonium hydroxide in presence of ammonium salts and in this case the presence of a considerable excess of the precipitant does not materially increase the solubility of the precipitate:

$$FeCl_3 + 3\,NH_4OH \rightleftarrows FeO_3H_3 + 3\,NH_4Cl.$$

The precipitate retains some of the acidic ion in the form of a basic salt, but this, if it is a chloride, nitrate, or sulphate, is dissociated on ignition. Like aluminic hydroxide, ferric hydroxide (or a basic salt) is also precipitable by the iodide-iodate mixture or by ammonium nitrite; but sodium thiosulphate reduces the ferric salt to the ferrous condition and fails to bring about precipitation. In fact, aluminium and iron may be separated approximately by the hydrolytic action of sodium thiosulphate upon the mixed salts. Iron in a ferrous salt may be determined by oxidation with a suitable oxidizer (chlorine, bromine, or nitric acid, or the iodide-iodate mixture) and treatment of the ferric salt as described.

Experimental Process: Determination of Iron Precipitated as Ferric Hydroxide and Weighed as Ferric Oxide. — Weigh out exactly about 1 grm. of clean crystals of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$; dissolve in water (100 $cm.^3$), add hydrochloric acid (5 $cm.^3$), and nitric acid (2 $cm.^3$). Boil the solution (with addition of more nitric acid, if necessary) until the precipitate formed on addition of a drop or two of ammonia is reddish — not black. Dilute the solution to a convenient volume (300 $cm.^3$), add ammonium hydroxide in slight excess, boil, filter on paper, wash with care, and ignite.

The Basic Acetate Process. — The acetates of iron and aluminium are hydrolyzed when heated in dilute solution and if a sufficient amount of a coagulant be present the hydroxides or basic salts may be precipitated in the hydrogel form. On the other hand, acetates of nickel, cobalt, zinc, and manganese are not so easily hydrolyzed. The basic acetate precipitation may therefore be applied to the separation of iron and aluminium from nickel, cobalt, zinc, and manganese as well as calcium, barium, strontium, magnesium, and the akali elements, although for aluminium unaccompanied by iron the separation is less satisfactory than for iron or for iron with aluminium.

After neutralizing the solution with great care by means of sodium carbonate, or ammonium carbonate, added dropwise in dilute solution until, after vigorous stirring, a faint permanent turbidity remains, hydrochloric acid is added dropwise, with long intervals between the additions and stirring, until the turbidity (which, if the solution is dark from much iron, may be better seen against a white background) is just dissolved. To the clear solution is then added 2 grm. to 3 grm. of sodium acetate, or ammonium acetate (made neutral), in solution, and a large volume (400 $cm.^3$ to 700 $cm.^3$) of boiling water. The liquid is boiled for some minutes, and then filtered hot without suction upon a filter protected for the subsequent application of suction, and washed with hot water containing a little sodium acetate or ammonium acetate. After the washing is complete suction is applied to compact the precipitate.

The precipitate obtained in the manner described may still retain traces of nickel, cobalt, zinc, and manganese, and traces of aluminium and iron will have been carried into the filtrate. The precipitate is, therefore, dissolved in hot hydrochloric acid (1 : 2) and reprecipitated by ammonium hydroxide to recover the iron hydroxide and aluminium hydroxide in purer condition; and from the combined filtrates the dissolved traces of these two hydroxides are recovered by concentration to the lowest convenient limit, treatment with a bare excess of ammonium hydroxide, and filtration.*

The Precipitation of Sulphides

Some insoluble sulphides are precipitable by hydrogen sulphide from water solution in the presence of free acid, and some only in alkaline solution.† Precipitated sulphides, however,

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* It should be noted that the precipitates found in the presence of phosphoric acid and arsenic acid contain aluminiac and ferric salts of these acids.

† In precipitating the latter ammonium sulphide is used as the precipitant, except in certain special cases. Such precipitations are often made to effect the separation of the precipitable sulphides from salts of the alkali-earth elements; and in these cases it is essential that the ammonium sulphide should be freshly made and free from ammonium carbonate. The ammonium sulphide may be prepared free from carbonate by saturating with hydrogen sulphide a solution of ammonium hydroxide which has been made by absorbing in water, freshly boiled and cooled in a cur-

are generally oxidizable in the air at moderately elevated temperatures, and if they are to be weighed as such, must be protected from oxidation in the preparation for weighing, by taking care to moderate the temperature of desiccation (as in drying mercury sulphide, and the arsenic sulphides), by heating (Fig. 21) in a current of pure carbon dioxide (as in determining antimony trisulphide, see p. 104), or by ignition in mixture with pure sulphur in a Rose crucible (Fig. 22) kept filled with hydrogen which is introduced through the perforated cover (as in determining copper, see p. 105). In some cases it is necessary to convert the precipitated sulphide to some other form for weighing.

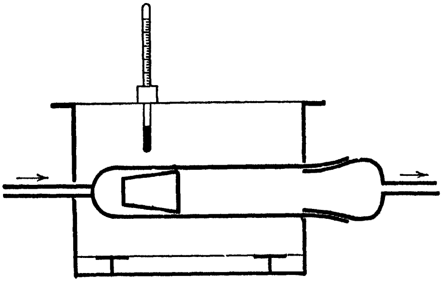
FIG. 21.

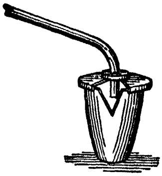
FIG. 22.

Sulphides Precipitable in Acid Solution

The Precipitation of Mercuric Sulphide by Hydrogen Sulphide. — The formation of insoluble mercuric sulphide by the action of hydrogen sulphide upon the mercuric salt in solution is a simple process well adapted to the determination of mercury, provided the solution does not contain nitric acid or other oxidizer which will set free sulphur from hydrogen sulphide. In the first action complex double compounds of light color are formed which are converted to the black mercuric

rent of purified air, the gaseous ammonia evolved from a solution of concentrated ammonium hydroxide first digested with lime and then brought to the boiling point.

sulphide when the liquid is thoroughly saturated with hydrogen sulphide.

$$(m+n)HgCl_2 + mH_2S = mHgS \cdot nHgCl_2 + 2\,mHCl.$$
$$mHgS \cdot nHgCl_2 + nH_2S = (m+n)HgS + 2\,nHCl.$$

The precipitate, after settling, is filtered on asbestos in the perforated crucible, washed with cold water, dried at 105 to 110 degrees and weighed as mercuric sulphide.

Experimental Process: Determination of Mercury in Mercuric Chloride. Dissolve 0.5 grm. of mercuric chloride in a little hot water, dilute to 100 cm.^{3} with cold water, and saturate the cold solution with hydrogen sulphide. Collect the precipitate upon asbestos in the perforated crucible, dry at 105 to 110 degrees to constant weight, and weigh as mercuric sulphide, HgS.

When mercuric nitrate is treated with hydrogen sulphide the sulphur set free in a secondary action between nitric acid and hydrogen sulphide may contaminate the precipitated sulphide and vitiate the result; and this effect is much magnified when the solution contains a considerable excess of nitric acid, as is often the case in practical analysis. In such cases the following more elaborate procedure is adopted.

The Precipitation of Mercuric Sulphide by Decomposition of the Sulphosalt. — The solution of the mercuric salt acid in reaction is treated with sodium carbonate nearly to neutralization, and then a mixture of freshly prepared ammonium sulphide and sodium hydroxide is added, with warming and stirring, until the soluble mercury sulphosalt is formed. Ammonium nitrate is added and the solution is boiled until the free ammonia is nearly all expelled:

$$\begin{aligned} Hg(NO_3)_2 + 4\,(NH_4)_2S + 4\,NaOH & \\ &= HgS + Na_2S + 2\,NaNO_3 + 4\,NH_4OH \\ &= Hg(SNa)_2 + 2\,NaNO_3 + 4\,NH_3 + 4\,H_2O, \end{aligned}$$
$$Hg(SNa)_2 + 2\,NH_4NO_3 = HgS + 2\,NaNO_3 + (NH_4)_2S.$$

The precipitated mercuric sulphide is settled, collected on asbestos in the perforated crucible, and washed with hot water; and admixed sulphur is extracted by pure carbon disulphide applied after washing away the repellant water from the precipitate by means of alcohol. A final washing with alcohol, followed by ether, prepares the precipitate for drying at 105 to 110 degrees in the air-bath.

The Precipitation of Arsenic Trisulphide, As_2S_3. — When the cold solution of compounds of arsenic in the trivalent condition is acidified strongly with hydrochloric acid, hydrogen sulphide precipitates arsenic trisulphide:

$$2\,AsCl_3 + 3\,H_2S \rightleftarrows As_2S_3 + 6\,HCl.$$

The excess of hydrogen sulphide is largely removed from the solution by a current of carbon dioxide and the arsenic trisulphide, collected upon asbestos in the perforated crucible, is dried to constant weight at 105 degrees.

The Precipitation of Arsenic Pentasulphide, As_2S_5. — If the solution of compounds of arsenic in quinquivalent form is *kept cool* (best by immersing the container in ice-water) while being treated with twice its volume of concentrated hydrochloric acid, the arsenic remains in solution as the pentachloride. By rapidly saturating such a solution with hydrogen sulphide, and allowing it to stand in a stoppered flask for a considerable period (two hours) arsenic pentasulphide is precipitated:

$$2\,AsCl_3 + 5\,H_2S \rightleftarrows As_2S_5 + 10\,HCl.$$

This precipitate may be collected on asbestos in the perforated crucible, washed with water and then with alcohol (to facilitate the removal of water), dried at 105 degrees, and weighed as the pentasulphide. It is essential, however, that the acidified solution be kept thoroughly cooled until the pentasulphide is precipitated, else the higher chloride will dissociate partially to arsenic trichloride and chlorine with the result that the precipitate will consist of arsenic trisulphide, arsenic pentasulphide, and sulphur in indefinite mixture, while some of the sulphur may be lost in the filtration or undergo oxidation in the drying.

The Precipitation of Antimony Trisulphide; Sb_2S_3. — *Antimonous Salts.* When a current of hydrogen sulphide acts upon a salt of trivalent antimony in a hot solution, sufficiently acidulated with hydrochloric acid (with addition of tartaric acid or without it, as may be preferred), to prevent the precipitation of an antimony oxychloride, antimony trisulphide is precipitated as an orange precipitate which grows redder and denser if the solution is kept at the boiling temperature while the current of hydrogen sulphide is passed for a considerable time:

$$2\,SbCl_3 + 3\,H_2S \rightleftarrows Sb_2S_3 + 6\,HCl.$$

The precipitate may be settled, collected upon asbestos in a perforated crucible, and washed with a hot 1 per cent (acid) solution of ammonium acetate containing hydrogen sulphide, followed in succession by alcohol, carbon disulphide, alcohol, and ether, and dried at 110 degrees for weighing.

If the boiling solution in which precipitation takes place is made up to contain a fourth of its volume of concentrated hydrochloric acid, the precipitate will become very dark, dense and crystalline upon prolonged boiling in the current of hydrogen sulphide and agitation (*Vortmann and Metzel*). Under these conditions the precipitation is not quite complete but may be made so by diluting the solution with an equal volume of water while continuing the operation a few minutes longer. The precipitate may be collected upon asbestos, and washed with hot water (without showing any tendency to pass into the hydrosol form) followed in succession by alcohol, carbon disulphide, alcohol, and ether, and dried at 110 degrees; or the precipitated antimony suphide may, after the washing with hot water, be heated in carbon dioxide, as described below.

Antimonic Salts. — By a procedure similar to that which has been described as applicable to the precipitation of antimony trisulphide from antimonous salts, the same product, mixed with sulphur, may be obtained from antimonic salts:

$$2\,SbCl_5 + 5\,H_2O \rightleftarrows Sb_2S_3 + 10\,HCl = Sb_2S_3 + 10\,HCl + S_2.$$

In this case the removal of the excess of sulphur may be best accomplished by volatilization. The precipitate is washed with aqueous ammonium acetate, or with water, heated in the filter crucible enclosed in a tube or other suitable apparatus (see p.

101), in an air-free atmosphere of carbon dioxide first at 100 to 130 degrees, and finally at 270 to 280 degrees, and weighed as antimony trisulphide.

The Precipitation of Cupric Sulphide and Weighing as Cuprous Sulphide. — In order that precipitated cupric sulphide may settle well it is precipitated from a solution containing a regulated amount of free acid. The solution should contain 5 per cent by volume of concentrated acid, preferably sulphuric acid. Hydrogen sulphide is passed into the hot solution and the current of gas is continued while the solution cools. The precipitate thus formed,

$$CuSO_4 + H_2S \rightleftarrows CuS + H_2SO_4,$$

is settled, collected upon a paper filter protected by a platinum point so that suction may be later applied without danger to the filter, although at the outset the filtration is best made without suction. It is washed with water charged with hydrogen sulphide and containing a little acetic acid. The filter should be kept full to the very last during the filtration and washing, to avoid oxidation of the sulphide to soluble form (sulphate and thiosulphate) which by reaction with the hydrogen sulphide will again form cupric sulphide in the hydrosol condition precipitable by coagulation in the filtrate. Finally, suction is applied to drain the precipitate which is dried on the paper at 90 to 100 degrees. The precipitate is transferred as completely as may be to a Rose crucible (p. 101); the paper is burned in a platinum spiral, and the ash, first collected on a crucible cover and reignited to burn all carbon, is introduced; pure sulphur (recrystallized) from carbon disulphide, so that it will leave no residue when volatilized, is added; the cover is put in place upon the crucible, and through the perforation hydrogen is introduced from a generator at the rate of about four bubbles per second in the wash bottle; the crucible is heated, gently at first and then so that the bottom shows faint redness, until the hydrogen flame shows no blue color of sulphur and emits no odor of sulphur dioxide:

$$2\,CuS = Cu_2S + S.$$

The crucible is cooled nearly to atmospheric temperature in an increased flow of hydrogen, placed in a desiccator to cool thoroughly, and weighed. The difference between the weight of the crucible and that of the crucible with the residue is the weight of the cuprous sulphide, Cu_2S.

The Precipitation of Zinc Sulphide. — Zinc may be precipitated as the sulphide from ammoniacal solutions or from solutions of regulated acidity.

A. According to the first procedure the solution, contained in an Erlenmeyer flask, is treated with sodium carbonate until some zinc carbonate is precipitated. The precipitate is dissolved by a very little ammonium hydroxide and to the solution is added ammonium acetate, or, better, ammonium thiocyanate, in the proportion of 5 grm. to every 100 $cm.^3$ (to coagulate the sulphide to be formed), and then freshly made ammonium sulphide in excess:

$$ZnCl_2 + (NH_4)_2S \rightleftarrows ZnS + 2\,NH_4Cl.$$

The mixture is diluted with boiled water, and the flask, nearly full and stoppered, is set aside to stand some hours (twelve to twenty-four). The clear liquid is decanted upon a filter; the precipitate is diffused through a 5 per cent solution of ammonium acetate or thiocyanate and again settled; and the liquid is poured upon the same filter while the filtrate is allowed to run into an empty beaker so that in case of necessity it may be refiltered apart from the first decantation. After several repetitions of the washing by decantation the precipitate is transferred to the filter, carefully washed with the coagulating mixture (keeping the filter full) and finally with water containing ammonium sulphide. The dried precipitate and the filter may be ignited apart, and the combined residues mixed with sulphur, ignited in hydrogen (see p. 101), and weighed as zinc sulphide, ZnS. Or the precipitated sulphide may be dissolved from the filter in hot dilute hydrochloric acid; the solution received and evaporated to dryness in a weighed crucible; the residue dissolved in a little water, mixed with pure (precipitated) mercuric oxide (*Volhard*); the mixture dried and gently ignited to volatilize the mercuric chloride formed and the mercury derived from the excess of mercuric oxide; and the residue weighed as zinc oxide:

$$\begin{aligned} ZnS + 2\,HCl &= ZnCl_2 + H_2S, \\ ZnCl_2 + HgO &= ZnO + HgCl_2. \end{aligned}$$

B. According to a second procedure (applicable to the separation of zinc from alkali and alkali-earth elements) ammonium chloride or sulphate (5 grm. to 100 cm.^{3}) and ammonium acetate (1 grm.) are added to the slightly acid solution and hydrogen sulphide is passed into the solution to saturation. The precipitate, which coagulates much better in presence of the acetic acid set free than in ammoniacal solution, is allowed to settle completely and then is collected upon paper and washed with a two per cent solution of acetic acid saturated with hydrogen sulphide; and the paper and precipitate are treated as described in the preceding paragraph:

$$ZnO_2\,(C_2H_3O)_2 + H_2S \rightleftarrows ZnS + 2\,HOC_2H_3O.$$

C. To precipitate zinc as sulphide while nickel and cobalt salts remain in solution requires the careful adjustment of a notable excess of acid. Instead of depending upon regulation of the amount of free acetic acid (as may also be done more or less successfully) it is better to rely upon a limited excess of hydrochloric acid to prevent precipitation of the nickel and cobalt sulphides and then to take advantage of the coagulating action of the neutral salt of a strong acid to precipitate the colloidal zinc sulphide.

To the acid solution from which zinc sulphide is to be precipitated, sodium carbonate is added until a slight permanent precipitate is formed. Hydrochloric acid (N/10) is added, with stirring, until the precipitate is just dissolved and then in excess amounting to 10 cm.^{3} of the N/10 acid (0.0365 grm.) in every 100 cm.^{3}. Next is added an electrolyte (2 grm. to 5 grm. in 100 cm.^{3}) to serve as a coagulant of the sulphide to be formed, best ammonium thiocyanate (*Zimmermann*), chloride, or sulphate (*Kramers*); the solution is heated to 50 or 60 degrees;

saturated with hydrogen sulphide, and allowed to stand unt the pure white precipitate has settled:

$$\mathrm{ZnCl_2 + NiCl_2 + CoCl_2 + n(NH_4Cl) + H_2S}$$
$$\rightleftarrows \mathrm{ZnS + NiCl_2 + CoCl_2 + nNH_4Cl + 2\,HC}$$

The precipitate is collected on paper, washed with a solutio of the coagulant (2 per cent), dried, ignited until the paper i ashed, reignited with sulphur in hydrogen and weighed a sulphide; or it may be converted to oxide and weighed as in *A*

Precipitation of Nickel Sulphide and Cobalt Sulphide i Acetic Acid Solution. — Nickel and cobalt may be precipitate nearly completely from a solution which is acid only wit acetic acid at not too great concentration:

$$\mathrm{NiO_2(C_2H_3O)_2 + H_2S \rightleftarrows NiS + 2\,HOC_2H_3O,}$$
$$\mathrm{CoO_2(C_2H_3O) + H_2S \rightleftarrows CoS + 2\,HOC_2H_3O.}$$

The process is adapted to the separation of these element from manganese as well as from the alkali and alkali-eart elements. The solution of small volume containing chloride or sulphates of these elements is treated with an excess c sodium carbonate, then made strongly acid with acetic aci diluted to a volume of 100 to 200 cm.^{3}, treated with ammoniu acetate (amounting to 5 per cent of the solution), heated t 70 or 80 degrees, and charged to saturation with hydroge sulphide. The precipitate of nickel sulphide and cobalt sulphide is filtered off and washed with hot water. In the filtrat will be found the manganese, the alkali and alkali-earth elements, with small amounts of nickel and cobalt which may b recovered by concentrating the solution, neutralizing wit ammonium hydroxide containing a little fresh ammoniu sulphide, making slightly acid with acetic acid, warming, an again filtering. The recovered traces and the main precipitat of nickel sulphide and cobalt sulphide are dried and ignite with the filters, and the residue of mixed oxides and sulphide is dissolved in *aqua regia.* Repeated evaporations with hydrochloric acid leave a residue of chlorides which may be treate by appropriate methods (see p. 112) for the separation an determination of nickel and cobalt.

The Precipitation of Stannous Sulphide and Stannic Sulphide, with Weighing as Stannic Oxide.—From stannous chloride in solution hydrogen sulphide precipitates brown stannous sulphide,

$$SnCl_2 + H_2S \rightleftarrows SnS + 2\,HCl,$$

which after standing a short time may be filtered off.

From stannic chloride, or metastannic chloride, hydrogen sulphide forms a colloidal precipitate of mixed composition, partly hydroxide and partly sulphide:

$$SnCl_4 + 2\,H_2S \rightleftarrows SnS_2 + 4\,HCl,$$
$$SnCl_4 + 3\,H_2O \rightleftarrows H_2SnO_3 + 4\,HCl.$$

This precipitate tends to assume the hydrosol condition in absence of coagulants; but, after the addition of ammonium nitrate and standing to settle, the precipitate may be collected on paper, washed with an acid solution of ammonium nitrate, and dried. The precipitate is removed from the paper as completely as possible and is put into a porcelain crucible. The paper is burned in a platinum spiral and the ash is added to the precipitate in the crucible. Upon ignition, gently at first to avoid loss of stannic sulphide which is volatile at high temperature, the hydroxide is dehydrated and the sulphide is converted to oxide containing some sulphate. To decompose the sulphate, the crucible is cooled, solid ammonium carbonate (1 grm.) is added, the cover of the crucible put on, and the ignition repeated. The residue is weighed as stannic oxide, SnO_2.

The Precipitation of Bismuth Sulphide, Bi_2S_3. — Bismuth sulphide, precipitated by saturating the slightly acid solution with hydrogen sulphide, may be collected upon asbestos in the perforated crucible, washed with water charged with hydrogen sulphide, freed from water (which repels the carbon disulphide to be applied later) by washing with alcohol, extracted with carbon disulphide to remove free sulphur, again washed with alcohol and with ether, dried at 100 degrees, and weighed as Bi_2S_3:

$$2\,Bi(NO_3)_3 + 3\,H_2S \rightleftarrows Bi_2S_3 + 6\,HNO_3.$$

The Precipitation of Lead Sulphide, PbS. — Lead sulphide may be precipitated completely from neutral and alkaline solution by ammonium sulphide and from cold and slightly acid solutions by hydrogen sulphide:

$$Pb(NO_3)_2 + H_2S = PbS + 2\,HNO_3.$$

The precipitate is prone, however, to retain some of the acidic ion of the soluble salt from which the sulphide is formed, and this is markedly so in the precipitation from solutions containing chlorides. The process is generally restricted to use in separations, other means for the determination of lead being preferred.

The Precipitation of Cadmium Sulphide, CdS. — Cadmium sulphide formed by precipitation, like lead sulphide, always includes products of the partial conversion of the soluble salt to the insoluble sulphide, such as Cd_2Cl_2S, Cd_2SO_4S, etc., and is therefore not adapted to the direct determination of cadmium. However, the complex precipitate which falls when hydrogen sulphide is passed into the solution of the cadmium salt, containing 2 to 7 per cent of concentrated sulphuric acid is easily filterable, readily converted to cadmium sulphate by evaporation with sulphuric acid, and may be brought to definite form for weighing by ignition in a crucible which is held within another crucible so that the walls of the crucibles are 1 cm. apart. The outer crucible may be heated to redness.

The Precipitation of Molybdenum Sulphide, MoS_3. — Molybdenum sulphide may be precipitated from the solution slightly acid with sulphuric acid (or, if necessary, with hydrochloric acid) by saturating the cold solution in a pressure flask and heating the closed flask on the water-bath until the precipitate settles. Or the ammoniacal solution of the molybdate may be charged with hydrogen sulphide until it is bright red and then acidified to bring about the precipitation of the sulphide. The precipitate is collected on asbestos in a perforated crucible, washed with acidulated water and then with alcohol, and dried at 100 degrees.

Sulphides Precipitable only in Alkaline Solution

Precipitation of Iron Sulphide. — Iron is precipitated as sulphide when it is desired to effect a separation from aluminium, chromium, titanium, and uranium which are not precipitable as sulphides or hydroxides in an ammoniacal tartrate solution. The acid solution containing tartaric acid to an amount three times that of the combined oxides is saturated with hydrogen sulphide, and then made just alkaline with ammonia to precipitate ferrous sulphide:

$$FeSO_4 + (NH_4)_2S \rightleftarrows FeS + (NH_4)_2SO_4.$$

After settling, the precipitated ferrous sulphide may be collected upon a filter, washed with water containing a little ammonium sulphide, dissolved in hydrochloric acid, and oxidized with nitric acid or other suitable oxidizer. From the solution of the oxidized salt ferric hydroxide may be precipitated by ammonium hydroxide.

Precipitation of Manganous Sulphide. — The precipitation of manganese as sulphide is a useful method of separating that element from the alkali-earth elements, magnesium, calcium, strontium, and barium.

If the amount of the alkali-earth elements is considerable the precipitation is made in the cold solution. To the slightly ammoniacal solution, contained in an Erlenmeyer flask and charged with a considerable amount of ammonium chloride or nitrate, a slight excess of freshly-made ammonium sulphide free from carbonates* is added; and the flask, nearly filled with previously boiled cold water and stoppered, is set aside for at least twenty-four hours; the clear supernatant liquid is poured off upon a filter; and the precipitate is washed several times by decantation, finally transferred to the same filter, and washed with water containing ammonium nitrate (5 per cent) with ammonium sulphide (1 per cent).

If only a small amount of the alkali-earth salts is present the precipitation may be made by adding the ammonium sulphide to the boiling solution and continuing the boiling until the color of the precipitate is a dirty green. After settling for some minutes the precipitate may be filtered off and washed with the washing mixture described above.

The precipitate and paper are dried and ignited separately, the paper being burned in a spiral of platinum wire. The ash and the precipitate may be ignited to constant weight in a crucible well enveloped in the oxidizing flame of a powerful

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* See foot-note on p. 100.

burner, and weighed as manganous manganite, Mn_3O_4; or the residue may be mixed with pure sulphur, heated in an atmosphere of hydrogen,* and weighed as manganous sulphide, MnS.

Precipitation of Nickel Sulphide and Cobalt Sulphide. — Nickel sulphide and cobalt sulphide may be precipitated by ammonium sulphide:

$$NiCl_2 + (NH_4)_2S \rightleftarrows NiS + 2\,NH_4Cl,$$
$$CoCl_2 + (NH_4)_2S \rightleftarrows CoS + 2\,NH_4Cl.$$

In this process (which is of value in making the separation of nickel and cobalt together from alkali and alkali-earth elements) the neutral solution of the salts (preferably chlorides) containing ammonium chloride is treated in a flask with freshly made ammonium sulphide free from carbonate,† added dropwise until no further precipitation takes place, and the flask is nearly filled with boiled water. After standing (12 hours), the precipitate is filtered off and washed with a solution of ammonium acetate (5 per cent) containing hydrogen sulphide. If too much ammonium sulphide is used in the precipitation traces of nickel sulphide will dissolve to form a brown solution from which the nickel sulphide may be recovered by acidifying with acetic acid and heating. In any event the filtrate should be acidified with acetic acid, heated to boiling, and treated with hydrogen sulphide and again filtered to recover traces of nickel sulphide which are to be added to the main precipitate. On ignition the precipitated sulphides of nickel and cobalt leave a mixture of sulphides and oxide which may be dissolved in *aqua regia,* converted to chlorides by repeated evaporations with hydrochloric acid, and made ready for the separation and determination of nickel and cobalt by appropriate methods.‡

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* See p. 101.

† See foot-note on p. 100.

‡ The metals may be determined together electrolytically, by the process described on p. 53 for the deposition of nickel. For the separation and determination of nickel and cobalt, see Treadwell-Hall: Analytical Chemistry, 3rd. ed., Vol. II, p. 161.

CHAPTER IV

PROCEDURES IN VOLUMETRIC ANALYSIS

In processes of Volumetric Analysis reactions are generally brought about by adding measured volumes of reagent solutions, made to contain known weights of reagents, to solutions of the substances to be determined; and the amounts of the substances to be determined are calculated from the amounts of reagent solutions employed. The process of measuring out the reagent solution is known as *titration.* According to the kind of reaction upon which they depend, nearly all processes of volumetric analysis may be classified as *Neutralization Processes, Oxidation Processes, Iodometric Processes, Precipitation Processes, Colorimetric Processes,* or *Gasometric Processes.*

Normal Solutions. — In any given reaction attention is naturally directed to the function of particular elements or ions. Thus, in reactions involving the neutralization of acids, such as the neutralization of hydrochloric acid by an alkali hydroxide,

$$\mathrm{HCl} + \mathrm{MOH} = \mathrm{MCl} + \mathrm{H_2O},$$

or

$$\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{M}} + \overset{-}{\mathrm{OH}} = \overset{+}{\mathrm{M}} + \overset{+}{\mathrm{Cl}} + \mathrm{H_2O},$$

attention is especially directed to the hydrogen ion, and to the hydroxyl-ion. In certain reactions of oxidation, such as oxidations by potassium permanganate in presence of sulphuric acid,

$$2\,\mathrm{KMnO_4} + 4\,\mathrm{H_2SO_4} = 2\,\mathrm{KHSO_4} + 2\,\mathrm{MnSO_4} = 3\,\mathrm{H_2O} + 5\,\ddot{\mathrm{O}},$$

it is the function of the available oxygen which is prominent. In some processes several elements or ions may demand consideration, as in the iodometric estimation of hydrochloric acid by the determination of the iodine which is liberated in the action of that acid upon a mixture of potassium iodide and iodate, the free iodine being determined by the action of sodium arsenite in presence of an alkali acid carbonate:

$$6\,HCl + KIO_3 + 5\,KI = 6\,KCl + 3\,H_2O + 3\,I_2,$$
$$2\,I_2 + As_2O_3 + n(NaHCO_3) = 4\,NaI + As_2O_5 + (n-4)NaHCO_3 + 2\,H_2O + 4\,CO_2.$$

In these reactions the elements or ions singled out for special consideration are the hydrogen of the hydrochloric acid, the iodine set free, and the oxygen which converts the arsenious oxide (present as an arsenite) to arsenic oxide (existing as an arsenate).

In order to arrange the concentrations of the solutions of hydrochloric acid, alkali hydroxide, potassium permanganate, arsenic trioxide (in the arsenite), and iodine (which is useful in estimating an excess of the arsenite in the titration process) so that they may correspond to one another volume for volume, it is necessary to take into consideration both the gram-equivalent weights of these reagents and the reaction valences of the elements or ions. To make solutions of corresponding concentrations there must be present, in equal amounts of solution, amounts of the reagents proportional to the quotients of their gram-equivalents by the sum of the active valences of the specially considered element or ion. For example, in preparing the reagents mentioned above in solutions of equal concentration in respect to the reactions specified, the solutions are so made that a given volume shall contain the reagents in amounts proportionate to the numerical values of the expressions

$$\frac{HCl}{1},\ \frac{NaOH}{1},\ \frac{Ba(OH)_2}{2},\ \frac{I}{1},\ \frac{2\,KMnO_4}{10}\ \text{or}\ \frac{KMnO_4}{5},\ \frac{As_2O_3}{4}.$$

When the solutions are made in each case to contain in 1 liter a weight of the reagent equal to the quotient obtained by dividing the gram-equivalent by the sum of the utilized valences of the specially considered element or ion in the specified reaction it is called a *normal solution.*

Standard Solutions. — The strengths of reagent-solutions are conveniently arranged in multiples or fractions of the normal strengths. It is customary to make use of normal, twice-normal, half-normal, fifth-normal, tenth-normal, etc., solutions, according to circumstances, indicating these solutions by N, 2 N, $\frac{N}{2}$ or N/2, $\frac{N}{5}$ or N/5, $\frac{N}{10}$ or N/10, etc.; and it is frequently convenient to make use of decimal coefficients, as in 1.8 N, 0.1 N, 0.52 N, etc., it being much easier to determine the exact value of solutions than to adjust them in the ratio of even numbers. Solutions of determined strengths of whatever value are called *standardized solutions* or *standard solutions*.

Varying Normality. — It is to be noted, however, that a solution which is normal, or which bears a certain relation to normality, for one sort of reaction may be of quite different concentration in respect to a reaction which proceeds on other lines. For example, as shown above, a normal solution of potassium permanganate for use in presence of sulphuric acid contains in 1 liter the number of grams indicated by the expression $\frac{KMnO_4}{5}$. When, however, oxidation is brought about by the permanganate in alkaline solution, as in Volhard's method of titrating a manganous salt in presence of zinc oxide,

$$3\,MnSO_4 + 2\,KMnO_4 + 7\,ZnO = 5\,ZnO_2MnO + K_2SO_4 + 2\,ZnSO_4,$$

three atoms of oxygen, instead of the five atoms which enter into the reaction of oxidation in presence of acid, are available from the $2\,KMnO_4$ for oxidizing the MnO of the manganous salt to the condition of MnO_2. For reactions of this sort, therefore, the normal solution of permanganate will contain in 1 liter a weight in grams of permanganate which is indicated by the expression $\frac{2\,KMnO_4}{6}$ or $\frac{KMnO_4}{3}$.

NEUTRALIZATION PROCESSES

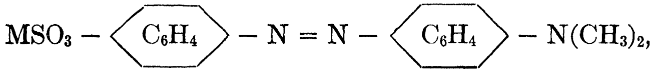
(*Acidimetry and Alkalimetry*)

The Use of Indicators. — In the determination of an acid by means of a neutralization process, a standard solution of base is required; and in the similar determination of a base a standard solution of acid is necessary. In such determinations, of either sort, the condition of exact neutralization, the *end-point*, is found by the aid of the *indicator*. The indicators commonly used to mark the end-point in processes of neutralization are organic substances, the colors of which are modified by the action of acids and bases, and of the numerous indicators which have been proposed, methyl orange and phenolphthalein are the most widely used and generally available.

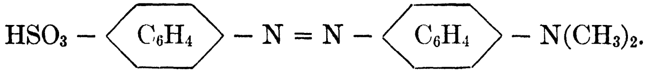
Methyl Orange (Helianthin). — Methyl orange gives to a solution containing free alkali a yellow color. Upon the addition of an excess of hydrochloric acid the color of the solution changes to red, and by treatment with a sufficient amount of alkali hydroxide the yellow color is restored.

The indicator solution is prepared by treating 0.02 grm. of the solid reddish violet methyl orange (the free acid) with 100 cm.^{3} of hot water, allowing the solution to cool, and filtering off any residue (metasulphonic acid); or 0.022 grm. of the yellow sodium salt may be treated with 100 cm.^{3} of hot water containing 0.67 cm.^{3} of N/10 hydrochloric acid, the solution being filtered after standing some time.

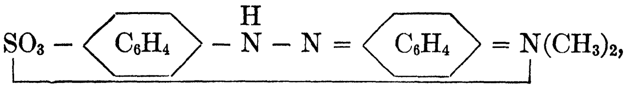
The color of alkaline solutions of methyl orange is due to the presence of *yellow* di-methyl-amino-azo-benzene sulphonate,

I 

which by the action of hydrochloric acid is changed to di-methyl-amino-azo-benzene sulphonic acid, also *yellow*,

II 

This substance, which is amphoteric, possessing the acidic group HSO_3 and the basic group $N(CH_3)_2$, may, according to accepted views,* rearrange to the isomeric form which is *red*,

III 

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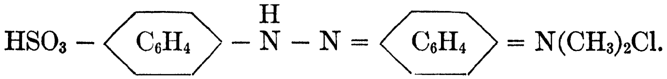
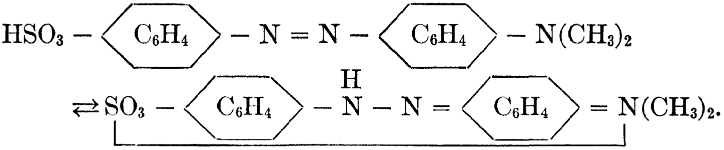
* Stieglitz: Jour. Am. Chem. Soc., **25**, 1112.

and this with hydrochloric acid forms a compound (chloride and sulphonic acid) also *red*,

IV 

The yellow color of the sulphonate and of the free sulphonic acid is ascribed to the presence of the special group $-N = N-$ known as the azo-chromophor, and the red color of the rearranged compounds is attributed to the presence of the quinoid group $=C_6H_4=$ which is known as the quinoid-chromophor.

When the reddish violet scales of the free sulphonic acid are dissolved in the least possible amount of water the solution takes a reddish orange color, due apparently to the existence of the azo-form (II), and the quinoid form (III) in equilibrium:



On dilution with water the solution becomes yellow, the azo form predominating; on addition of a trace of hydrochloric acid the solution takes the red color due to the quinoid form and its salt (IV). Upon further dilution, if the amount of acid has not been excessive, the red changes again to yellow, in consequence of the hydrolytic action of water upon the quinoid salt (IV) and the reversion of the quinoid acid (III) thus set free to the azo form II.

BEHAVIOR OF REPRESENTATIVE ACIDS AND BASES TOWARD METHYL ORANGE

Acids.		Indeterminate.	Bases.	
Active.	Inactive.		Active.	Inactive.
HCl HNO_3 H_2SO_4 H_3PO_4* H_2SO_3†	HCN H_2CO_3 H_2S H_3AsO_3*	Organic acids in general. H_3BO_3	$NaOH$ KOH CaO_2H_2 SrO_2H_2 BaO_2H_2 MgO_2H_2 NH_4OH $CH_3NH_2(H_2O)$ $C_2H_5NH_2(H_2O)$	$C_6H_5NH_2$ $CH_3 \cdot C_6H_4 \cdot NH_2$ C_6H_5N etc.

* Forming H_2MPO_4. † Forming $HMSO_3$.

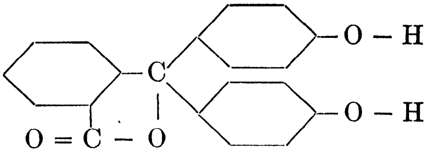
Methyl orange is a sensitive and reliable color indicator for a few of *the stronger acids* (showing red); and it is a good indicator for *nearly all the common bases* (showing yellow). It may therefore be used to indicate the mutual neutralization of such acids and such bases.

Inasmuch, however, as the change of color depends not only upon the relation between the amounts of base and acid present but also upon the concentrations of acid and indicator, it is essential that standardizations and titrations should be made at similar concentrations and the amount of the indicator used should be the least possible. In a volume of 100 cm.^{3} the change in color is distinct when titrations are made with fifth-normal (or stronger) solutions, while with tenth-normal solutions the change at the point of neutrality is less characteristic. A few drops (five or six) of a 0.02 per cent solution of methyl orange should be a suitable amount of the indicator. In titrating an acid with standard alkali the end-point of the titration should be determined by matching the color of the solution with that obtained by adding a similar amount of the indicator to 100 cm.^{3} of water, and this point is reached when an amount of alkali exactly equivalent to the acid has been added; but in the reverse process, the titration of an alkali by standard acid, a slight excess of acid is necessary to overcome the hydrolytic effect of the water upon the methyl-orange salt. Theoretically, the results should be more accurate when acid is titrated by alkali than when alkali is titrated by acid. Practically, it is easier for most observers to see the change from yellow to red rather than the reverse change from red to yellow.

Phenolphthalein. — The indicator solution of phenolphthalein is prepared by dissolving 1 grm. of pure phenolphthalein in 100 cm.^{3} of 86 per cent alcohol.

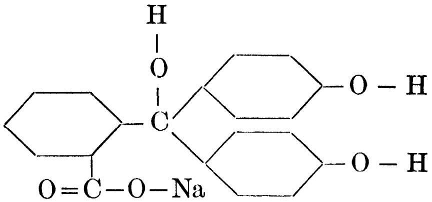
Phenolphthalein (I), the lactone of a tribasic acid, is colorless. From it may be prepared, by the action of sodium hydroxide, a tribasic salt (IV) which is colorless, a dibasic salt (III) which is red, and a monobasic salt (II), which is colorless. The red color of the dibasic salt appears to be associated with chromophoric group $=C_6H_4=$. The relations of phenolphthalein and these derivatives are shown in the following symbols.*

(I)



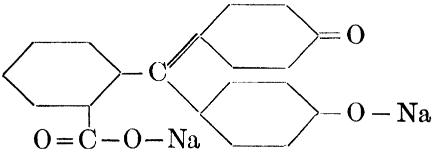
Phenolphthalein
(Colorless lactone)

(II)



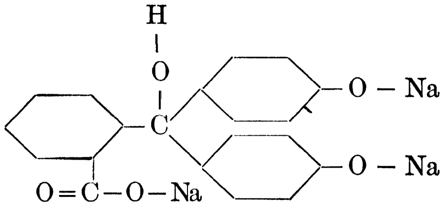
Monobasic salt
(Colorless)

(III)



Dibasic salt
(Red)

(IV)



Tribasic salt
(Colorless)

The use of phenolphthalein as an indicator depends upon the formation of a red dibasic salt by the action of a strong base and the production of a colorless monobasic salt (or the lactone

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* Kober and Marshall: Jour. Am. Chem. Soc., **33,** 59, 1780. **34,** 1424.

of the free acid) by the action of an acid. It is to be noted, however, that the red color of the dibasic salt which is produced when an alkali hydroxide is added to a solution containing phenolphthalein may be made to disappear with the formation of a tribasic salt upon excessive addition of the reagent and to return when the dibasic salt is reproduced by hydrolysis on suitably diluting the solution. When dissolved in water, the colorless monobasic salt which is formed in the first stage of the neutralization by the base is also slowly acted upon by water with the formation of colorless phenolphthalein and the red dibasic salt which is the most stable of these salts in the water solution. It is obvious, therefore, that standardizations and titrations should be executed under similar conditions. *Phenolphthalein* does not form stable salts with weak bases and is not available in the titration of such bases nor of ammonia, but *is a good indicator for strong bases and for many acids, organic and inorganic.* It is even sensitive to carbonic acid, and (at 0 degree and in presence of sodium chloride) may be used to indicate the point at which neutral sodium carbonate is converted to sodium hydrogen carbonate (see p. 127).

The Preparation of Standards

Many methods have been proposed for the standardization of solutions used in the neutralization processes. For most purposes it is convenient to make the acid the primary standard and to fix by reference to it the standard of the alkali. Hydrochloric acid in solution of suitable strength makes a convenient primary standard solution for use with either methyl orange or phenolphthalein as the indicator.

The Standard Solution of Hydrochloric Acid. — To make a solution of hydrochloric acid of approximately standard strength it is only necessary to dilute the concentrated acid suitably with water. If pure concentrated hydrochloric acid is diluted until the specific gravity of the solution is about 1.020 a nearly normal solution is obtained, containing approximately 1 grm. mol. or 36.468 grm. to the liter. From such a solution more dilute solutions of strength suitable for use in titrimetric processes, N/5 or N/10, may be made by properly diluting measured portions with water. The strength of such solutions is then determined exactly by precipitating and weighing in the manner previously described for the gravimetric determination of the chloride ion,* the silver chloride obtained from an exactly measured portion of the solution.

Experimental Process: Standardization of Hydrochloric Acid. — From an approximately N/10 solution of hydrochloric acid, made by diluting 10 cm.^{3} of the concentrated acid of sp. gr. 1.02 to a liter, draw from a burette a 100-cm.^{3} portion, dilute it with water to a volume of 300 cm.^{3}, add a few drops of nitric acid and then (gradually and with constant stirring to coagulate the precipitate) a 5 per cent solution of silver nitrate, until no further precipitation takes place. Heat the liquid to boiling and set the whole aside (in the dark) to cool. When completely settled, the precipitate is filtered off on asbestos in a perforated crucible, previously weighed, washed thoroughly with water containing a few drops of nitric acid to the liter and then with a little pure water. Dry first at 100 degrees and then in an air-bath heated to at least 130 degrees or over a low flame at a temperature not exceeding the fusing point of silver chloride. From the weight of silver chloride found calculate the corresponding weight of hydrochloric acid and the weight of that reagent in a liter of the solution analyzed. State the results in the following form:

Solution of HCl taken.	AgCl found.	HCl		Normality of solution.
		corresponding to AgCl found.	in 1 liter of solution.	
Cm^3.	Grm.	Grm.	Grm.	

The Standard Solution of Sodium Hydroxide. — *A*. It is not necessary that sodium hydroxide should be entirely free from carbonate if the solution is to be used in the neutralization of hydrochloric acid (or other strong acid) with methyl orange as the indicator. For this purpose the solution may be prepared by washing the surface of a suitable amount of sodium hydroxide, sticks or lumps, with water (to remove the outer coating

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* See p. 67.

of carbonate) and dissolving the washed hydroxide in water. To make a nearly normal solution, about 1 grm. mol. of sodium hydroxide (40 grm.) is dissolved in a liter of water, and more dilute solutions, N/5 or N/10, may be made by diluting with water. The necessary degree of dilution may be fixed approximately by titrating a small portion, roughly measured, against the standardized hydrochloric acid, with methyl orange as the indicator, and the exact standard of the diluted solution may then be fixed by a similar titration carefully executed.

Experimental Process: Standardization of NaOH. — Weigh out approximately 10 grm. of sodium hydroxide in sticks, wash away the superficial coating of carbonate, and dissolve the rest in 200 cm.^{3} of water.

A. Measure from a burette 4 cm.^{3} of the strong solution just made, add a few drops of the methyl orange indicator, and run in N/10 hydrochloric acid to the point of neutralization. From the result calculate how much of the strong solution of sodium hydroxide must be taken to make an N/10 solution (40.01 grm. to the liter) and make up a suitable amount of an approximately N/10 solution.

B. Draw from a burette 40 cm.^{3} of the approximately N/10 solution of sodium hydroxide, carefully mixed and at the laboratory temperature, add a few drops of the methyl orange indicator and titrate to the end-point with N/10 hydrochloric acid. Calculate the exact value of the sodium hydroxide solution and label it in terms of "value per cm.^{3}" and in terms of normality.

B. For titration against acids in presence of phenolphthalein used as the indicator, the standard solution of sodium hydroxide must be prepared free from carbonate, since the carbon dioxide set free in the process of neutralization is capable of converting the red dibasic sodium salt into the colorless monobasic sodium salt, thus vitiating the apparent balance between the alkali hydroxide and the standard acid.

For use with phenolphthalein the N/10 solution is most convenient and accurate. Such a solution of sodium hydroxide, free from carbonate, is best prepared by the action of water vapor upon clean metallic sodium in absence of carbon dioxide.

A device for this purpose (*Küster*) is shown in Fig. 23. A tubulated bell-jar sealed at the bottom by water in a flatbottomed dish and standing upon a glass triangle, to give a vent through the water to the hydrogen evolved in the reaction, makes a suitable isolating chamber. A cone of nickel gauze, suspended over the nickel vessel which is to receive the sodium hydroxide as it is formed, serves to contain the sodium. In using this apparatus, a suitable amount of sodium, freshly cut to give a clean surface, is put in the gauze cone and the funnel, the dish containing water, and the vessel to receive the sodium hydroxide are arranged as shown. As the sodium is attacked by the water vapor sodium hydroxide is formed and, dissolving in the vapor, drops into the vessel below. The operation may be hastened by gently heating the water in the dish upon a steam radiator, *after the air has been replaced by the hydrogen.* The solution of sodium hydroxide in the containing vessel is suitably diluted with distilled water, free from carbon dioxide, so that a liter of the solution shall contain the hydroxide produced by 2.3 grm. of sodium, and is transferred as quickly as possible to a bottle provided, as shown in Fig. 24,

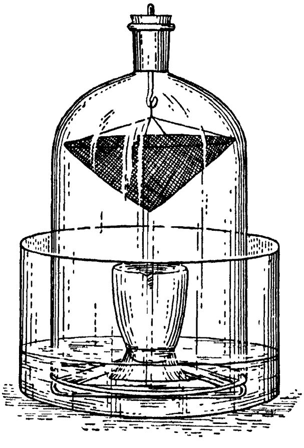

FIG. 23.

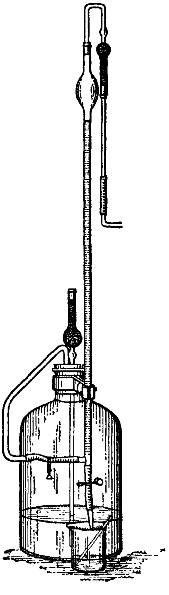

FIG. 24.

with a protecting tube filled with soda-lime, a side-neck burette fitted with a pinch-cock or the Bunsen bead-tap,* and a siphon-tube for filling the burette. The exact standard of the solution is fixed by titration with the standard acid.†

The Standard Solution of Barium Hydroxide. — For many purposes, the more easily prepared solution of barium hydroxide may be substituted for the solution of sodium hydroxide free from carbonate. Such a solution may be easily made by dissolving crystallized barium hydroxide in a suitable amount of water, diluting to the volume desired, allowing the solution to stand until all barium carbonate has settled out, and siphoning into a bottle filled with air free from carbon dioxide, protected by a soda-lime tube, and provided with burette and siphon, as shown in Fig. 24. The exact standard of the solution may be determined by titration with standard hydrochloric acid.

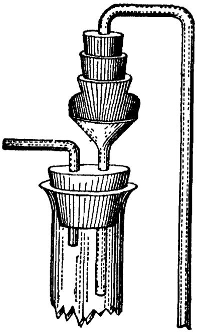

FIG. 25.

Experimental Process: Standardization of Barium Hydroxide, with Phenolphthalein. — Weigh out about 20 grm. of crystallized barium hydroxide and dissolve it in a suitable amount of water contained in a closed flask. Let the solution stand for a day or two, until the precipitated barium carbonate has settled completely. Fill the bottle to be used as a container with water and displace the water by air freed from carbon dioxide. Draw the solution of barium hydroxide through a siphon filter (made from a perforated crucible with the asbestos filter, stopper, and tube, as shown in Fig. 25) into the container, adjust the protecting tube, siphon, and burette, as shown in Fig. 24. To fix the standard, a 50-cm.^{3} portion of N/10 hydrochloric acid is placed in a flask, a drop of phenolphthalein is added, and barium hydroxide is run in from the burette until the red color of the dibasic salt appears. Calculate the strength of the solution in terms of standard hydrochloric acid and state the results in the following form:

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* To draw liquid from the burette the tube is held between the thumb and forefinger over the bead and by gentle pressure the tube is deformed so that the liquid may flow.

† See Experimental Process, p. 122.

HCl solution taken.	$Ba(OH)_2$ solution used.	$Ba(OH)_2$ solution corresponding to 1 cm.^{3} of HCl solution.	$Ba(OH)_2$ in 1 cm.^{3} of solution.	Normality of $Ba(OH)_2$ solution.
Cm.^{3}	Cm.^{3}	Cm.^{3}	Grm.	

Experimental Process: Determination of Stronger Acids in Dilute Solution. — Measure out roughly 25 cm.^{3} of N/10 sodium hydroxide or barium hydroxide, introduce methyl orange, and, from a pipette graduated to tenths of a cubic centimeter, add portions of the dilute hydrochloric acid, nitric acid, or sulphuric acid of unknown strength (e.g., the desk supply) until the end-point is reached. Then from the results of this rough comparison calculate the volume of the acid necessary to make 100 cm.^{3} of acid of approximately N/10 concentration. Measure this calculated volume of the original acid into a counterpoised 100-cm.^{3} graduated flask, weigh carefully, and dilute to the mark.

A. Measure from a burette 40 cm.^{3} of the prepared solution. Add methyl orange and titrate to the end-point with standard sodium hydroxide, approximately N/10. From the amount used of the sodium hydroxide solution calculate the percentage strength (by weight) of the original acid. Tabulate the results in the form given below.

Acid used.	Weight of original acid in 100 cm.^{3} of the prepared solution.	Volume of prepared solution taken.	Standard solution of alkali used.	Weight of NaOH or $Ba(OH)_2$ used.	Weight of acid equivalent to NaOH or $Ba(OH)_2$ used.		Concentration of original acid by weight.
			A				
	Grm.	Cm.^{3}	Cm.^{3}	Grm.	Grm.	Per cent.	Per cent.
HCl HNO_3 H_2SO_4							
			B				
HCl HNO_3 H_2SO_4							

B. Measure from a burette 40 cm.^{3} of the prepared solution made to contain a known weight of the original acid, add phenolphthalein, and titrate to the end-point with standard barium hydroxide, approximately N/10. From the amount used of the standard barium hydroxide solution calculate the percentage strength (by weight) of the original acid.

Experimental Process: Determination of Sodium Hydroxide and Sodium Carbonate in Crude Caustic Soda. —Weigh out exactly about 5 grm. of crude caustic soda, dissolve it in water, and make up the solution to 1 liter at the atmospheric temperature.

Process I. — *A*. Of this solution, draw 50 cm.^{3} from a burette, add five or six drops of methyl orange, and add nearly N/10 hydrochloric acid to apparent neutralization. Reactions take place according to the equations

$$NaOH + HCl = NaCl + H_2O,$$
$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2O + CO_2.$$

With standard solutions stronger than fifth-normal the dissolved carbon dioxide does not affect the end-point with methyl orange; but with tenth-normal solutions the end-point is somewhat hastened by the carbon dioxide. To obviate this error, it is only necessary to expel the carbon dioxide by boiling, to cool the solution (now yellow) and to add the slight amount of standard hydrochloric acid necessary to produce the end-color. The amount of hydrochloric acid used is the measure of the sodium present as hydroxide and as carbonate.

B. Draw 50 cm.^{3} of the solution from the burette, add more than enough barium chloride in solution to affect the transformations shown in the following equations:

$$Na_2CO_3 + BaCl_2 = 2\,NaCl + BaCO_3 \text{ (insoluble)},$$
$$2\,NaOH + BaCl_2 \rightleftarrows 2\,NaCl + Ba(OH)_2 \text{ (soluble)}.$$

Add phenolphthalein to the mixture and titrate by standard hydrochloric acid very slowly and with constant stirring; for, unless proper precaution is taken in respect to the gradual addition of the hydrochloric acid some of the insoluble barium carbonate may be attacked before the indicator shows the end-point. If the titration is properly conducted, the hydrochloric acid should be used up in the reactions

$$NaOH + HCl = NaCl + H_2O,$$
$$Ba(OH)_2 + 2\,HCl = BaCl_2 + 2\,H_2O.$$

The amount of acid used in *B* measures the amount of sodium hydroxide originally present. The amount of acid used in *A* measures the amount of sodium hydroxide and sodium carbonate present. The difference between the amounts of acid used in *A* and *B* measures the sodium carbonate originally present.

State the results in the following form:

Solution $NaOH+$ Na_2CO_3 taken.	Standard HCl used for complete neutralization. (A)	Standard HCl used in neutralizing the hydroxide. (B)	Standard HCl used in neutralizing carbonate. ($A-B$)	NaOH in 50 cm.^{3} of solution.	Na_2CO_3 in 50 cm.^{3} of solution.	In crude soda.	
						NaOH	Na_2CO_3
Cm.^{3}	Cm.^{3}	Cm.^{3}	Cm.^{3}	Grm.	Grm.	Per cent.	Per cent.

Process II. — *A.* Draw from a burette 50 cm.^{3} of the solution. Add 5 grm. of sodium chloride and chill the solution to 0 degree. Add phenolphthalein and titrate with N/10 hydrochloric acid to colorlessness:

$$n\mathrm{NaOH} + \mathrm{Na_2CO_3} + (n+1)\mathrm{HCl} = (n+1)\mathrm{NaCl} + \mathrm{NaHCO_3} + n\mathrm{H_2O}.$$

B. To the solution just titrated add methyl orange and titrate with N/10 hydrochloric acid to the end-color (brownish red):

$$\mathrm{NaHCO_3} + \mathrm{HCl} = \mathrm{NaCl} + \mathrm{H_2O} + \mathrm{CO_2}.$$

Twice the amount of hydrochloric acid used in the methyl orange titration (B) will measure the sodium carbonate; and the difference between the amount of acid used in the phenolphthalein titration (A) and that used in the methyl orange titration (B) will measure the sodium hydroxide. State the results in the following form:

Solution of nNaOH $+Na_2CO_3$ taken.	Standard HCl used with phenolphthalein. (A)	Standard HCl used with methyl orange. (B)	Na_2CO_3 indicated.	NaOH indicated.	In crude soda.	
					Na_2CO_3	NaOH
Cm.^{3}	Cm.^{3}	Cm.^{3}	Grm.	Grm.	Per cent.	Per cent.

The Determination of Boric Acid. — Many of the ordinary indicators, even methyl orange, are more or less sensitive to the action of boric acid in fairly concentrated solutions and fail, therefore, to indicate with accuracy the exact point at which a stronger acid in presence of free boric acid may be removed by neutralization with a standard alkali. The mixture of an iodide with an iodate, sensitive to the action of stronger acids, is not acted upon by boric acid when present to the extent of the equivalent of 0.1 grm. of boric anhydride in 25 cm.^{3} of solution. When a solution containing boric acid, of suitable concentration, and hydrochloric acid is treated with an iodide-iodate mixture, and the liberated iodine taken up by sodium thiosulphate, the solution will contain only neutral chloride, neutral iodide, tetrathionate, possibly a slight excess of thiosulphate, and free boric acid. Carbonic acid, which if present would interfere with the subsequent use of phenolphthalein as an indicator, may be removed as barium carbonate by the addition of barium chloride in presence of the iodide-iodate mixture:

$$\begin{aligned} 5\,KI + KIO_3 + 4\,HCl + BaCl_2 + CO_2 + H_3O_3B \\ = BaCO_3 + 6\,KCl + H_3O_3B + 2\,H_2O + 3\,I_2. \end{aligned}$$

When boric acid and mannite (or glycerine in suitably large proportion) are mixed in solution, a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, its acid taste (comparable to that of citric acid) is much stronger than that of boric acid alone, and the solution shows greater electrical conductivity and a lower freezing point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities. If, therefore, mannite is added to the solution of boric acid after treatment with the iodide-iodate mixture and thiosulphate, and with barium chloride, the boromannite compound of strongly acid properties is formed, and this may be titrated with an alkali hydroxide in presence of phenolphthalein.

In the practical procedure, the solution in which boric acid is present to an amount not exceeding 0.1 grm. in 25 cm.^{3} is made slightly acid to litmus by hydrochloric acid and is treated with 5 cm.^{3} of a 10 per cent solution of barium chloride. To the iodide-iodate mixture just bleached (as is generally necessary) by a dilute solution of sodium thiosulphate a single drop of the solution to be analyzed is added. If the iodine color develops, the solution is known to be acidic with hydrochloric acid and all the boric acid is in free condition. If no color develops the borate solution must be carefully acidified with hydrochloric acid until a drop of the solution will liberate iodine from the iodide-iodate mixture. Then, the iodide-iodate mixture, containing about 2 grm. of potassium iodide with 0.5 grm. of potassium iodate, is added to the solution of the boric acid, and the liberated iodine is bleached with sodium thiosulphate. A few drops of the phenolphthalein indicator are now added, and N/5 sodium hydroxide is run in until a strong red coloration is produced. The addition of a pinch of mannite, 1 grm. or 2 grm., has the effect of bleaching the color and the alkali solution is run in again until a faint color, permanent on the addition of more mannite, is obtained.

Neither silica nor fluorides will interfere with the correctness of this process. The best results are obtained in cold solution of final volumes not greater than 50 $cm.^3$. *

Other Standards and Indicators. — Other acids — such as nitric acid, sulphuric acid, and oxalic acid — are sometimes used with advantage as standard solutions in neutralization processes, and these solutions are best standardized by titration against a standard alkali solution, itself standardized against standard hydrochloric acid or against weighed portions of pure succinic acid, $H_2O_2C_4H_4O_2$, dried in air or over sulphuric acid, with phenolphthalein as the indicator.

In certain cases, standard solutions of potassium hydroxide or of ammonia may advantageously replace the more usual standard solutions of sodium hydroxide or barium hydroxide.

Other indicators are sometimes substituted for methyl orange and phenolphthalein.

OXIDATION PROCESSES

Oxidation processes, or processes of oxidimetry, present three distinct phases of procedure:

(I) The substance to be determined may be oxidized definitely by direct titration with a standard oxidizer. (II) The substance may be first reduced to a definite condition and then reoxidized

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* Jones: Methods in Analysis, Gooch, p. 206.

definitely by the standard oxidizer. (III) The substance may be reduced to an inert form by a definite amount of a reagent taken in an excess which is then titrated with the standard oxidizer to find (by difference) a measure of the substance reduced.

Use of Potassium Permanganate. — The most generally applicable reagent containing oxygen directly available for oxidizing purposes in volumetric analysis is potassium permanganate in solutions of suitable concentrations — commonly tenth-normal. Solutions made by dissolving the crystallized potassium permanganate in water, especially if hot water is used to hasten the process of going into solution, invariably contain in suspension manganese dioxide or an insoluble potassium manganite. If the higher manganese oxide, or the manganite, is removed by filtering the solution through asbestos * (paper will produce further reduction of the permanganate) such solutions may remain essentially unchanged for months, provided they are kept free from dust and are not exposed to the action of direct sunlight. The standard of such solutions should, nevertheless, be redetermined from time to time. In presence of a suitable acid, such as sulphuric acid, potassium permanganate acts as an oxidizer according to the equation

$$2\,KMnO_4 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,\ddot{O},$$

and, in a solution devoid of free acid, in the sense of the expression

$$2\,KMnO_4 + H_2O = 2\,MnO_2 + 2\,KOH + 3\,\ddot{O}.$$

For most purposes of volumetric analysis potassium permanganate is made to react in presence of acid and a solution of tenth-normal strength is generally suitable. Two gram-molecules of potassium permanganate liberate 5 gram-atoms of oxygen, each atom having a valence of two, in reactions which take place in presence of acid. A normal solution will there-

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* A simple form of asbestos filter may be made by plugging a funnel with glass wool and covering the latter with an emulsion of asbestos such as is used in the perforated crucible.

fore contain in 1 liter that weight of the permanganate which equals two gram-molecules divided by ten:

$$\frac{2\,KMnO_4}{10} = \frac{KMnO_4}{5} = \frac{158.03}{5} = 31.61 \text{ grm.}$$

A solution of N/10 concentration for use in acid solution is therefore made to contain 3.161 grm. in the liter, or $\frac{1}{50}$ gram-molecule of potassium permanganate.

Potassium permanganate is exceedingly sensitive to the action of the organic matter almost always present in water even when it has been distilled, and the oxide of manganese produced in such action behaves as a catalyzer in promoting further decomposition of the permanganate. In making an approximately N/10 solution it is customary to weigh out about 3.16 grm. of potassium permanganate, dissolve it in 1 liter of hot distilled water, filter on an asbestos filter, set aside for several days and then filter again.

Standardization of Potassium Permanganate. — Many modes of standardizing the nearly N/10 solution of potassium permanganate have been proposed and applied, but the most convenient method is based upon the use of sodium oxalate which may now be obtained of certified purity.* The principle upon which this process of standardization depends is the oxidation of the oxalic acid liberated by the action of sulphuric acid upon the sodium oxalate.

$$\begin{aligned} &2\,KMnO_4 + 5\,Na_2C_2O_4 + 8\,H_2SO_4 \\ &\quad = K_2SO_4 + 2\,MnSO_4 + 5\,Na_2SO_4 + 5\,H_2C_2O_4 + 3\,H_2O + 5\,\ddot{O} \\ &\quad = K_2SO_4 + 2\,MnSO_4 + 5\,Na_2SO_4 + 10\,CO_2 + 8\,H_2O. \end{aligned}$$

A weighed amount of sodium oxalate is dissolved in water heated to 80 or 90 degrees, sulphuric acid is added, and the hot solution is titrated with the nearly N/10 permanganate solution. At first the action is slow and the permanganate, contained in a glass-stoppered burette, should be added so gradually that the color imparted by each drop shall disappear before the addition of the next. After a small amount of manganous sulphate has

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* Purchaseable from the Bureau of Standards, Washington, D. C.

been produced, the speed of the reaction is very much increased (by the catalytic action of this substance) and the permanganate may then be run in with rapidity. From the weight of sodium oxalate taken and the amount of the permanganate solution used the "oxygen equivalent per cm.^{3}" of the latter may be calculated.

Experimental Process: Preparation and Standardization of N/10 Permanganate. — *A.* Make a solution of potassium permanganate (of approximately 1/50 gram-molecular strength in 1 liter; N/10 for use in presence of acid) by dissolving 3.16 grm. of potassium permanganate in hot water, filtering on an asbestos filter, setting aside for some days, refiltering into a liter flask, and making up to the 1 liter mark.

B. Dissolve about 0.25 grm. of sodium oxalate in 250 cm.^{3} of water heated to 80 or 90 degrees and contained in a 400-cm.^{3} beaker. Add 10 cm.^{3} of [1 : 1] sulphuric acid. Titrate immediately with the nearly N/10 solution of potassium permanganate, stirring continually and taking care not to run in the permanganate at a rate greater than 10 cm.^{3} to 15 cm.^{3} per minute and to add the last 1 cm.^{3} dropwise, allowing time for full decolorization between successive drops until the end-color (which should match that given by a single drop of the permanganate solution to 300 cm.^{3} of water containing 10 cm.^{3} of (1 : 1) sulphuric acid) remains. The reaction proceeds according to the equation

$$Na_2C_2O_4 + H_2SO_4 + O = Na_2SO_4 + 2\,CO_2 + H_2O.$$

From the weight (w) of sodium oxalate taken and the number of cubic centimeters (n) of the solution of potassium permanganate employed in oxidizing the oxalic acid produced to carbon dioxide and water, calculate weight of oxygen used and the "oxygen value" per cubic centimeter of the permanganate.

$$Na_2C_2O_4 : O = 134 : 16 = w : x = \text{oxygen used.}$$

$$\frac{x}{n} = \text{“oxygen value per cm.}^3\text{.”}$$

State the results in the following form:

$Na_2C_2O_4$ taken.	Permanganate solution used.	Oxygen employed in oxidation.	"Oxygen value per cm.^{3}" of permanganate.
Grm.	Cm.^{3}	Grm.	Grm.

Other Modes of Standardizing Potassium Permanganate.— Solutions of potassium permanganate may sometimes be exactly standardized to advantage by titration against a ferrous salt made from a weighed amount of electrolytic iron,* or against a weighed amount of arsenic trioxide,† or by absorbing and weighing with molecular silver the iodine set free by the permanganate from potassium iodide in an acidified solution.‡

Direct Oxidations by the Permanganate Solution

Many useful analytical processes depend upon the use of the standard solution of potassium permanganate for the direct oxidation of the substance to be determined: (I) in presence of free acid; (II) in absence of free acid. Examples of such processes are found in (I) the determination of oxalates, iron in ferrous salts, and hydrogen dioxide by titration in presence of dilute acid; and of nitrous acid in concentrated sulphuric acid; and (II) the determination of manganese and formates by titration in absence of free acid.

Determination of Oxalates. — By the reversal of the process by which potassium permanganate is standardized by means of sodium oxalate various oxalates may be determined. Moreover, many elements capable of yielding by precipitation oxalates of definite constitution may be thus estimated, either by direct titration with standard permanganate or, indirectly, by titration of the excess remaining from a definite amount of oxalic acid or a soluble oxalate used to precipitate them. Elements which may be estimated in this manner are calcium, strontium, barium, copper, lead, zinc, mercury (in the mercurous form), cerium, and lanthanum.§

Experimental Process: Determination of Copper. — Weigh out carefully about 0.5 grm. of pure, crystallized copper sulphate, $CuSO_4 \cdot 5\,H_2O$, and, dissolve it in 50 cm.^{3} of 50 per cent acetic acid. Dissolve 4 grm. of pure

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, pp. 93–97.

† Gooch and Peters: Methods in Analysis, Gooch, pp. 41, 42.

‡ Perkins: Ibid., pp. 42, 361, 362.

§ See Methods in Analysis, Gooch, pp. 123, 131, 181–184, 187, 197, 218, 248, 254.

oxalic acid in 40 cm.^{3} of 50 per cent acetic acid, add 10 cm.^{3} of concentrated nitric acid,* and pour this solution into that of the copper sulphate. Collect the precipitate, after standing over night, upon asbestos in a perforated crucible and wash carefully with small amounts of water applied successively. Place the crucible with its contents in a beaker, cover it with about 200 cm.^{3} of hot water containing 25 cm.^{3} of dilute sulphuric acid (1 : 3), and titrate the solution with N/10 permanganate. From the oxygen value of the permanganate used calculate the copper in the copper oxalate, CuC_2O_4, titrated.

State the results in the following form:

$CuSO_4 \cdot 5\,H_2O$ taken.	Copper in $CuSO_4 \cdot 5\,H_2O$.	N/10 $KMnO_4$ used.	"Oxygen value" of $KMnO_4$.	Copper found.	Error.
Grm.	Grm.	Cm.^{3}	Grm.	Grm.	Grm.

Determination of Iron in Ferrous Sulphate.† — When ferrous sulphate is acted upon by potassium permanganate in

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* The acetic acid is used to increase the insolubility of the copper oxalate and the nitric acid is added to induce a favorable condition for the crystallization. For a discussion of this procedure, and for its application in the separation of copper from certain other elements, see Methods in Analysis, Gooch, p. 123.

† Instead of potassium permanganate, standard potassium dichromate (Penny's Method) may be used as the oxidizing agent in the determination of iron in the ferrous condition, the reaction taking place in the cold solution and in presence of either hydrochloric acid or sulphuric acid:

$$K_2Cr_2O_7 + 6\,FeSO_4 + 8\,H_2SO_4$$
$$= 2\,KHSO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O$$

or,

$$K_2C_2O_7 + 6\,FeCl_2 + 14\,HCl = 2\,KCl + 2\,CrCl_3 + 6\,FeCl_3 + 7\,H_2O.$$

The end of the reaction is not indicated by any characteristic change in color in the solution, but is found by noting the point where a drop of the solution taken out on the end of a clean stirring rod and added to a drop of a freshly prepared solution of potassium ferricyanide fails to give with the reagent the blue which shows the presence of a ferrous salt. The dichromate method is less accurate than the permanganate method of oxidation, but it may sometimes be used with advantage when solutions are clouded by the presence of insoluble colored material in suspension which would have the effect of obscuring the permanganate end-color.

presence of free sulphuric acid, oxidation takes place according to the reaction

$$\begin{aligned}2\,KMnO_4 + 10\,FeSO_4 + 9\,H_2SO_4 &= 2\,KHSO_4 + 2\,MnSO_4\\ &+ 5\,Fe_2(SO_4)_3 + 8\,H_2O.\end{aligned}$$

The relations between the oxygen derived from the permanganate and the iron, ferrous oxide, and ferric oxide involved are shown in the condensed expression

$$2\,FeO + \ddot{O} = Fe_2O_3,$$

and from the "oxygen value" of the permanganate used the amounts of the other substances may be calculated.

In the practical application of this reaction to the determination of iron in a ferrous salt (*the method of Margueritte*), the solution diluted so that the concentration shall not exceed 1 : 1000 in respect to iron, is treated with 10 cm.^{3} of sulphuric acid (1 : 1) for every 100 cm.^{3} of solution, and is then titrated in the cold with N/10 potassium permanganate.

Experimental Process: Iron in Ferrous Ammonium Sulphate. — Weigh out carefully about 0.7 grm. of ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$ (Mohr's salt), and dissolve it in cold water. Dilute the solution to a volume of 200 cm.^{3}, add 20 cm.^{3} of sulphuric acid (1 : 1), and run in N/10 potassium permanganate to coloration. From the "oxygen value" of the permanganate calculate the weight and percentage of iron in the salt taken. State the details of the determination in the following form:

$(NH_4)_2FeSO_4 \cdot 4\,H_2O$ taken.	Theory for iron.		$KMnO_4$ taken.	Oxygen value per cm.^{3} of $KMnO_4$ used.	Iron found.		Error in iron found.	
Grm.	Grm.	Per cent.	Cm.^{3}	Grm.	Grm.	Per cent.	Grm.	Per cent.

Determination of Hydrogen Dioxide. — Hydrogen dioxide in sufficiently dilute solution (0.001 per cent) and in presence of sulphuric acid at sufficient concentration (1 per cent) may be determined by direct titration with N/10 permanganate, by means of the following reaction:

$$2\,KMnO_4 + 4\,H_2SO_4 + 5\,H_2O_2 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2{}^*.$$

Determination of Nitrous Acid or Nitrites. — Nitrous acid is oxidized to nitric acid according to the equation:

$$2\,KMnO_4 + 5\,HNO_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,HNO_3.$$

In the analysis, the nitrous acid taken in solution in concentrated sulphuric acid (on account of the volatility of nitrogen oxides from the aqueous solution) is measured from a burette into the solution of a known amount of N/10 permanganate, diluted to about 400 cm.^{3}, and warmed to 40 degrees, the decoloration of the solution being the end-point. Toward the end the bleaching takes place tardily and the nitrous acid or nitrite must be added slowly. Nitrites may be similarly determined by adding the neutral or alkaline solution to a known amount of N/10 permanganate, suitably diluted and acidified with sulphuric acid, to the point of decoloration.

Determination of Manganese in Manganous Sulphate. — When potassium permanganate is added to a hot and neutral solution of manganous sulphate a reaction takes place (*the Guyard reaction*) in which the low oxide MnO of the manganous salt is oxidized at the expense of the high oxide Mn_2O_7 of the permanganate with the formation of intermediate hydrated oxides. For example,

$$\begin{aligned} Mn_2O_7 + 3\,MnO &= 5\,MnO_2, \\ Mn_2O_7 + 8\,MnO &= 5\,Mn_2O_3, \\ Mn_2O_7 + 13\,MnO &= 5\,Mn_3O_4. \end{aligned}$$

These higher hydrated oxides appear to be manganous acid or salts of manganous acid, H_2MnO_3. When the conditions are

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* Should it happen in thus testing a solution for hydrogen dioxide that the first drop of the permanganate gives a permanent color to the solution more sulphuric acid should be added before concluding that no hydrogen dioxide is present.

favorable and a suitable salt of another element (e.g., zinc) is present, a manganite of this element is precipitated which, though variable in composition, contains the manganese in the quadrivalent form. In the presence of zinc oxide, a weak base, the free acid is taken up and the precipitation of the manganese is made complete. The manganese of manganous sulphate may therefore be determined by titration of the solution, heated to boiling and containing zinc sulphate with zinc oxide, until the supernatant liquid remains pink. The course of the reaction may be represented typically by the following equations:

$$4\,KMnO_4 + 5\,ZnSO_4 + 6\,MnSO_4 + 14\,H_2O$$
$$= 4\,KHSO_4 + 7\,H_2SO_4 + 5\,ZnH_2O_4(MnO)_2,$$
$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

In this process (*Volhard's Method*) two equivalents of the permanganate, $KMnO_4$, supply three equivalents of oxygen, and the relation of the available oxygen to the manganese in manganous form is shown in the condensed expression:

$$MnO + \ddot{O} = MnO_2.$$

The "oxygen value per cm.^{3}" of the permanganate solution when used in this process would, if the reaction were perfectly exact, be three-fifths of that found by the standardization in the presence of acid. Practically, it is more exact to standardize the permanganate solution against a known weight of anhydrous manganous sulphate, treated exactly as in the process of titration by which the unknown manganous salt is to be determined.*

Dilution and the presence of free acid tend to limit this reaction and this is why the solution remains clear for a considerable time at the end-point of titrations by permanganate in presence of a suitable amount of sulphuric acid (10 cm.^{3} of the [1 : 1] in 100 cm.^{3} of solution), and why such solutions may ultimately become brown and cloudy upon long standing after the end-point is passed.

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., p. 612.

Determination of Formates. — The determination of formates may serve as an example of oxidation by permanganate in alkaline solution. In cold acid solutions the action is very slow and from hot acid solutions formic acid may escape by volatilization. An excess of sodium carbonate is therefore added, the solution is heated to induce the settling of the precipitate to be formed, and the permanganate is run in until the clear liquid above the settled precipitate shows the end-color.

$$2\,KMnO_4 + 3\,NaOCOH = K_2CO_3 + Na_2CO_3 + NaHCO_2 + CO_2 + MnO_2.$$

The Effect of Hydrochloric Acid in Permanganate Titrations. — Although hydrochloric acid and potassium permanganate do not react by themselves with evolution of chlorine at the concentrations employed in processes of titration, chlorine is evolved, a portion of the permanganate is wasted, and the indication for iron is too high when hydrochloric acid is present during the titration of a ferrous salt.* The same is true to a less degree in respect to the titration of oxalic acid, and other oxidizable substances, in the presence of hydrochloric acid. It has been found, however, that the introduction of a suitable amount of a manganous salt into the solution before titration will not only prevent the secondary action by which chlorine is evolved but will very markedly hasten a reaction of oxidation when it is slow to start.

That the hastening of the process is due to an intervention of the Guyard reaction, described above, by which intermediate oxides of manganese (MnO_2, Mn_2O_3, Mn_3O_4, more sensitive than the permanganate to the action of a reducing agent) are produced in the action of permanganate upon a manganous salt, is clearly shown in the titration of oxalic acid by permanganate. When the permanganate is added drop by drop to the hot solution containing oxalic acid and sulphuric acid

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* This effect may, however, be regulated and the error eliminated, by making the titration in very dilute solution and calculating the results by use of a standard obtained by matching the permanganate against a known amount of ferrous salt under similar conditions.

the solution remains colored for several seconds after the addition of each of the first few drops, during which process a manganous salt is formed, and then the rate of decolorization increases gradually and rapidly. If a suitable amount of manganous sulphate is added to the solution of oxalic acid and sulphuric acid before titration the color of the permanganate disappears immediately upon the addition of the first drop and the titration may be pushed rapidly, even in the cold solution; but if too much manganous salt be present the end reaction is marked by the advent of a brownish-red precipitate (due to the Guyard reaction) rather than the clear pink of the soluble permanganate.

The explanation of the protective action of a manganous salt in respect to the evolution of chlorine on the process of titration is not so obvious, although it would seem probable that the manganous salt is instrumental in destroying an oxidizer which is formed in this reaction and is sensitive enough to act upon hydrochloric acid as well as upon the substance to be oxidized. Neither permanganic acid nor any of the persistent oxides of the Guyard reaction will evolve chlorine from hydrochloric acid in the concentrations employed in the processes of titration. Manganic acid, H_2MnO_4, the oxide of which (MnO_3) stands next in the series of manganese oxides to that (Mn_2O_7) of permanganic acid, undergoes spontaneous decomposition when it is formed by the action of sulphuric acid upon an alkali manganate, with the production of the more stable manganous acid and permanganic acid,

$$3\,H_2MnO_4 = 2\,HMnO_4 + H_2MnO_3 + H_2O.$$

Moreover, chlorine is evolved when hydrochloric acid is added to the solution of an alkali manganate. In order to explain the evolution of chlorine in a permanganate titration it is sufficient, therefore, to make the not unnatural assumption that in the decomposition of the permanganic acid any one of the known oxides of manganese between Mn_2O_7 and MnO may be formed momentarily as a transition step, all reducible by the substance to be oxidized. If the oxide of manganic acid, MnO_3, is formed it will act upon hydrochloric acid as well as upon another oxidizable substance, but if the amount of the other oxidizable substance is sufficiently preponderant the action upon hydrochloric acid will be insignificant. A manganous salt, capable of acting with manganic acid, as well as with permanganic acid, to form the persistent oxides of the Guyard reaction, is such an oxidizable substance.

In using a manganous salt for the purpose of regulating the velocity of the oxidizing reaction or for preventing action upon hydrochloric acid, it is important to adjust, according to the conditions, the amounts used, in order that these desirable effects may be secured without interference with the end-reaction by the persistence of the Guyard reactions.

Experience has shown that in titrating oxalic acid, 1 grm. of the manganous salt ($MnSO_4 \cdot 5\,H_2O$ or $MnCl_2 \cdot 4\,H_2O$) should be present in order to push the reaction at the ordinary temperature with reasonable speed, and that this amount is enough to so affect the conditions of equilibrium that titrations in presence of hydrochloric acid (5 $cm.^3$ to 15 $cm.^3$ of the strong acid) in moderate volumes (100 $cm.^3$ to 500 $cm.^3$) may be conducted safely and with reasonable rapidity, with or without sulphuric acid.

In titrating a ferrous salt, which acts more rapidly than oxalic acid upon the oxides produced in the Guyard reaction, a considerable amount of the manganous salt may be present without interfering with the regularity of the titration. When much of the iron salt is present hydrochloric acid may bring out the yellow color of ferric chloride which is detrimental to the delicacy of the end-reaction, but this difficulty may be overcome by the addition of phosphoric acid.* In a volume of 500 $cm.^3$, which may contain as much as 15 $cm.^3$ of strong hydrochloric acid, 2 grm. of the manganous salt (sulphate or chloride) will be sufficiently protective and 4 $cm.^3$ of phosphoric acid of sp. gr. 1.7 with the usual amount of sulphuric acid (10 $cm.^3$ of the (1 : 1) acid to 100 $cm.^3$ of solution) will serve to correct the color.

Oxidations by the Permanganate Solution after a Preliminary Reduction

In processes of analysis, based upon the oxidation of the substance to be determined after reduction to a condition from which potassium permanganate will reoxidize definitely the

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* Reinhardt. See Analytical Chemistry: Treadwell-Hall, 3rd. ed., Vol. II, p. 607.

product of reduction, *the product of reduction may be definite and reasonably stable on exposure to air; the reduction product may be sensitive to the action of air; the action of the reducer may be excessive, the over-reduction being corrected by the use of an oxidizer of limited power before the titration with the standard oxidizer.*

Reduction to Stable Condition

Determination of Iron in Ferric Salts. — The reduction of ferric salts for the purpose of determining the iron by subsequent reoxidation from the ferrous condition with standard permanganate may be effected by any one of several reducing agents, of which the one most commonly used is zinc. Other available reducing agents are hydrogen sulphide, sulphur dioxide, stannous chloride, and titanous sulphate.

I. *Reduction by Zinc.* — In the reduction of the ferric salt by zinc in presence of free acid both the metal and nascent hydrogen may take part in the reduction:

$$\begin{aligned} Zn + 2\,FeCl_3 &= ZnCl_2 + 2\,FeCl_2, \\ Zn + 2\,HCl &= ZnCl_2 + 2\,\dot{H}, \\ 2\,FeCl_3 + 2\,\dot{H} &= 2\,HCl + 2\,FeCl_2. \end{aligned}$$

When a ferric salt is accompanied by a salt of titanium (as frequently happens in the analysis of titaniferous iron ores and rocks) the latter is also reduced by the action of zinc in presence of acid and left in condition to vitiate the determination of iron, but by treatment of the solution containing the products of the reduction by zinc — the ferrous salt and the titanous salt — with bismuth oxide only the titanous salt is oxidized,

$$3\,Ti_2(SO_4)_3 + Bi_2O_3 + 3\,H_2SO_4 = 6\,Ti(SO_4)_3 + 2\,Bi + 3\,H_2O.$$

After filtering off the precipitated bismuth, with the excess of bismuth oxide, the ferrous salt may be titrated in the usual manner. To prevent the error which may be caused by the presence of the titanous salt it is, therefore, only necessary to shake the solution containing the ferrous and titanous salts reduced in the flask (*A*) or in the reductor (*B*), with a little bismuth oxide, allow the mixture to stand a few minutes, and filter quickly with the aid of the suction pump, and titrate as usual the ferrous salt in the filtrate.* There is little danger of reoxidation of the ferrous salt when the cold solution free from dissolved oxygen † is allowed to stand for a short time.

II. *Reduction by Hydrogen Sulphide.* — For the determination of iron in ferric salts by the reduction and subsequent titration of the ferrous salt the method of reducing by zinc is not applicable if other substances similarly reducible and oxidizable are present. In such cases, notably in the determination of iron in presence of titanic acid (derived from titaniferous ores) it is sometimes customary to use hydrogen sulphide as the reducer, the reduction taking place according to a reaction like the following:

$$Fe_2(SO_4)_3 + H_2S = 2\,FeSO_4 + H_2SO_4 + S.$$

In this process, the acidified solution of the ferric salt is placed in a stoppered flask provided with a tube for the introduction of hydrogen sulphide from a generator and another tube for the exit of unused gas. The contents of the flask are heated to boiling, hydrogen sulphide is passed in until it has completely decolorized the ferric salt and is then replaced by carbon dioxide until the excess of the hydrogen sulphide has been expelled from the boiling solution and the escaping gas no longer blackens lead acetate paper. The solution is cooled in the atmosphere of carbon dioxide and the ferrous salt is titrated with the usual precaution to dilute well and to add a manganous salt if hydrochloric acid is present.‡ The precipitate of sulphur (if free from sulphides) does not reduce permanganate in the cold, dilute solution.

III. *Reduction by Sulphur Dioxide.* — A ferric salt is not completely reduced by sulphur dioxide if much free acid is present in the solution. The free acid is therefore nearly neutralized by sodium carbonate, sulphur dioxide is bubbled through the boiling solution, contained in a reduction flask similar to that used in the process of reduction by hydrogen sulphide, until the reduction is completed and is then replaced by carbon dioxide until the gas escaping from the boiling solution will no longer decolorize a solution containing dilute sulphuric acid and a drop or two of N/10 permanganate. The

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* Gooch and Newton: Methods in Analysis, Gooch, p. 500.

† Peters and Moody: Methods in Analysis, Gooch, p. 371.

‡ See p. 138.

ferrous salt is titrated after cooling the solution in an atmosphere of carbon dioxide.

$$Fe_2(SO_4)_3 + SO_2 + 2\,H_2O = 2\,FeSO_4 + 2\,H_2SO_4.$$

IV. *Reduction by Stannous Chloride.*[*] — Ferric chloride in hot solution and in presence of hydrochloric acid is easily reduced by stannous chloride. The stannous chloride is added cautiously, drop by drop, until the solution is decolorized. After thorough cooling of the solution mercuric chloride is added, and after a short interval, the titration is made very slowly in the diluted solution containing a manganous salt.[†]

$$\begin{aligned} 2\,FeCl_3 + SnCl_2 &= 2\,FeCl_2 + SnCl_4, \\ SnCl_2 + 2\,HgCl_2 &= SnCl_4 + Hg_2Cl_2. \end{aligned}$$

V. *Reduction by Titanous Sulphate.* — When a solution of titanous sulphate is added to the cold solution of ferric sulphate the reduction of the ferric salt is immediate.

$$Fe_2(SO_4)_3 + Ti_2(SO_4)_3 = 2\,FeSO_4 + 2\,Ti(SO_4)_2.$$

The excess of the titanous salt is immediately oxidized upon shaking the solution with a little bismuth oxide

$$3\,Ti_2(SO_4)_3 + Bi_2O_3 + 3\,H_2SO_4 = 3\,Ti(SO_4)_4 + 2\,Bi + 3\,H_2O,$$

and, after filtering off the bismuth and the excess of bismuth oxide, and diluting the solution, the ferrous sulphate may be titrated with permanganate in the usual manner.[‡] This method [§] is, of course, directly applicable to the determination of iron in ferric salts containing a salt of titanium. A solution of titanous sulphate of convenient strength may be made by mixing 20 grm. of commercial titanic acid with three times its own weight of a mixture of sodium and potassium carbonates and fusing it in a platinum crucible, treating the melt (after being finely ground) in a platinum dish with hot concentrated sulphuric acid, cooling, diluting a little, filtering through asbestos, treating with zinc until reduction is accomplished, and, while zinc is still left in the flask, filtering the solution quickly through a perforated platinum cone into about two liters of freshly boiled water contained in a small reservoir connected with a burette and a hydrogen generator.

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[*] Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 609.

[†] See p. 138.

[‡] See p. 134.

[§] Newton: Methods of Analysis, Gooch, p. 502.

Experimental Processes: Iron in Hematite.—Extraction. Weigh out into each of several small beakers a 1-grm. portion of the finely ground iron ore. To each portion, add 10 cm.^{3} of concentrated hydrochloric acid (and, if the ore contains carbonaceous matter, a pinch of potassium chlorate), cover the beaker with a watch-glass, and digest at a temperature just below the boiling of the liquid until there seems to be no further solvent action. Very few iron ores are completely decomposed by hydrochloric acid, and, unless it is known that the iron of the ore under examination may be completely dissolved by hydrochloric acid, the insoluble residue should be treated further to extract the iron in the insoluble residue. To this end, remove the watch-glass (washing any spatters upon it into the beaker), evaporate the solution, and desiccate the residue to render the silica insoluble. Treat the residue with hydrochloric acid (5 cm.^{3}), dilute with water (40 cm.^{3}), settle, decant as much as possible of the clear liquid and filter the rest through a small filter, washing repeatedly and thoroughly, but with as little water as may be. Ignite the filter and siliceous residue in a platinum crucible, add sulphuric acid (about 1 cm.^{3}) and hydrofluoric acid (about 2 cm.^{3}) and evaporate off the silicon fluoride and the hydrofluoric acid, to the fuming point of the sulphuric acid. Cool the liquid, dilute with a little water, and if no dark specks of undecomposed ore remain add the liquid to the hydrochloric acid solution. Should any undecomposed ore still remain, filter the solution into the flask, through a little filter, made with rough edges (by tearing the edge off the rim), so that it will fit the funnel tightly even when it is covered with liquid. Ignite the filter and residue, fuse with acid potassium sulphate until the latter is quite liquid and fuming freely. Cool, dissolve the residue in hot water and a few drops of hydrochloric acid, and add the solution to the main portion of the ferric solution.

Reduction by Zinc. — *A.* If the zinc at hand is not iron-free, as is ordinarily the case, it must be used in (roughly) weighed amounts and the excess of it entirely dissolved by the addition of sufficient acid. In this case, correction must also be made for the iron content of the zinc, found by dissolving a weighed portion of it in acid by itself as described below, and titrating the solution with permanganate.

FIG. 26.

To the cold solution contained in a small flask, of 50 cm.^{3} to 75 cm.^{3} capacity, add 3 grm. of granulated zinc, close the flask with a diminutive funnel (Fig. 26), and introduce hydrochloric acid (if necessary) until a brisk evolution of hydrogen takes place. Keep up the rapid evolution of hydrogen by warming judiciously and adding more hydrochloric acid as the occasion may require, until the characteristic yellow color of ferric chloride has disappeared and does not return upon the addition of a few drops more of the acid. The use of hydrochloric acid in the reduction, rather than sulphuric acid, is desirable because the color of ferric chloride is deeper than that of ferric sulphate and the vanishing of it a better indication of complete reduction. Add gradually dilute sulphuric acid, 30 cm.^{3} of the (1 : 2) acid, and when the zinc has completely disappeared wash down the neck of the flask, and the funnel, with a fine jet of water until the flask is nearly filled. Stand the flask in cold water, transfer the cool solution to a large volume of cold water (best contained in a white dish) and make up the solution to a liter. Add in solution 1 grm. of manganous sulphate and titrate the ferrous salt in the solution in the usual way.

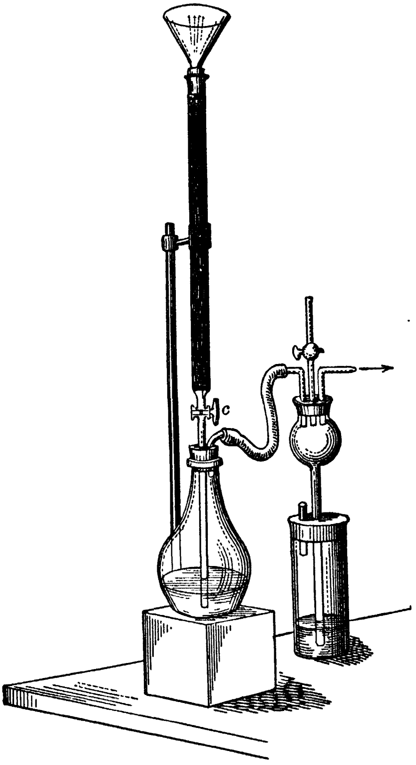

Fig. 27.

B. If iron-free zinc is at hand the process of dissolving the excess of zinc may be omitted. In this case, add to the solution of the ferric salt contained in a small flask (50 cm.^{3} to 75 cm.^{3}) a suitable amount of the iron-free granulated zinc, close the flask with a small funnel, add hydrochloric acid (if necessary) until the evolution of hydrogen is brisk, and keep up the action until the characteristic color of ferric chloride has disappeared. Then, while the evolution of hydrogen continues, cool the flask in water, strain the solution through a funnel fitted with a platinum cone of perforated foil or gauze. Add the washings of the flask and the zinc, dilute the solution, add manganous sulphate (1 grm.) and syrupy phosphoric acid (4 cm.^{3} of sp. gr. 1.7), and titrate the ferrous salt in the usual manner by permanganate.

C. When many reductions are to be made the work is very much facilitated by the use of the *Jones reductor*. This instrument, shown in Fig. 27, is so arranged that the reduction may be effected by means of a column of granulated zinc, 20 to 30 mesh, — that is, in grains which will pass the sieve of twenty meshes to the linear inch or eight to the centimeter, but will not pass the sieve of thirty meshes to the inch or twelve to the centimeter — previously amalgamated by first cleaning it with a little hydrochloric acid and then adding mercuric chloride in solution until the evolution of hydrogen ceases. This amalgamated zinc, though scarcely attacked by dilute hydrochloric or sulphuric acid, is capable of easily effecting the reduction of ferric salts, and other reducible substances. The reductor tube to contain the zinc has (for this purpose) a length of 40 cm., and an inside diameter of 18 mm. It is constricted at one end and sealed to a stop-cock tube. The tube is set in vertical position, a cone of perforated platinum foil or a spiral or platinum wire is inserted (or a layer of glass beads) upon which is placed a plug of asbestos or glass wool. Above the plug is put a thin layer of asbestos suitable for use in the perforated crucible, and the tube is filled with the amalgamated zinc to a point 5 $cm.^3$ from the top. The reductor tube and the flask to receive the reduced solution are arranged so that the reduced liquid may be introduced into water without contact with air, as shown, and connection is made with the suction pump and a pressure regulator which will keep the pressure inside less than the atmospheric pressure by an amount equal to a 20-cm. column of water.

In making use of the Jones reductor, first pour warm 2.5 per cent sulphuric acid into the tube until the zinc is well covered, start the pump, adjust the stop-cock so that the liquid will run slowly into the receiver (best cooled in running water) and, keeping the zinc always covered by the liquid (so that hydrogen dioxide may not be produced by the action of the nascent hydrogen upon the oxygen of the air), pass 100 $cm.^3$ of the dilute acid through the column. Next pass the solution of the ferric salt, diluted with 100 $cm.^3$ of warm 2.5 per cent sulphuric acid, through the column and wash the zinc with 200 $cm.^3$ of the warm dilute acid followed by 100 $cm.^3$ of hot water. Cool the solution, dilute with boiled water, and, after adding manganese sulphate (since hydrochloric acid is present), titrate in the usual manner with permanganate.

The presence of traces of iron in the zinc will, of course, introduce error into determinations made with the Jones reductor, and all determinations made with this instrument should be corrected by taking into consideration the reducing effect noted in a blank determination in which the other reagents are run through the reductor without the ferric salt and titrated with potassium permanganate.

From the number of cubic centimeters (n) of the permanganate used and its oxygen value per $cm.^3$ (o), the weight (w) of the iron indicated may be found by means of the expressions:

$$2\,FeO + \ddot{O} = Fe_2O_3,$$

$$no : w = O : 2\,Fe = 16 : 111.68,$$

$$w = \frac{no \times 111.68}{16}.$$

Calculate and state results in the following form:

	Iron ore taken.	$KMnO_4$ used.	Oxygen value per cm.³ of $KMnO_4$	Iron found.	
	Grm.	Cm.³	Grm.	Grm.	Per cent.
A..........					
B..........					
C..........					

Determination of Vanadic Acid reduced by Sulphur Dioxide. — When sulphuric acid is added to a solution which contains vanadic acid or a vanadate, the passing of sulphur dioxide into the boiling solution will bring about the reduction of the vanadic acid to the blue vanadyl salt, corresponding to vanadium tetroxide, which is perfectly stable in the air:

$$V_2O_5 + SO_2 = SO_3 + V_2O_4.$$

The excess of sulphur dioxide is removed by boiling the solution, while replacing the current of sulphur dioxide by a current of carbon dioxide, until the escaping gas no longer bleaches permanganate. The hot solution is titrated by N/10 permanganate and the calculation is made according to the equation

$$V_2O_4 + \ddot{O} = V_2O_5.$$

When small amounts of vanadium are involved the pink end-point is easily recognizable and the determinations are fairly accordant and exact. Wider variations, due to the difficulty of catching the pink end-reaction in presence of the reddish yellow color of vanadic acid at high concentration, are inherent in the permanganate process of titration when large amounts of vanadic acid are formed.

Reduction Products Sensitive to the Action of Air

In certain processes the reduction is definite but the product is so sensitive to the action of the atmospheric oxygen that direct titration by the permanganate solution in air leads to incorrect results. In such cases the reduced solution may be received directly in the solution of a reagent which will immediately oxidize it with the simultaneous formation of a product which is less sensitive to atmospheric action, though easily acted upon by the permanganate solution and capable of acting as a register of the reduction previously brought about in the substance to be determined. Examples of such processes are the determination of molybdic acid reduced by the zinc reductor and received in ferric sulphate, and the similar determination of vanadic acid * and titanic acid.†

Determination of Molybdic Acid and Phosphomolybdic Acid. — Molybdic acid may be reduced by zinc in the presence of sulphuric acid to the condition of the oxide Mo_2O_3 but this condition is not stable in presence of air. When, however, the solution containing molybdic acid and sulphuric acid is passed through the Jones reductor ‡ and then directly into a solution of ferric sulphate placed in the receiver, the sensitive molybdic compound is partially oxidized by the ferric salt with the formation of a corresponding amount of ferrous salt, less sensitive than the molybdic compound to the atmospheric actions.§ The molybdenum compound is green as it passes through the lower part of the reductor but on coming in contact with the ferric salt it is changed to a bright red. The solution, decolorized by phosphoric acid,|| is titrated while still hot with N/10 permanganate. The result may be calculated from the expression

$$Mo_2O_3 + 3\,\ddot{O} = 3\,MoO_3.$$

The molybdenum trioxide contained in ammonium phosphomolybdate may be similarly reduced and determined by the procedure first outlined; and from the amount of permanganate used in the titration of ammonium phosphomolybdate precipitated under definite conditions the phosphoric pentoxide, or the phosphorus, contained in the precipitate may be estimated.

Experimental Process: Determination of Phosphorus in Iron and Steel. — Of steel drillings weigh out 1 grm. or 2 grm. (according as the steel contains more or less than 0.15 per cent of phosphorus) into a 250-cm.^{3} Erlen-

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* Gooch and Edgar: Methods in Analysis, Gooch, p. 349.

† Newton: Ibid., p. 242.

‡ See p. 145.

§ Randall: Methods in Analysis, Gooch, p. 424.

|| See p. 140.

meyer flask. Add a mixture of 25 cm.^{3} of nitric acid (sp. gr. 1.42) and 75 cm.^{3} of water. Hang in the neck of the flask a small funnel and heat until the metal has dissolved and the nitrogen oxides have been expelled. Add in concentrated solution 0.15 grm. of potassium permanganate and boil the solution until the characteristic permanganate color has disappeared. Dissolve the precipitated higher oxides of manganese by adding a solution of sulphurous acid, boil out the excess of this reagent, and filter the solution. Add 40 cm.^{3} of ammonia (sp. gr. 0.96), mix thoroughly to dissolve in the free acid the precipitated ferric hydroxide, and to the solution, at a temperature of 40 degrees, add 40 cm.^{3} of "molybdate solution,"* close the flask with a rubber stopper, and shake vigorously for five minutes. Settle the precipitate, filter (best on asbestos in a perforated crucible), and wash with a solution of ammonium acid sulphate (15 cm.^{3} of ammonia, 25 cm.^{3} of sulphuric acid, and 1 liter of water). Wash out the flask with a solution of 20 cm.^{3} of water and 5 cm.^{3} of ammonia, and use this mixture to dissolve the precipitate off the filter. Acidify the solution and washings with 10 cm.^{3} of strong sulphuric acid and pass the acidified solution through the reductor into the receiver, containing 2 grm. to 3 grm. of ferric alum and 4 cm.^{3} of syrupy phosphoric acid, preceded by 100 cm.^{3} of hot water and followed by 200 cm.^{3} of the hot dilute acid with 100 cm.^{3} of water. Titrate the reduced solution immediately with approximately N/10 permanganate. On the assumption that the ammonium phosphomolybdate contains phosphorus and molybdenum in the proportion given by the symbol $(NH_4)_3PO_4 \cdot 12\,MoO_3$, and that the reduction proceeds to the condition represented by the symbol Mo_2O_3, the weight of phosphorus may be calculated from the number of cubic centimeters of permanganate used (n) and the oxygen value per cm.^{3} (o) of that reagent.

$$no : w = 18\,\mathrm{O} : \mathrm{P} = 288 : 31.$$

$$w = \frac{no \times 31}{288}.$$

State the results in the following form:

Weight of steel taken.	KMnO$_4$ used.	Oxygen value per cm.^{3} of KMnO$_4$.	Weight of P found.	Per cent of P in steel.
Grm.	Cm.^{3}	Grm.	Grm.	

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* Made by stirring 100 grm. of molybdenum trioxide, MoO_3, into 80 cm.^{3} of concentrated ammonia, adding 400 cm.^{3} of water, filtering, pouring the solution into a mixture of 400 cm.^{3} of nitric acid (sp. gr. 1.42) with 600 cm.^{3} of water, treating with 0.05 grm. of microcosmic salt, $HNaNH_4PO_4 \cdot 4\,H_2O$, standing twenty-four hours, and filtering.

Over-reduction and Correction

Excessive and irregular effects of a reducing agent, employed to prepare a substance for determination by the permanganate oxidation, may sometimes necessitate corrective treatment before the titration is made. The action of zinc upon vanadic acid and uranyl salts will serve to illustrate this point.

Determination of Vanadic Acid Reduced by Zinc. — The reduction of vanadic acid by zinc in presence of sulphuric acid, for example, proceeds farther than the condition of the oxide V_2O_4 and under favorable conditions may reach that of V_2O_2. The lavender solution thus obtained turns blue on exposure to air, in consequence of the formation of a blue vanadyl salt which corresponds to the tetroxide; but the action of molecular oxygen is insufficient to bring about complete oxidation of the lower unstable oxides to the condition of the stable oxide V_2O_4 within a reasonable time. Ordinary oxidizers attack the tetroxide as well as the lower oxides. It has been found, however, that silver oxide and silver salts are sufficiently active to affect the lower oxides while leaving the tetroxide intact, and silver sulphate appears to be the most convenient form in which to use the silver compound.*

When the solution of vanadic acid is subjected in presence of sulphuric acid, as in the reduction of a ferric salt, to the action of a 40-cm. column of the Jones reductor and is received in a flask charged with a saturated solution of silver sulphate a muddy deposition of finely divided silver is formed. Upon boiling the mixture the silver gathers into a single spongy mass and leaves the solution so clear that, were it not that spongy silver is susceptible to the action of the permanganate, the titration of the vanadium, now definitely in a condition corresponding to V_2O_4, might be made without previous filtration. The solution is filtered upon asbestos in the perforated crucible, diluted to about 700 cm.^{3}, heated to the boiling point, and titrated with N/10 permanganate. The result is calculated from the expression

$$V_2O_4 + \ddot{O} = V_2O_5.$$

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* Gooch and Gilbert: Methods in Analysis, Gooch, p. 346.

Determination of Uranium in Uranyl Sulphate. — When uranyl sulphate in dilute sulphuric acid is subjected to the action of the zinc column of the Jones reductor, reduction takes place to a degree dependent upon the conditions.* The sulphuric acid should have during the action the concentration of the (1 : 6) acid, since with less concentration of acid the reduction is delayed while a greater concentration produces a too violent evolution of hydrogen. With the acid of the concentration named, fifteen minutes or more should be allowed for the passage of the uranium solution containing as much as 0.2 grm. of uranic oxide and for 0.3 gram half an hour or more should be allowed. The reduction is carried under this condition beyond the uranous stage, represented by the oxide UO_2, and if the reduced solution is received and titrated in an atmosphere of carbon dioxide the indication for uranous oxide is too high. Brief exposure of the solution to air, as it comes from the reductor, is, however, sufficient to correct the over-reduction, and the contents of the receiving flask, which after the reduction are olive-green, immediately become sea-green (the characteristic color of uranous salts) when poured out into an open dish. In the titration of the hot solution of uranous sulphate with permanganate, the solution becomes more and more yellowish green as the highest condition of oxidation is approached. If only small amounts of uranium are present the addition of a single drop of N/10 permanganate in excess will bring out the pink end-color, but with large amounts of uranium the end-color is a yellowish pink.

The uranyl sulphate solution amounting to 100 cm.^{3} or 150 cm.^{3}, and containing enough sulphuric acid to make the concentration 1 : 6, is heated nearly to the boiling point. Preceded by a few cubic centimeters of acid of the same strength, the solution is drawn by gentle suction very slowly through the 40-cm.^{3} column of 20-inch amalgamated zinc, and is followed by more of the same acid and then by 250 cm.^{3} of hot water. The contents of the receiving flask are poured through the air into an open porcelain dish, diluted with about 200 cm.^{3} of hot

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* Pulman: Methods in Analysis, Gooch, p. 430.

water, and titrated with N/10 potassium permanganate. The reaction takes place according to the equations

$$UO_2SO_4 + Zn + 2\,H_2SO_4 = ZnSO_4 + U(SO_4)_2 + 2\,H_2O,$$
$$2\,KMnO_4 + 5\,U(SO_4)_2 + 2\,H_2O = 2\,KHSO_4 + 2\,MNSO_4 + H_2SO_4 + 5\,UO_2SO_4,$$

and the result is calculated from the expression

$$UO_2 + \ddot{O} = UO_3.$$

Oxidations by Permanganate of a Reagent Used in Excess

Some processes rest upon the oxidizing action of the substance to be determined upon a suitable reducing agent, the excess of which may be determined by titration with the permanganate solution, the reduced product of the substance being inactive toward the permanganate. Examples of such processes are the determinations of the higher oxides of lead and manganese by means of their reaction upon oxalic acid or upon ferrous sulphate, the excess of which may be determined, and determinations of chloric acid and of nitric acid by means of the similar reaction upon ferrous sulphate under carefully defined conditions.

Determination of Higher Lead Oxides. — Lead dioxide, in presence of nitric acid, is capable of acting upon oxalic acid with the formation of lead nitrate which is not susceptible to the oxidizing action of the permanganate in acid solution:

$$PbO_2 + H_2C_2O_4 + 2\,HNO_3 = Pb(NO_3)_2 + 2\,H_2O + 2\,CO_2.$$

The other higher oxides of lead, Pb_3O_4 (red lead) and Pb_2O_3, are resolved into lead nitrate and hydrated lead dioxide by the action of 2 N nitric acid:

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + H_2O + H_2PbO_3.$$

These characteristics make it possible to determine the purity of lead dioxide, or the condition of oxidation of any of the higher oxides of lead, by acting with nitric acid (8 per cent) upon the oxide, treating with a known amount of standard oxalic acid in excess of that required for the reaction, and titrating in the hot solution the excess of the oxalic acid by means of standard permanganate.

If the standard of the oxalic acid solution is stated in terms of the oxygen required to oxidize 1 cm.^{3} of it (its "oxygen equivalent per cm.^{3}") and the standard of the permanganate is given in terms of the oxygen available in 1 cm.^{3} of it (its "oxygen value per cm.^{2}"), the calculation of the amount of lead dioxide indicated is simple.

If o = the oxygen value of the permanganate per cm.^{3},
o' = the oxygen equivalent of the oxalic acid per cm.^{3},
n = the number of cm.^{3} of permanganate used,
n' = the number of cm.^{3} of oxalic acid used,
x = amount of lead dioxide indicated,

then

$$\mathrm{O} : \mathrm{PbO_2} = 16 : 239.1 = n'o' - no : x,$$

$$x = \frac{239.1\,(n'o' - no)}{16}.$$

Determination of Higher Oxides of Manganese.* — I. *Reduction by Ferrous Sulphate.* Manganese dioxide and other high oxides of manganese react with ferrous sulphate in presence of sulphuric acid to form ferric sulphate and manganous sulphate:

$$MnO_2 + FeSO_4 + 2\,H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\,H_2O.$$

If the total oxygen value of the amount of ferrous sulphate used is known (that is, the amount of oxygen required to convert the ferrous salt to the ferric condition), and the oxygen equivalent of the excess remaining after the reaction be determined, the difference, Δ, will measure the active oxygen of the amount of manganese dioxide taken. The weight, w, of manganese dioxide indicated will be given by the proportion

$$\mathrm{O} : \mathrm{MnO_2} = 16 : 86.93 = \Delta : w,$$

$$w = \frac{\Delta \times 86.93}{16}.$$

II. *Reduction by Oxalic Acid.* Manganese dioxide is attacked by oxalic acid, in presence of sulphuric acid, with the formation of manganous sulphate:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2\,H_2O + 2\,CO_2.$$

Other high manganese oxides are reduced similarly and if the reduction is brought about by a known amount of oxalic acid (N/5) taken in excess of the amount which will take part in the reaction, the determination of the excess of oxalic

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* Treadwell-Hall: Analytical Chemistry, 3rd. ed., Vol. II, p. 624.

acid will provide the data necessary for the calculation of the available oxygen of the high manganese oxide and of the equivalent amount of the dioxide MnO_2.

If o = the oxygen value of the permanganate per cm.^{3},
o' = the oxygen equivalent per cm.^{3} of the oxalic acid,
n = the number of cm.^{3} of permanganate used,
n' = the number of cm.^{3} of oxalic acid used,
then $n'o' - no$ = available oxygen of the MnO_2.
If x = weight of MnO_2 indicated,
then

$$O : MnO_2 = 16 : 86.93 = n'o' - no : x,$$

$$x = \frac{86.93\,(n'o' - no)}{16}.$$

Determination of Chlorates. — The determination of a chlorate may be effected by taking advantage of its reaction with ferrous sulphate, in presence of sulphuric acid in boiling solution.* The chlorate, in amounts up to 0.5 grm., is treated with a known amount of approximately N/5 ferrous sulphate of known oxygen equivalent, in excess of the amount theoretically necessary to register the oxidizing power of the chlorate, according to the reaction,

$$MClO_3 + 6\,FeSO_4 + H_2SO_4 = MCl + 3\,Fe_2(SO_4)_3 + 3\,H_2O,$$

with 15 cm.^{3} of sulphuric acid (1 : 3), in a flask trapped to prevent mechanical loss. The mixture is brought to the boiling point, cooled to the room temperature, diluted to a volume of about 600 cm.^{3}, and titrated with N/10 permanganate after the addition of 2 grm. to 3 grm. of manganous chloride.

From the total oxygen value, P, of the permanganate used the weight of chlorate is found from the proportion

$$3\,O : MClO_3 : P : w,$$

$$w = \frac{P \times 1\ \mathit{grm. mol.}\ MClO_3}{3 \times 16}.$$

Determination of Nitrates. — Soluble nitrates, in presence of sulphuric acid, are decomposed by ferrous sulphate in the sense of the equation

$$2\,MNO_3 + 6\,FeSO_4 + 5\,H_2SO_4 = 2\,MHSO_4 + 3\,Fe_2(SO_4)_3 + 4\,H_2O + 2\,NO.$$

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* Phelps: Methods in Analysis, Gooch, p. 258.

The reaction may be utilized for the determination of a nitrate by the estimation of the amount of ferrous sulphate taken and the amount of that reagent remaining after the action is completed, provided means are adopted to remove the nitrogen dioxide so that it may not act as a carrier of oxygen from the air to the ferrous sulphate and may not itself be acted upon by permanganate in the process of titration.

The estimation of nitrates may be accomplished successfully by the following procedure.*

The apparatus which is used consists of a 250-cm.^{3} boiling flask, closed with a rubber stopper carrying a separating funnel of 50 cm.^{3} capacity to serve as an inlet tube and a glass tube of 0.8-cm. bore to serve as an outlet tube. The inlet tube is constricted at the lower end, and the outlet tube is enlarged just above the stopper to a small bulb (to prevent mechanical loss during the boiling) and bent twice at right angles. The flask is supported on a wire gauze above a Bunsen burner and the outlet tube dips under mercury contained in a test-tube.

Of the nitrate to be analyzed, amounts up to 0.5 grm. are introduced with water into the flask, the stem of the separating funnel being left full of water, the outlet tube is adjusted to just touch the surface of the mercury in the tube, and the air is expelled from the flask by boiling the solution to small volume. A definite amount of standardized ferrous sulphate solution known to be in excess of that required to break up the nitrate is introduced into the separating funnel. The outlet tube is plunged a centimeter or two deep into the mercury (which is readily accomplished by changing the position of the flask on the wire gauze), and the flame is withdrawn until the diminution of pressure due to cooling is made evident by the rise of mercury in the outlet tube. By applying and withdrawing the flame, while regulating inflow of the solution, the ferrous salt may be introduced, without admitting air. The funnel is carefully washed with a volume of hydrochloric acid nearly enough to equal that of the liquid previously in the flask and the washings are similarly introduced. After the pressure has been restored in the apparatus by heating the flask, the outlet tube is again raised to the surface of the mercury, and the solution in the flask is boiled down, beyond the point at which the dark compound of nitrogen dioxide and ferrous sulphate is

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* **Phelps: Methods in Analysis, Gooch, p. 462.**

broken up, to a volume of 10 cm.^{3} to 15 cm.^{3}. After dilution with 600 cm.^{3} of cool, boiled water and addition of 2 grm. to 3 grm. of manganous chloride, the ferrous salt remaining is titrated with N/10 permanganate. The weight of nitrate, w, may be calculated from the total oxygen value, P, of the permanganate used, by means of the proportion

$$3\,\ddot{O} : 2\,MNO_3 = P : w,$$

$$w = \frac{P \times 2\ \mathit{grm.\ mol.}\ MNO_3}{3 \times 16}.$$

IODOMETRIC PROCESSES

The measurement of the iodine involved in definite reactions affords a basis for many valuable processes of volumetric analysis. *Iodine may be used in standard solution to bring about a definite reaction; or iodine may be a product of reaction and determined by some suitable standardized reagent.* Analytical processes which depend upon the measurement of definite amounts of iodine used as a reagent or obtained as a product of reaction are known as *iodometric processes.*

The estimation of sulphurous acid by titration with a standard solution of iodine in potassium iodide until the solution shows color, according to Dupasquier's original method,

$$I_2 + H_2SO_3 + H_2O = 2\,HI + H_2SO_4,$$

is typical of reactions of the first sort. The estimation of free chlorine by the use of a standardized solution of sulphurous acid for the purpose of bleaching the iodine set free when the chlorine comes into contact with potassium iodide may serve as an example of the second sort:

$$(a) \qquad Cl_2 + 2\,KI = 2\,KCl + I_2,$$
$$(b) \quad H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2\,HI.$$

Iodine and Sulphurous Acid. — As a matter of fact this illustrative method reaction of iodine with sulphurous acid is only realized ideally, as Bunsen found, when the iodine is presented to sulphurous acid of a concentration no greater than 0.04 per cent. Nevertheless, upon the use of standard iodine and standard sulphur dioxide in suitably dilute solution (standardized by comparison with the standard solution of iodine) Bunsen founded many determinative methods resting upon the estimation of iodine set free from potassium iodide either by the direct action of the determined substance upon that reagent or by the action of the chlorine liberated in a reaction between the substance and hydrochloric acid.

In Bunsen's procedure the standard iodine was made by dissolving a known weight of purified and dried iodine in a concentrated solution of potassium iodide, or by dissolving similarly a known weight of ordinary iodine of value determined by analysis. Dilute sulphurous acid, of about 0.03 per cent strength, was standardized against a solution of iodine of known value. Potassium iodide was made up for use in a solution of 10 per cent strength. Dilute, clear starch solution was used to indicate the presence of an excess of iodine in the process of titration. With these reagents Bunsen demonstrated a number of typical processes, such as the determination of free sulphurous acid (of strength not exceeding 0.04 per cent); of iodine (dissolved in potassium iodide); of chlorine and bromine (allowed to act upon potassium iodide to set free the equivalent amount of iodine); of chlorites and hypochlorites (decomposed by hydrochloric acid and potassium iodide, with evolution of iodine); of chromates, chlorates, and the higher oxides of lead, manganese, nickel, and cobalt (by treating each of these substances in a diminutive distillation flask with hydrochloric acid, collecting the evolved chlorine in potassium iodide, and estimating the iodine set free). Bunsen pointed out that iodates, vanadates, selenates, manganates, ferrates, ozone, etc., should be determinable by similar procedure. Cerium was determined in presence of lanthanum by a chlorine oxidation in alkaline solution, treatment of the precipitate containing cerium dioxide with hydrochloric acid in the distillation flask, absorption of the chlorine evolved in potassium iodide, and titration of the liberated iodine. Ferrous salts and arsenious acid, or arsenites, were oxidized by known amounts of potassium chromate and the excess of the last, determined by the procedure indicated for chromates, gave by difference the amount used in the oxidation.

These demonstrations were sufficient to point the way to the iodometric estimation of many substances capable of acting upon potassium iodide with liberation of iodine or of acting upon hydrochloric acid with evolution of chlorine which is determinable from the iodine set free when that reagent is brought into contact with potassium iodide.

The chief inconveniences of Bunsen's procedure — the necessity of using very dilute solutions of sulphurous acid in the titration of iodine and the tendency of the standard sulphurous acid to change in strength on account of spontaneous and continuous oxidation — were obviated when Schwarz replaced the sulphurous acid by sodium thiosulphate.

Iodine and Thiosulphate. — Sodium thiosulphate acts definitely with iodine, in neutral or faintly acid solutions of any reasonable concentrations, with the formation of sodium tetrathionate and sodium iodide:

$$I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI.$$

Though definite and complete in the neutral or acid solution, the action of iodine upon sodium thiosulphate is in alkaline solution irregular and excessive, even when the alkalinity is due to a bicarbonate.

Iodine and Arsenic Trioxide. — The reaction between iodine and arsenious acid,

$$I_2 + H_3AsO_3 + H_2O \rightleftarrows 2\,HI + H_3AsO_4,$$

is, however, reversible and can be made to proceed to completion, in either direction, by attention to the conditions of action. If the hydriodic acid formed in the reaction is neutralized as fast as it is formed the forward action will proceed to completion, but in order that no secondary reaction between iodine and the neutralizing reagent may intervene the latter must be properly selected.

When iodine and an alkali hydroxide meet the reaction results in the formation of an iodide, a hypoiodite, and ultimately an iodate:

$$\begin{aligned} 6\,I + 6\,KOH &= 3\,KI + 3\,KOI + 3\,H_2O \\ &= 5\,KI + KIO_3 + 3\,H_2O. \end{aligned}$$

The reaction between iodine and a neutral carbonate is similar, proceeding to an equilibrium,

$$2\,I + 2\,K_2CO_3 + H_2O \rightleftarrows KI + KOI + KHCO_3.$$

But upon acid carbonates in solution iodine has no appreciable action, and upon a mixture of monoalkali arsenite and the dialkali arsenite — which exist in the solution saturated with carbon dioxide — the only action of iodine is that of simple oxidation.

The reaction between iodine and an alkali arsenite (arsenic trioxide in presence of an alkali bicarbonate),

$$I_2 + NaH_2AsO_3 + 2\,NaHCO_3 = NaH_2AsO_4 + 2\,NaI + 2\,CO_2 + H_2O,$$

is practically as complete and definite as that between iodine and sodium thiosulphate.

The ease with which arsenic trioxide may be prepared and weighed in a state of purity, the stability of a properly made arsenite solution for long periods, and the definiteness of the reaction between iodine and the arsenite solution make the use of pure arsenic trioxide as a primary standard, in place of pure iodine, most convenient and desirable. But the relations discussed above make it imperative that, in making up the standard arsenite solution, care be taken to use a regulated amount of alkali hydroxide (or to neutralize the excess subsequently) and to have acid carbonate present for the neutralization of the hydriodic acid formed in oxidation of the arsenite by the iodine.* By comparison with the arsenite solution, carefully made and used as primary standard, the standard of iodine solutions made up approximately may be readily fixed; and, by comparison with iodine solutions thus standardized, the exact standard of solutions of sodium thiosulphate, made up approximately, may be determined. With these three standard solutions — the arsenite, the iodine, and the thiosulphate — and a properly made solution of starch to be used as an indicator of free iodine, many problems of quantitative analytical chemistry may be easily and accurately solved.

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* For the discussion of these relations from the point of view of the ionic theory, see Washburn: Jour. Am. Chem. Soc., **30**, 21 (1908).

Iodine, Iodate, and Hydrochloric Acid. — Iodine, free or evolved in reaction, may sometimes be conveniently determined by conversion to colorless iodine chloride formed in the reaction of this iodine with suitable concentrated hydrochloric acid and an oxidizer. The oxidizer best adapted to the purpose is potassium iodate in standard solution.*

When a solution of potassium iodide and potassium iodate is acidified with dilute hydrochloric acid iodine is set free, according to the expression

$$5\,KI + KIO_3 + 6\,HCl = 6\,KCl + 3\,I_2 + 3\,H_2O.$$

If, however, the hydrochloric acid is present in sufficient concentration (60 per cent of the concentrated acid) with the proper amount of iodate iodine enters into union with chlorine:

$$KIO_3 + 6\,HCl + 2\,I_2 = KCl + 5\,ICl + 3\,H_2O,$$

the entire reaction being expressed by the equation

$$KIO_3 + 2\,KI + 6\,HCl = 3\,KCl + 3\,ICl + 3\,H_2O.$$

The end-point of the reaction is best indicated by the disappearance of the iodine color from a small amount of chloroform (5 $cm.^3$) when the mixture in a stoppered bottle is thoroughly shaken in the intervals between successive additions of the standard iodate.

The Starch Indicator

While in colorless solutions of small volume (100 $cm.^3$) the yellow color produced by a single drop of N/10 iodine is distinct, it is, nevertheless, desirable in most cases to increase the delicacy of the end-reaction by the use of a sensitive indicator. The "starch blue" which is formed when iodine and pure starch come together in presence of an iodide is a very delicate indicator for free iodine.

The End-Color. — In the literature of iodometric titration frequent mention is made of the fact that a red color may sometimes appear, as well as the blue, when starch is used as

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* Andrews: Jour. Am. Chem. Soc., **25**, 796 (1903).

an indicator for iodine. It may happen, also, that in certain processes in which the red coloration appears, notably the titration of an arsenite or of an antimonite (tartar emetic), in presence of an alkali bicarbonate, loss of iodine will occur, outside the main reaction, when the readings are delayed beyond the first appearance of the red coloration. It has been found,* however, that neither the loss of iodine nor the red coloration takes place when a freshly made solution of pure starch is employed. Whenever it is impracticable to make use of a fresh and pure product it is best to add the starch indicator only at the end-point of the titration. In this way the end-color may be made a clear blue, even with an impure starch.

It appears that ordinary starch, or a once pure starch which has undergone partial hydrolysis, is liable to contain amidulin, which like starch gives a blue coloration, and erythrodextrin which gives a red coloration with iodine; these substances being the first two dextrins produced, in the order mentioned, when starch, either in the solid state or in solution, undergoes hydrolytic change. Amidulin is readily changed under the influence of an oxidizer to erythrodextrin and to this action must be ascribed the simultaneous production of the red coloration and disappearance of iodine sometimes noted in titrimetric processes. With an impure starch, the reading from the first permanent color, whether red or blue, is nearest to the correct value; and the titration should be made in well-diluted solutions — 150 cm.^3 to 200 cm.^3 — since the production of red is at a minimum and the loss of iodine small at high dilutions.

The Influence of Iodides. — The formation of the starch blue, as well as the delicacy of the iodine yellow, is conditioned by the presence of an iodide, and the influence of iodides upon the delicacy of the end reaction is obviously a matter of considerable importance analytically. Experience shows that the presence of 0.3 grm. of potassium iodide in volumes not exceeding 300 cm.^3 is sufficient to bring out the maximum sharpness of readings made either by means of the iodine yellow or by the starch blue, and that the indications are then quite as delicate at the ordinary room temperature as at the temper-

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* Hale: Methods in Analysis, Gooch, p. 29.

ature of ice-water. The addition of more potassium iodide (though not harmful, within reasonable limits) renders the readings no sharper for any given volume within that range of dilution. It is to be noted that the delicacy of the indication turns also upon the concentration of the iodide and that the amount of iodine necessary to bring out the starch blue in presence of a suitable amount of potassium iodide increases with the dilution.

According to the experimental evidence* it would appear that the group $KI \cdot I_4$ is characteristic of the blue starch iodide formed in presence of potassium iodide, and that the delicacy of the starch blue coloration depends upon keeping a concentration of potassium iodide suitable for the production of this group. On the other hand, the excessive concentration of the potassium iodide may be detrimental since it tends to change the group $KI \cdot I_4$ into two groups $KI \cdot I_2$, characteristic of a starch red which, however, reverts to the condition of the starch blue on further dilution of the solution.

Preparation of the Starch Solution. — The statement has been made that preparations of starch from different sources will show different capacities for absorbing iodine. This is incorrect. Any variety of pure starch (e.g., potato, rice or arrowroot) will serve for the preparation of the starch indicator. The "starch solution" may be made by grinding a suitable amount of starch (2 grm.) to a paste with a little cold water, pouring the mixture into boiling water (1 liter), and continuing the boiling for five or ten minutes so that a translucent solution is obtained. Only the clear supernatant liquid, or the clear solution after filtration, is to be used. The solution thus prepared will soon deteriorate in consequence of the growth of mould and, unless fresh solutions are to be prepared as needed, means must be taken to keep the starch in condition for use, — as may be done by adding 10 mgrm. of mercuric iodide in the process of grinding in cold water (*Gastine*); or, by filling into small bottles, the cold, filtered solution, sterilizing by heating these for two hours in a water-bath at 100

* Hale: Methods in Analysis, Gooch, p. 37.

degrees, closing the bottles by means of soft, sterilized stoppers, and keeping the individual bottles to be opened as the occasion may require (*Stokes*).

The Preparation and Use of Standards

Arsenic Trioxide, a Primary Standard. — Carefully sublimed and anhydrous arsenic trioxide serves as the most exact primary standard in iodometric processes. It may be prepared by subliming the commercially pure oxide from a large porcelain crucible (or small porcelain dish) upon a watch-glass, rejecting the first (or successive) portions of the sublimate in case it shows the red color of selenium or the yellowish color of arsenic trisulphide. Impure arsenic trioxide may also be purified by dissolving it in hot hydrochloric acid, filtering hot, crystallizing out the pure product, drying in the air, and resubliming.

To oxidize a gram-equivalent of arsenic trioxide (As_2O_3) in alkaline solution four gram-atoms of iodine (I) are required:

$$As_2O_3 + 2\,I_2 + 5\,H_2O = 2\,H_3O_3AsO + 4\,HI.$$

Solutions of the same degree of normality will be obtained when the arsenic trioxide and the iodine are taken in the proportion of $\frac{As_2O_3}{4} : I = \frac{197.92}{4} : 126.92 = 4.948 : 12.692$ for the same volume of solution.

Preparation of N/10 Arsenite. — A convenient method for the preparation of the N/10 solution of arsenite is to dissolve 4.948 grm. of pure arsenic trioxide in a concentrated solution of 4 grm. of potassium hydroxide and make up the solution to 1 liter by adding 100 cm.^{3} of a saturated solution of potassium hydrogen carbonate and enough water to complete the volume. The standard of the arsenite solution is most conveniently expressed in terms of the iodine which is equivalent to the arsenic trioxide contained in 1 cm.^{3} of the solution. The "iodine equivalent per cm.^{3}" of the carefully made N/10 arsenite solution is exactly equal to the "iodine value per cm.^{3}" of the N/10 iodine solution, or 0.012692 grm. The arsenic trioxide dissolves much more readily in the alkali hydroxide than in the acid carbonate alone, and the proportion given is not enough to convert the trioxide entirely into dipotassium hydrogen arsenite but more than enough to form dihydrogen potassium arsenite. Should more alkali hydroxide be used in effecting solution, it should be neutralized by a suitable amount of acid (sulphuric acid or hydrochloric acid) before the final addition of the acid carbonate in excess; but it is important to obtain the neutralization without the addition of any indicator containing alcohol, which is susceptible to the action of iodine in an alkaline solution. The neutralization is easily accomplished without the use of any indicator if attention is paid to the amount of alkali hydroxide employed. With this standard arsenite solution the standardization of iodine dissolved in potassium iodide is effected by titration with or without starch as an indicator, according to circumstances.

The Standard Iodine Solution. — To prepare a solution of iodine a weighed amount of potassium iodide is dissolved in as little water as possible, and to this solution is added a weight of iodine not greatly exceeding one-half that of the dissolved iodide. Upon shaking the mixture, the iodine will go into solution, and when this has been accomplished the solution is suitably diluted with water. An approximately N/10 solution of iodine may be made by thus dissolving 25 grm. of potassium iodide in a liter flask, adding 12.7 grm. of iodine, shaking until the iodine is completely in solution, and diluting to the mark. The solution is best standardized exactly by titration against the standard solution of the arsenite in presence of starch; or it may be standardized against a thiosulphate solution of previously determined standard.*

Experimental Process: Standardization of Iodine Against N/10 Arsenite. — Into an Erlenmeyer beaker containing 100 cm.^{3} of water draw a convenient portion (45 cm.^{3}) of the standard N/10 arsenite solution, and into this run from a burette the nearly N/10 iodine solution to be standardized until the liquid becomes visibly yellow from the slight excess of iodine. Then add 2 cm.^{3} or 3 cm.^{3} of starch solution, bleach the starch blue by the addition of a drop or two of the standard arsenite and then restore a distinct reading color by the careful addition of the iodine solution, the sensitiveness of the color reaction being greater in this direction. From the "iodine equivalent per cm.^{3}" (i = 0.012692 grm.), the number of cubic centimeters (n) of the arsenite solution, and the number of cubic centimeters of the iodine solution diminished by the amount of the single drop

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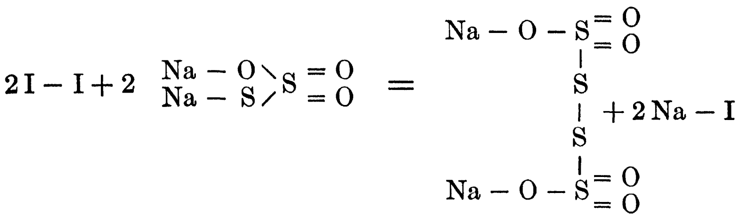
* See pp. 166, 167.

in excess (0.03 cm.^{3}) required to bring out the starch color (n'), the "iodine value per cm.^{3}" of the latter (i') may be found from the expression

$$ni = n'i',$$
$$i' = \frac{n\,(0.012692)}{n'}.$$

Iodine solutions of lower concentrations — for example, N/100 solutions — may be easily made by suitably diluting the standardized iodine solution of nearly N/10 concentration.

The Standard Thiosulphate Solution. — Sodium thiosulphate reacts with iodine in neutral solution, or when added with stirring to the slightly acid solution, according to the equation



In alkaline solution the reaction between sodium thiosulphate and iodine goes farther and is irregular.

Sodium thiosulphate is acted upon by free acids with the ultimate formation of sulphurous acid and sulphur:

$$\begin{aligned} Na_2S_2O_3 + 2\,HX &= 2\,NaX + H_2S_2O_3 \\ &= 2\,NaX + H_2SO_3 + S. \end{aligned}$$

It is even susceptible to the action of carbonic acid, and in a freshly made solution is subject to slight decomposition in consequence of the action of dissolved carbon dioxide; but when, after an interval of some days, the carbon dioxide has become fixed in the form of an acid carbonate the solution will keep its value for a considerable time. It is to be noted that if any sulphurous acid is produced by the decomposition of the thiosulphate this acid has a capacity to react with iodine twice greater than that of the thiosulphate from which it is derived. The amount of iodine which may enter into the reaction with the thiosulphate is dependent to a very marked degree, therefore, upon the concentrations of the thiosulphate and the free acid, as well as upon the duration of the reaction and the temperature. When considerable amounts of thiosulphate are to be titrated by iodine in an acidified solution the conditions under which the reaction takes place must be carefully guarded. The concentration of the acid should be restricted, the temperature should be reduced as nearly as possible to 0 degrees, and the iodine should be added promptly. So long as the thiosulphate present does not exceed a concentration equivalent to that of the N/100 solution a rapid titration proceeds in the cold solution with fair regularity in presence of hydrochloric acid in concentrations not greater than that of the N/4 solution of that acid. In most iodometric processes involving the use of the thiosulphate in acid solution it is possible to add that reagent gradually to the solution so that it may be acted upon by iodine in the normal way as fast as it is introduced. Under such conditions the danger of interaction with acid is avoided and the titration may be made at the ordinary laboratory temperature.

An approximately N/10 solution is made by dissolving in a liter of water 25 grm. of the crystallized sodium thiosulphate, $Na_2S_2O_3 \cdot 5\,H_2O$, about one-tenth of the gram-equivalent; but the standard of the thiosulphate may not be permanent until the solution has been allowed to stand for some days. The solution may be standardized by titration against (I) iodine in a solution previously standardized against the standard arsenite, or (II) against iodine specially prepared and weighed out, or (III) against iodine set free from an iodide by standard potassium permanganate, and several other less exact methods have been proposed.

Experimental Process: Standardization of Thiosulphate against Standard Iodine. — Into an Erlenmeyer flask containing 100 cm.^{3} of water draw a convenient portion (45 cm.^{3}) of the standardized solution of iodine and run in the thiosulphate solution to be standardized until only a pale yellow tinge remains of the original iodine color. Add starch solution (2 cm.^{3} or 3 cm.^{3}) and bleach the starch blue to the vanishing point by the careful addition of more of the thiosulphate. Find, from the number of cubic centimeters (n) of the iodine solution of known "iodine value per cm.^{3}" (i)

and the number of cubic centimeters (n') required to bleach the iodine color with starch, the "iodine equivalent per cm.³" (i') of the thiosulphate:

$$i' = \frac{ni}{n'}.$$

Experimental Process: Standardization against Weighed Iodine. — Pure iodine may be prepared from commercial iodine (which may contain chlorine, bromine, and cyanogen, as impurities) by mixing it with potassium iodide and subliming it from the iodide (which will remove the impurities) and then resubliming it to get rid of traces of iodide which may be carried with the iodine in the first sublimation. In carrying out this operation, heat the mixture in a beaker which is closed by a conical or cylindrical flask filled with luke-warm water.* Loosen the sublimed iodine which collects upon the condenser in the form of a crystalline crust by replacing the water in the condenser by cold water, thus chilling and contracting the glass. Remove the crust of iodine, and resublime it similarly by itself to get rid of traces of iodide. Grind it in an agate mortar and dry in a desiccator (with joints ungreased) over calcium chloride. This drying agent is preferable to sulphuric acid because the latter absorbs the vapor of iodine and may then evolve contaminating volatile products. The desiccator is used without grease lest the latter form with the iodine vapor hydriodic acid to be absorbed by the solid iodine.

In weighing out the iodine for use as the standard of reference, with necessary precaution against volatilization, place a portion (0.4 grm. to 0.5 grm.) in a weighed tube, provided with a glass stopper and containing potassium iodide (2 grm. to 2.5 grm.) moistened with a very little water (0.5 cm.³), put the stopper in place and weigh again. Loosen the stopper of the tube containing the iodine dissolved in the concentrated solution of the iodide and allow the tube, followed by the stopper, to slide down the side of an Erlenmeyer beaker held at an inclination and containing 200 cm.³ of water. Titrate the solution, thus prepared, with precaution against volatilization of the weighed iodine with the thiosulphate to be determined and find the "iodine equivalent per cm.³" of the thiosulphate.

Experimental Process: Standardization against Iodine Set Free by Standard Permanganate. — When potassium permanganate acts upon an acidified excess of potassium iodide, iodine is set free according to the equation

$$2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 2\,MnCl_2 + 8\,H_2O + 5\,I_2,$$

and the relation of the available oxygen to the iodine evolved is shown in the expression

$$5\,\ddot{O} + 10\,HI = 5\,H_2O + 10\,I,$$

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* For a specially designed apparatus see Treadwell-Hall: Analytical Chemistry, 3rd. ed., Vol. II, p. 646.

from which it appears that the "iodine equivalent per cm.^{3}" (i) of the permanganate will be to the oxygen value per cm.^{3} (o) in the relation 126.92 : 8.

To standardize an approximately N/10 solution of sodium thiosulphate by the use of standard permanganate, dissolve a suitable amount of potassium iodide (3 grm.) in water (200 cm.^{3}), add hydrochloric acid (5 cm.^{3}), and (if the solution remains colorless) a measured amount of standard permanganate (45 cm.^{3} N/10), and titrate with the thiosulphate solution the iodine set free, using starch as the indicator. Should the addition of acid to the solution of the iodide set iodine free before the permanganate is added, the solution may be made colorless again by the cautious addition of the exact amount of the thiosulphate required to bleach the iodine. Thereafter the permanganate may be immediately added. Of course, only the amount of the thiosulphate added after the permanganate is to be taken into account in the calculation of the relation between the permanganate and the thiosulphate. From the number of cubic centimeters of the permanganate taken (n), the number of cubic centimeters of the thiosulphate (n') used in taking up the iodine liberated by the permanganate, and the "oxygen value per cm.^{3}" of the permanganate (o), the "iodine equivalent per cm.^{3}" of the thiosulphate (i'), may be calculated

$$i' = \frac{no\,(126.92 \div 8)}{n'}.$$

The Standard Iodate Solution. — The standard solution of iodate may be made up by dissolving in water a carefully weighed amount (conveniently 10.7 grm. (about $\frac{1}{20}$ mol.) to the liter) of pure potassium iodate, KIO_3, neutral to litmus. If not at hand, pure potassium iodate may be made * by dissolving potassium permanganate (40 grm.) in hot water (1 liter), adding potassium iodide (20 grm.), heating for half an hour, adding alcohol drop by drop until decoloration of the excess of permanganate takes place, filtering, washing the residue with hot water, adding acetic acid to plainly acid reaction, evaporating to small volume (50 cm.^{3}), cooling to solution, and washing the crystallized product repeatedly with strong, pure alcohol. The oxidation of the iodide takes place according to the equation

$$KI + 2\,KMnO_4 + H_2O = KIO_3 + 2\,KOH + 2\,MnO_2.$$

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* Gröger: Zeit. Anorg. Chem., **1994**, 13.

In determining free iodine in presence of strong hydrochloric acid, by means of the iodate solution,

$$KIO_3 + 6\,HCl + 2\,I_2 = KCl + 5\,ICl + 3\,H_2O,$$

the relation between the iodate used and the iodine converted to iodine chloride is given by the expression

$$KIO_3 \Bumpeq 4\,I.$$

When the action takes place between the iodate and an iodide in presence of strong hydrochloric acid,

$$KIO_3 + 2\,KI + 6\,HCl = 3\,KCl + 3\,ICl + 3\,H_2O,$$

the relation between the iodate and the iodine combined in an iodide is given by the expression

$$KIO_3 \Bumpeq 2\,I.$$

The standard of an iodate solution may also be fixed by determining, as in the process of standardizing iodine (see p. 164), the amount of iodine which is set free when a given amount of the iodate is acted upon in slightly acidified solution by an excess of potassium iodide,

$$KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2,$$

in which reaction

$$6\,I \Bumpeq KIO_3.$$

The Determination of Iodine

Iodine in free condition or evolved in reaction may be dissolved in potassium iodide and determined, under suitable conditions, by means of standard arsenite (as in the experimental standardization of iodine against $N/10$ arsenite) or standard thiosulphate (by a process the reverse of the experimental standardization of thiosulphate against weighed iodine).

From the iodine equivalent per $cm.^3$ (i) of the standard solution and the number of cubic centimeters of it (n), the weight (w) of the iodine to be determined may be found from the expression $w = ni$; or, in case the iodine is determined by an exactly N/10 standard, by the expression $w = n \times 0.012692$.

The standard iodate solution may be used for the determination of free iodine in a strong solution of hydrochloric acid. See pp. 178, 180.

Processes Based upon Oxidation by Standard Iodine

As implied in the standardization of iodine against arsenic trioxide and in the similar standardization of sodium thiosulphate against iodine determinations of arsenic trioxide and of thiosulphates may be made by direct titration with standard iodine.

Direct Titration by Iodine

Determination of Arsenic Trioxide. — The determination of arsenic trioxide combined in the form of an alkali arsenite is made by titration with standard iodine in solution alkaline with an alkali hydrogen carbonate precisely as in the determination of the relation between iodine and the standard arsenite in the process of standardization of the former.* The reaction takes place according to the equation

$$KH_2AsO_3 + I_2 + 2\,NaHCO_3 = KHAsO_4 + 2\,NaI + H_2O + 2\,CO_2,$$

and the relation between arsenic trioxide and iodine is given by the expression

$$As_2O_3 + 2\,I_2 + 2\,H_2O = As_2O_5 + 4\,HI.$$

The solution of pure starch will give a sharp end-reaction, while with impure starch there may be an over use of iodine accompanying the production of reddish coloration. If only an impure starch is available the reading should be first made without starch in presence of enough potassium iodide to bring out sharply the yellow iodine color (see p. 161). The reading with starch may then be confirmed by adding the starch solution which, though impure, will then give only the pure blue color.

Determination of Thiosulphates. — Soluble thiosulphates may be determined by titration with iodine in the neutral or acid (not alkaline) solution, as in the standardization of the

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* See p. 164.

sodium thiosulphate solution.* When occurring in association with sulphides or sulphydrates the thiosulphate may be titrated after treatment of the mixture with freshly precipitated cadmium carbonate and filtration of the solution from the precipitated cadmium sulphide and the excess of cadmium carbonate.

Determination of Antimony Trioxide. — Another example of oxidation processes, based upon a direct titration by standard iodine, is the determination of antimony in the trivalent condition. In determining antimony trioxide, in a soluble compound, the titration is made by standard iodine in presence of an alkali hydrogen carbonate exactly as in the titration of an arsenite. It is necessary, however, to have the antimony in such combination that it may resist precipitation as antimonious acid (or an oxy-salt), due to the hydrolytic action of water or to the action of the alkali hydrogen carbonate, and this purpose is accomplished by adding tartaric acid or an alkali tartrate (such as Rochelle salt) to the liquid in which the antimony compound (e.g., antimony trichloride) is to be dissolved:

$$Sb_2O_3 + 2\,I_2 + 2\,H_2O = Sb_2O_5 + 4\,HI.$$

Reverse Titration

Determination of Sulphurous Acid. — According to Bunsen, when the concentration of the sulphur dioxide is very low — not exceeding the limit of 0.04 per cent of the solution — Dupasquier's method of oxidizing sulphurous acid to sulphuric acid proceeds ideally according to the reaction

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2\,HI.$$

In more concentrated solutions of sulphur dioxide the reaction may result in the formation of dithionic acid instead of sulphuric acid exclusively:

$$2\,H_2SO_3 + I_2 = H_2S_2O_6 + 2\,HI.$$

Moreover, a reaction may set in between the sulphur dioxide and the hydriodic acid produced or present in consequence of the

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* See p. 166.

action of the sulphuric acid upon the potassium iodide of the standard iodine solution. In this secondary reaction iodine and sulphur are set free:

$$SO_2 + 4\,HI = 2\,I_2 + 2\,H_2O + S.$$

When the conditions of reaction are so adjusted that there is no excess of sulphur dioxide to react with iodine or with hydriodic acid the subsidiary reactions cannot take place; and this is the case when the solution of sulphurous acid is slowly added to the iodine solution or when the solution of a sulphite is slowly added to the iodine solution previously acidulated. In determining sulphurous acid or a sulphite the usual course of the iodine titration is therefore reversed; the solution of the substance to be determined is made up to a known volume, and of this solution a measured portion of the standard iodine, suitably acidified, is added to the point of decoloration.*

Action of Iodine in Excess and Titration of the Excess

Determination of Soluble Sulphides. — Iodine reacts with hydrogen sulphide, according to the equation

$$H_2S + I_2 = 2\,HI + S,$$

but in the practical determination of the volatile hydrogen sulphide by means of this reaction, direct titration by gradual addition of standard iodine is not feasible. The process may, however, be made successful by introducing the solution of hydrogen sulphide into a solution of standard iodine, so diluted that the separated sulphur will not coagulate to a film, and determining by standard sodium thiosulphate the excess of the latter. Sulphides and sulphydrates which evolve hydrogen sulphide if brought into contact with dilute hydrochloric acid may be similarly determined by introducing them into the diluted solution of standard iodine containing also hydrochloric acid — or, by acting upon them with acid and conducting the evolved hydrogen sulphide into the acidulated and

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* See, also, Ashley: Methods in Analysis, Gooch, p. 366.

dilute solution of standard iodine — the iodine in excess being titrated by standard thiosulphate.

Processes Based upon Liberation of Iodine in Solution

Determination of Bromine. — With an excess of potassium iodide, bromine reacts according to the equation

$$Br_2 + 2\,KI = 2\,KBr + I_2.$$

When bromine in water solution (best faintly acidulated with hydrochloric acid) is added to the solution of potassium iodide the iodine set free measures the bromine. To avoid loss by volatilization in the process the bromine solution should be delivered from a pipette, the opening of which is held close to the surface of the iodide solution contained in a flask or bottle provided with a glass stopper. Upon shaking the liquids together in the stoppered bottle the reaction is completed immediately and the free iodine, which may be titrated by standard thiosulphate or with standard arsenite after the addition of an excess of alkali hydrogen carbonate, measures the bromine originally free, according to the equation above.

When the bromine is in gaseous form, as when it is dissolved in air, it must be introduced into the solution of potassium iodide in a way to preclude danger of mechanical loss in the process of absorption by the iodide solution.

A convenient method for the manipulation of such gaseous substances is to place them, contained in a glass stoppered pipette or Chancel flask, between a carbon dioxide generator and a trapped absorption bottle, of the form shown in Fig. 28, charged with a solution of potassium iodide. The gas may then be passed bubble by bubble into the solution of potassium iodide which reacts with the bromine and retains most of the iodine set free, while any traces of bromine or iodine which may escape from the bottle are caught in the trap also charged with potassium iodide.

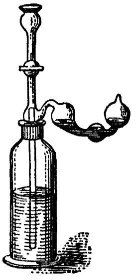

FIG. 28.

From the number of cubic centimeters (n) and the iodine equivalent per cm.[3] (i) of the thiosulphate or arsenite, the weight of bromine (w) may be calculated from the proportion

$$w : ni = \text{Br} : \text{I} = 79.97 : 126.92,$$

$$w = \frac{ni \times 79.97}{126.92}.$$

Determination of Chlorine. — Chlorine in water solution or in gaseous form may be determined by procedures exactly like those described for the determination of bromine, the chlorine reacting with an excess of potassium iodide according to the equation

$$\text{Cl}_2 + 2\,\text{KI} = 2\,\text{KCl} + \text{I}_2,$$

in accordance with which the amount of chlorine may be calculated from the iodine liberated and determined by titration with the standard thiosulphate or the standard arsenite.

From the number of cubic centimeters (n) and the iodine equivalent per cm.[3] (i) of the thiosulphate or arsenite, the weight (w) of chlorine is given by the formula

$$w = \frac{ni \times 35.45}{126.92}.$$

The Reaction between an Iodide and an Iodate in Presence of Dilute Acid. — From iodides the iodine may be liberated by the action of iodic acid or of an iodate and a suitable acid, e.g., dilute sulphuric acid; from iodates (and periodates) the iodine may be liberated by the action of a suitable acid and an iodide. In either process iodic acid and hydriodic acid enter into the reversible reaction

$$\text{HIO}_3 + 5\,\text{HI} \rightleftarrows 3\,\text{I}_2 + 3\,\text{H}_2\text{O}.$$

Under suitable conditions this reaction may be utilized for the determination of iodine in iodides or in iodates. At all volumes ordinarily used in analysis the direct action is practically complete when the hydriodic acid is in moderate excess. In order that the reaction given above may be realized when the iodic acid is in excess attention must be paid to limiting the volume of the water solution in which the reaction takes place. In presence of an appreciable amount of hydrochloric acid, or a chloride, a secondary reaction takes place which results in the formation of iodine chloride; and this action may be complete in presence of a suitable amount of hydrochloric acid: *

$$2\,I_2 + KIO_3 + 5\,HCl = 5\,ICl + 3\,H_2O.$$

Determination of Iodates. — When potassium iodide in excess and dilute hydrochloric acid, or dilute sulphuric acid, are added to the solution of an iodate, iodine is immediately set free according to the equation

$$MIO_3 + 5\,KI + 6\,HCl = 5\,KCl + MCl + 3\,H_2O + 3\,I_2.$$

The iodine set free may be titrated at once by standard sodium thiosulphate, or it may be absorbed by an excess of standard arsenite, this excess being determined by titration with standard iodine. In these operations

$$MIO_3 \approx 3\,I_2.$$

Experimental Process: Determination of Iodate by Thiosulphate Titration of Iodine. — Weigh out exactly about 0.15 grm. of potassium iodate, dissolve it in water (about 100 cm.^{3}), add in solution an excess of potassium iodide (1 grm.) and acidulate the mixture with dilute hydrochloric acid or sulphuric acid. Titrate at once the free iodine by means of N/10 thiosulphate. Find the weight of iodate (w) from the number of cubic centimeters (n) and the iodine equivalent per cm.^{3} (i) of the thiosulphate solution by the proportion

$$ni : w = 6 \times 126.92 : 1 \text{ grm. mol. } MIO_3,$$
$$w = \frac{ni \times 1 \text{ grm. mol. } MIO_3}{6 \times 126.92}.$$

Tabulate the details of the determination.

Experimental Process: Determination of Iodate by Arsenite Absorption of Iodine. — When the iodine set free in the reaction between an iodate, an iodide, and hydrochloric acid is estimated by acting upon it with standard arsenite in excess and titrating this excess by standard iodine, precaution must be taken to prevent any escape of iodine with the carbon dioxide evolved in the process of neutralization. A suitable apparatus for the application of the process is a reaction-bottle of 500 cm.^{3} or 1000 cm.^{3} capacity (Fig. 28, p. 173) provided with a stopper carrying a stop-cock and thistle fused to the inlet tube and a Will and Varrentrapp absorption trap sealed to the outlet tube.

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* See p. 178.

Put the iodate to be determined (about 0.15 grm. of KIO_3) into the bottle with more than the equivalent amount of potassium iodide (3 grm.) and adjust the volume of the liquid to about 150 cm.^{3}. Set the stopper in place, and charge the trap with a solution (5 per cent) of potassium iodide. Introduce sulphuric acid (5 cm. of the [1 : 3] mixture) through the thistle tube and agitate the solution thoroughly by a rotary motion of the bottle, to bring about the mixture of the acid, the iodate, and the iodide. Add an amount of sodium hydroxide in solution sufficient (as previously determined) to neutralize the larger part of the free acid, shake thoroughly, and add a saturated solution of potassium hydrogen carbonate, $KHCO_3$, to an amount about 10 cm.^{3} more than sufficient to neutralize all the sulphuric acid. Close the stop-cock and shake the solution carefully until the last traces of iodine vapor have been absorbed by the liquid. Run the solution in the trap into the bottle and add the washings of trap, tubes, and stopper. Now, introduce standard N/10 arsenite to the bleaching point of the iodine, add starch solution, and titrate the excess of arsenite with N/10 iodine (usually only a few drops) to coloration. Calculate the weight of the iodate (w) from the number of cubic centimeters (n) and the iodine equivalent per cm.^{3} (i) = (0.012692) of the N/10 arsenite solution, with the number of cubic centimeters of the standard iodine (n') and its iodine value per cm.^{3} (i), by the proportion

$$ni - n'i' : w = 6 \times 126.92 : 1 \text{ grm. mol. } MIO_3,$$

$$w = \frac{(ni - n'i') \times 1 \text{ grm. mol. } MIO_3}{6 \times 126.92}.$$

Tabulate the details of the operation.

Determination of Periodates. — *Action of an Iodide in Presence of Acid.* Periodates may be analyzed by procedure similar to that described above for the determination of iodates, the decomposition taking place according to the equation

$$MIO_4 + 7\,KI + 8\,HCl = 7\,KCl + MCl + 4\,I_2.$$

If the process of direct titration of the free iodine by standard thiosulphate is followed, the calculation may be made from the number of cubic centimeters (n) of the thiosulphate used and the iodine equivalent per cm.^{3} (i) of that reagent, according to

$$w = \frac{ni \times 1 \text{ grm. mol. } MIO_4}{8 \times 126.92}.$$

If the titration of the free iodine is made by using standard arsenite in excess (n cubic centimers of iodine equivalent i), and estimating the excess by standard iodine (n' cubic centimeters of iodine value i') the calculation may be made by the formula

$$w = \frac{(ni - n'i') \times 1 \text{ grm. mol. } MIO_4}{8 \times 126.92}.$$

Action of an Iodide in Alkaline Solution. The decomposition of a periodate may also be effected by potassium iodide in presence of an alkali hydrogen carbonate, according to the equation

$$MIO_4 + 2\,KI + 2\,MHCO_3 = MIO_3 + K_2CO_3 + M_2CO_3 + H_2O + I_2.$$

The solution of the periodate is made barely alkaline to phenolphthalein with the use of an alkali hydroxide or hydrochloric acid as may be necessary, and is then treated with sodium hydrogen carbonate (10 cm.^{3} of the cold saturated solution) and potassium iodide. The iodine liberated immediately may be titrated by standard N/10 arsenite which is not affected by the iodate, and this reaction may be utilized for the determination of the iodine of a periodate in presence of an iodate.

If n cubic centimeters of arsenite having an iodine equivalent per cm.^{3} i are used, the weight w of periodate is given by the following expression:

$$w = \frac{n \times 0.012692 \times 1 \text{ grm. mol. } MIO_4}{2 \times 126.92}.$$

Determination of Iodates and Periodates in Association. — The weight of iodine (w) of an iodate associated with the periodate may be determined by combining the result of the titration of the iodine set free (from the periodate) in the alkaline solution with that of the titration of the iodine (from the iodate and periodate) set free in acid solution.

Denoting by n the number of cubic centimeters used of the N/10 arsenite and by n' the number of cubic centimeters of thiosulphate containing the iodine equivalent per cm.^{3} i',

$$w = \frac{(n'i' - 4\,[n \times 0.012692]) \times 1 \text{ grm. mol. } MIO_3}{6 \times 126.92}.$$

Determination of Iodides. — *Action of the Iodate in Slightly Acid Solution.* In applying the reaction

$$5\,HI + HIO_3 \rightleftarrows 3\,H_2O + 3\,I_2,$$

to the analysis of an iodide, it is obvious that if the iodine set free in presence of an excess of the iodate is to be determined in the solution and made the measure of the iodide it must be determined by a reagent which will not be affected also by the excess of iodate. Sodium thiosulphate is not available for this purpose, since in acid solution it reacts with the iodate while in alkaline solution its reaction with iodine is irregular. But it is possible to so arrange the process that the action between the iodate and the iodide takes place in acid solution and the determination of the liberated iodine is made in alkaline solution by means of the standard arsenite, which is unaffected by the excess of the iodate.* The reaction between an iodide, iodate and acid may also be applied in such fashion that the difference between the amount of iodate taken in excess and the amount of it which remains after boiling out the free iodine (see p. 179) shall be made the measure of the iodine to be determined.†

In either of these processes, the presence of any considerable amount of chloride or bromide interferes with the accuracy of the analytical process, since chlorides and bromides are appreciably attacked by iodic acid and iodine in association, with the formation of iodine chloride and iodine bromide.

Action of the Iodate in Presence of Strong Hydrochloric Acid

The iodine set free in the reaction between a standard solution of iodate and an iodide (see also p. 180) may be converted to iodine monochloride by further action of the iodate in presence of sufficiently concentrated hydrochloric acid, and the amount of iodine acted upon may be found from the amount of iodate required to complete this reaction,‡ according to the equation

$$KIO_3 + 2\,KI + 6\,HCl = 3\,KCl + 3\,ICl + 3\,H_2O.$$

The vanishing of the iodine color from chloroform shaken up with this solution marks the end-point of the reaction. This

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* Gooch and Walker: Methods in Analysis, Gooch, p. 454.

† Dietz and Margosches: Analytical Chemistry, Treadwell-Hall, 3rd ed., Vol. II, p. 671.

‡ Andrews: Jour. Am. Chem., **25**, 756 (1903).

process has the advantage that the reagent which sets free the iodine determines it also, and that the presence of chlorides or bromides does not interfere with the accuracy of the determination.

Experimental Process: Arsenite Determination of Iodine Set Free from Iodide by Iodate. — Draw from a burette in a reaction bottle (Fig. 28), an amount of an approximately N/10 solution of potassium iodide equivalent to about 0.4 grm. of the iodide. Add more than equivalent amount (about 0.2 grm.) of potassium iodate in solution and make up the volume of liquid to 150 cm.^{3}. Insert the stopper and charge the trap with a solution (5 per cent) of potassium iodide. Introduce sulphuric acid (5 cm.^{3} [1 : 3]) through the thistle tube and mix the solution. Then add slowly a saturated solution of potassium hydrogen carbonate, in amount (10 cm.^{3}) somewhat in excess of that needed to neutralize the sulphuric acid. After the neutralization, which prevents interaction when the iodide in the trap and the iodate in the bottle come into contact, bleach the free iodine in the bottle and trap by N/10 arsenite, add starch, and titrate with N/10 iodine the very slight excess of the arsenite used in the bleaching. From the iodine equivalent per cm.^{3} of the standard arsenite (i) and the number of cubic centimeters of it used (n), with the iodine value per cm.^{3} of the standard iodine (i'), and the number of cubic centimeters of it used (n'), calculate the weight (w) of the iodine given by the proportion

$$ni - n'i' : w = 3I_2 : 5\,MI,$$

$$w = \frac{5\,(ni - n'i')\,(1 \text{ grm. mo. MI})}{6 \times 126.92}.$$

Fix the standard of the solution of iodide.

Experimental Process: Determination of Iodide from Excess of Iodate Used.— First, make a solution of potassium iodate of nearly N/10 value in respect to the iodine which will be evolved by its reaction with an iodide in presence of acid (containing in a liter 1grm. mol. ÷ 6 × 10 of KIO_3) and determine the exact iodine equivalent per cubic centimeter by treating a measured portion with potassium iodide in excess, adding sulphuric acid, and titrating by N/10 thiosulphate the iodine set free. From the iodine equivalent per cm.^{3} of the thiosulphate (i) and the number of cubic centimeters used (n), with the number of cubic centimeters (n') of the iodate, the iodine equivalent per cm.^{3} of the iodate (i') solution will be given by the expression

$$i' = \frac{ni}{n'}.$$

Next, treat the solution of the iodide to be determined with a measured volume of the iodate solution (now of known iodine value per cm.^{3}), acidify with hydrochloric acid, introduce a piece of calcite, and boil until the free iodine is expelled. In this process the iodide is completely broken up in accordance with the equation

$$KIO_3 + 5\,MI + 6\,HCl = 5\,KCl + MCl + 3\,H_2O + 3\,I_2,$$

the amount of iodide to be determined being equivalent to five-sixths of the iodate which disappears. Find the amount of the iodate which remains by treating the cooled solution with an excess of potassium iodide and titrating with the standard thiosulphate the iodine liberated, as in the determination of the iodine of the iodate.

If the iodine equivalent per cm.^{3} of the thiosulphate is denoted by i, the number of cubic centimeters used in titrating the iodine liberated by the excess of iodate by n, the iodine equivalent per cm.^{3} of the iodate by i', and the number of cubic centimeters of iodate used by n', the amount of iodine liberated by the iodate which disappeared in reaction with the iodide to be determined will be given by the expression $n'i' - ni$, and five-sixths of this amount will be the iodine equivalent of that iodide. The weight of iodide determined is given by the proportion

$$5/6\,(n'i' - ni) : w = I : MI = 126.92 : 1 \text{ grm. mol. MI},$$

$$w = \frac{5\,(n'i' - ni)\,(1 \text{ grm. mol. MI})}{6 \times 126.92}.$$

Tabulate the details of the operation.

Experimental Process: Determination of Iodide by Direct Action of Standard Iodate. — Draw from a burette 20 cm.^{3} of the approximately N/10 solution of potassium iodide into a 250-cm.^{3} glass bottle provided with a glass stopper. Add 5 cm.^{3} of chloroform and 30 cm.^{3} of concentrated hydrochloric acid. Into the mixture measure from a burette successive portions of the standard iodate solution, inserting the stopper and shaking the contents of the bottle vigorously between the additions of the iodate, until the violet color of iodine in the chloroform just disappears. Calculate the standard of the iodide solution from the relation

$$KIO_3 \simeq 2\,KI.^*$$

Other Substances (Oxidizers) Reactive with Iodide or Hydriodic Acid. — Like the iodates and periodates, certain other substances enter into complete reactions with potassium iodide or with hydriodic acid (produced in the interaction of an excess of potassium iodide and a suitable acid), so that exact determinations of these substances may be based upon the immediate titration of the iodine thus set free. Examples of such

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* See p. 178.

substances are hydrogen dioxide, the soluble hypochlorites, bromates, chromates, permanganates, the higher oxides of lead and cerium, gold tri-chloride, ferric chloride, and cupric salts.

Determination of Hydrogen Dioxide. — In dilute solution and in presence of free acid, hydrogen dioxide liberates iodine from potassium iodide according to the equation

$$2\,HI + H_2O_2 = 2\,H_2O + I_2.$$

If a suitable amount of hydrogen dioxide (10 cm.^{3} of a 0.6 per cent solution) is added gradually to dilute (1:20) sulphuric (200 cm.^{3}) containing an excess (2 grm.) of potassium iodide, the iodine set free after a short interval (5 minutes) may be titrated with N/10 thiosulphate and taken as the measure of the hydrogen dioxide.

Determination of Hypochlorites.[*] — The reaction between hypochlorous acid and hydriodic acid is immediate, so that in the determination of a hypochlorite it is only necessary to add it to a solution of potassium iodide, acidify the hydrochloric acid, and titrate the free iodine with sodium thiosulphate.

$$HOCl + HCl + 2\,KI = 2\,KCl + H_2O + I_2.$$

Determination of Bromates. — Bromic acid and hydriodic acid, formed in the interaction of potassium iodide, sulphuric acid, and potassium bromate, react together according to the equation

$$6\,HI + HBrO_3 = HBr + 3\,I_2.$$

Time of action, proportion of iodide to bromate, excess of acid, and the concentrations are all within limits determining factors,

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[*] In presence of a chlorate the determination of the hypochlorite is best made otherwise, since the former may take part to some extent in the evolution of iodine from the iodide. By the action of standard arsenite the hypochlorite may be reduced while the chlorate is not affected:

$$2\,NaOCl + As_2O_3 = As_2O_5 + 2\,NaCl.$$

In the technical analysis of "chloride of lime," which may also contain chlorate, it is customary to titrate the emulsion of this substance in water with standard arsenite to the point at which a single drop of the solution, removed on a rod, fails to set free iodine and produce a blue coloration of test-paper made by impregnating it with starch and potassium iodide and drying. In this process the reaction involving iodine is only employed to indicate the end-point.

but if free acid and a considerable excess of potassium iodide are present the reaction proceeds to completion within a reasonable time. When an amount of potassium bromate not exceeding 0.14 grm. in 100 cm.^{3} of solution is put in the reaction bottle (Fig. 28), with 2.5 cm.^{3} of sulphuric acid (1 : 1), or an equivalent amount of hydrochloric acid, and about four times the amount of iodide theoretically required (3 grm.) the reaction is complete in half an hour and the determination of the liberated iodine serves to measure the bromate quite exactly.*

Determination of Chromates. — Chromic acid is immediately reduced by potassium iodide in presence of hydrochloric acid, to the green chromic chloride, with evolution of an amount of iodine which is equivalent to the oxygen lost by the chromic acid. Chromates and dichromates behave similarly:

$$2\,K_2CrO_4 + 6\,KI + 16\,HCl = 10\,KCl + 2\,CrCl_3 + 8\,H_2O + 3\,I_2,$$
$$K_2Cr_2O_7 + 6\,KI + 14\,HCl = 8\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,I_2.$$

The iodine set free is a measure of the chromate or dichromate entering into the reaction. After suitably diluting the solution, so that the green color may not mask the disappearance of the starch blue in the end reaction, the greater part of the iodine is bleached by standard thiosulphate, starch is added, and the titration by the thiosulphate is continued until the color of the solution changes from blue to green.

Permanganates. — Upon contact with a solution of potassium iodide containing hydrochloric acid, permanganates are reduced with the formation of manganous chloride and the liberation of iodine:

$$2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 2\,MnCl_2 + 8\,H_2O + 5I_2.$$

The iodine liberated, which is the measure of the permanganate originally present, may be titrated by the process previously described for the standardization of the thiosulphate solution by means of potassium permanganate. (See p. 167.)

Determination of Lead Dioxide. — In presence of 5 per cent acetic acid, sodium acetate, and potassium iodide, lead dioxide,

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* Gooch and Blake: Methods in Analysis, Gooch, p. 471.

finely ground (if dry) or in hydrated form, is decomposed according to the equation

$$PbO_2 + 4\,HI = PbI_2 + 2\,H_2O + I_2.$$

If a large excess of the acetate is present with not too much potassium iodide the lead iodide will not precipitate, and upon further dilution the dissolved iodine may be titrated with standard thiosulphate.

Suitable proportions are about 0.5 grm. of lead dioxide, 1.2 grm. of potassium iodide, 10 grm. of sodium acetate, and 5 cm.^{3} of 5 per cent acetic acid. If lead iodide is precipitated it should be dissolved by more sodium acetate with a little water. After dilution to a volume of about 25 cm.^{3}, the still clear solution of iodine is titrated with the thiosulphate.

Determination of Cerium Dioxide. — Anhydrous cerium dioxide, prepared by the ignition of the oxalate or the hydroxide, is very slowly acted on by hydrochloric acid, especially when free from the oxides of lanthanum and didymium. By digesting cerium dioxide with potassium iodide and hydrochloric acid the decomposition of the dioxide is brought about and iodine is set free in accordance with the reaction

$$2\,CeO_2 + 8\,HCl + 2\,KI = 2\,CeCl_3 + 2\,KCl + 4\,H_2O + I_2.$$

In this procedure, a weighed portion of the cerium dioxide is placed in a small glass-stoppered bottle (of about 100 cm.^{3} capacity), with 1 grm. of potassium iodide and a few drops of water. Carbon dioxide is passed into the bottle to expel the air, concentrated hydrochloric acid (10 cm.^{3}) is added, the stopper is inserted, and the bottle is heated gently upon a steam radiator for about an hour, until the dioxide is completely dissolved. After cooling, the solution in the bottle is carefully washed into a considerable volume of water and titrated with N/10 thiosulphate. Correction should be made for the amount of iodine set free from potassium iodide by hydrochloric acid, without the addition of cerium dioxide, under similar conditions of treatment, but this correction should not exceed a few hundredths of a cubic centimeter if the process is carefully conducted.

Determination of Gold Trichloride. — When potassium iodide reacts at suitable concentrations with minute amounts of gold trichloride in solution, the reaction takes place regularly along the line of the following equation:

$$AuCl_3 + 2\,KI = AuCl + 2\,KCl + I.$$

The iodine liberated may be determined by N/100 or N/1000 sodium thiosulphate and the amount of the gold may be calculated from the proportion of the equation given.* In a similar process in which the reduction of gold chloride is effected by potassium iodide and the free iodine titrated with sulphurous acid, larger amounts of gold may be determined (*Lenher*).

Determination of Ferric Chloride. — The reaction between ferric chloride and hydriodic acid is reversible:

$$2\,FeCl_3 + 2\,HI \rightleftarrows 2\,FeCl_2 + 2\,HCl + I_2.$$

In order that the direct action between ferric chloride, potassium iodide, and hydrochloric acid may proceed to completion it is necessary to have a considerable excess of the iodide present and to remove from time to time the iodine set free while protecting the acid solution of the iodide from action of atmospheric oxygen during the protracted titration.

The solution of ferric chloride, or ferric sulphate, containing a slight excess of free hydrochloric acid is placed in a trapped reaction-bottle like that shown in Fig. 28, p. 173. The stopper carrying the inlet tube with thistle and stop-cock and the outlet tube with its trap charged with a solution of potassium iodide is put in place; the air in the bottle is replaced by carbon dioxide introduced through the thistle tube; a solution of potassium iodide (5 grm.) is introduced through the thistle tube and mixed with the ferric chloride by a rotary movement of the bottle; and the mixture is allowed to stand for twenty minutes. The liberated iodine is nearly bleached by titration with sodium thiosulphate introduced through the thistle tube, starch is added, and the titration is continued until the starch-iodide blue disappears. If upon further standing the blue color returns, more iodine must be added, and the process of standing and titrating repeated.

Determination of Copper in Cupric Salts. — When potassium iodide is added to the solution of a cupric salt, cuprous

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* Gooch and Morley: Methods in Analysis, Gooch, p. 146.

iodide is precipitated, while iodine is liberated in an amount which is equivalent to the cuprous iodide:

$$2\,CuSO_4 + 4\,KI = 2\,K_2SO_4 + Cu_2I_2 + I_2.$$

This reaction has been made the basis of an iodometric method for the determination of copper.* To obtain the best results, attention must be paid to the concentrations of the reagents and of free acid.

The procedure best suited to the determination of an amount of copper not exceeding 0.3 grm. seems to be covered by the following directions.† The solution of the cupric salt, containing no more than 3 cm.^{3} of concentrated sulphuric acid, hydrochloric acid, nitric acid (free from nitrogen oxides) or 25 cm.^{3} of 50 per cent acetic acid, is made up to a volume of 100 cm.^{3} and treated with 5 grm. of iodate-free potassium iodide. The iodine liberated is titrated by sodium thiosulphate with the use of starch indicator at the end of the titration. When as much as 25 cm.^{3} of the N/10 sodium thiosulphate has been used in the titration without bleaching all the iodine 2 grm. or 3 grm. more of potassium iodide should be added before continuing the titration.

Titration of Iodine after Extraction from Aqueous Solution

When iodine is liberated in association with substances which interfere with the direct titration by means of sodium thiosulphate or by an alkali arsenite, it is sometimes possible to estimate the iodine by titration after extracting it from the aqueous solution in a non-miscible solvent, such as carbon disulphide or chloroform. In applying the process of extraction the general principle which governs the division of a solute between two non-miscible solvents should be borne in mind.‡ The experimentally determined ratio of the concentration per cm.^{3} of the iodine in water to that in the carbon disulphide is

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* Originally proposed by DeHaen, discussed by many investigators, modified and advocated by Low. For review and references, see Methods in Analysis, Gooch, p. 118: for the application to the technical analysis of copper ores, see Treadwell-Hall: Analytical Chemistry, 3rd ed., pp. 682–684.

† Gooch and Heath: Methods in Analysis, Gooch, p. 121.

‡ See p. 56.

1 : 400. For the distribution of iodine between water and carbon disulphide, the general expression, in which x_0 is the amount of iodine in the water and x_n the amount of iodine in the carbon disulphide after n shakings of the water solution of volume V with n portions of carbon disulphide of volume v, takes the form

$$x_n = x_0\left(\frac{\frac{1}{400}V}{v + \frac{1}{400}V}\right)^n = x_0\left(\frac{V}{V + 400\,v}\right)^n.$$

The amounts of iodine remaining from 0.0500 grm. after shaking its solution in 100 cm.^3 of water with 5 cm.^3 portions of carbon disulphide will be given by the expression

$$x_n = 0.05\left(\frac{100}{100 + 2000}\right)^n = 0.05\left(\frac{1}{21}\right)^n.$$

After one shaking the amount of iodine remaining in the water separated by means of a stoppered funnel will be 0.0024 grm.; after two shakings, 0.0001 grm.

Decomposition of Iodides by Nitrous Acid. — The determination of iodine liberated from iodides by the action of nitrous acid,

$$2\,HI + HNO_2 = 2\,H_2O + NO + I_2,$$

and titrated with sodium thiosulphate after absorption by shaking the aqueous mixture with carbon disulphide or with chloroform rests upon this principle. This process is subject to irregularities which preclude the use of a solution of the thiosulphate standardized in the ordinary way; but if use be made of an *empirical standard* determined by matching the thiosulphate against the iodine set free by nitrous acid from a known amount of iodide closely like that of the iodide to be determined, the process may be made serviceable in the determination of small amounts of iodides in association with relatively large amounts of chlorides and bromides.

Processes Depending upon the Determination of Iodine Volatilized to the Distillate

The non-reversible reactions in which hydriodic acid or an iodide is completely broken up with evolution of iodine by oxidizers generally involve a further reaction in which a portion of the iodine is oxidized to iodic acid. To remove the iodine completely from an iodide and leave it free so that it may be volatilized to the distillate it is necessary to employ a reaction in which a product of reduction is sensitive enough to oxidation to prevent the formation of iodic acid, and such reactions prove to be reversible in respect to this liberation of iodine from an iodide. When the iodine evolved is made the measure of the oxidizer, it is essential to exclude oxygen from the boiling solution containing hydriodic acid in order that iodine may not be set free apart from the main reaction, and this is accomplished by performing the operation in an atmosphere of carbon dioxide made as free as possible from air by acting in the Kipp generator upon previously boiled marble with boiled hydrochloric acid charged with cuprous chloride.

Determination of Iodine in Iodides. — Arsenic acid is capable of expelling iodine from hydriodic acid without forming iodic acid. The reversible reaction between arsenic acid in excess and hydriodic acid,

$$H_3AsO_4 + 2\,HI \rightleftarrows H_3AsO_3 + H_2O + I_2,$$

may be made complete in the forward direction by volatilizing the iodine, and if the iodine volatilized be absorbed in the distillate it may be easily determined by titration and made the measure of the iodide acted upon.

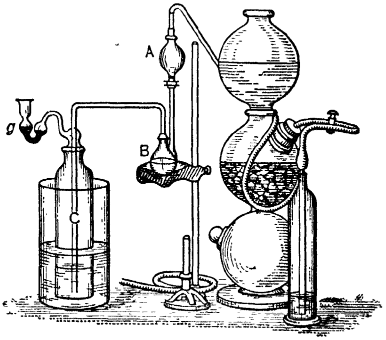

Fig. 29.

A suitable form of distillation apparatus,* constructed with sealed or ground joints of glass whereever contact with iodine is a possibility, as shown in Fig. 29, may be easily made by sealing together a separating funnel *A*, a Voit flask *B*, a Drechsel wash-bottle *C*, and a bulbed trap *g*. Upon the side of the distillation flask *B* is pasted or etched a graduated scale by means of which the

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* Gooch and Norton: Methods in Analysis, Gooch, p. 418.

volume of the liquid in the flask may be known. The bottle used as the receiver and the trap are charged with a solution of potassium iodide (3 grm. of iodide in 200 cm.^{3} of water). The iodide, in solution, is placed in the distillation flask and the connection of the latter with the receiver is adjusted. A mixture of 20 cm.^{3} of sulphuric acid (1 : 1) and 2 grm. of dihydrogen potassium arsenate is introduced through the stoppered funnel followed by enough water to make up the total volume of liquid to about 50 cm.^{3}. Carbon dioxide, produced in a Kipp generator by the action of hydrochloric acid upon marble, is passed through the apparatus, to facilitate the transfer of the iodine from the distillation flask to the receiver. The liquid is boiled until the volume has decreased to 35 cm.^{3}, when the operation should be stopped and the iodine in the receiver and trap titrated by sodium thiosulphate or, after the addition of an excess of hydrogen potassium carbonate, with the standard arsenite.

Approximative Determinations of Arsenic, Antimony, Vanadium, Molybdenum, Cerium, and Selenium. — Incomplete and reversible reactions between certain oxidizers and potassium iodide in excess, in the presence of an acid, may also be made complete by the removal of the iodine which appears as a volatile product of the reaction. Determinations based upon such procedure may be made to depend upon finding the amount of iodine distilled and collected in the distillate; but, in this case, it is necessary to carry on the process of distillation in an atmosphere of carbon dioxide, so that the hydriodic acid may not be acted upon by atmospheric oxygen with the consequent liberation of iodine outside the main reaction. Furthermore, solutions containing hydriodic acid tend to withhold iodine from volatilization, and that in proportion to the concentration of this acid. If the concentration is considerable it is impracticable to remove to the distillate the last traces of iodine set free by an oxidizer from an iodide used in excess. In such cases, a determination of the oxidizer must generally be made to depend upon determining the free iodine in the residue as well as in the distillate. In this manner determinations may be made of arsenic, antimony, vanadium, molybdenum, and cerium, in compounds showing the highest valence of these elements, and of selenium in selenious and selenic acids. These processes, which involve the distillation and determination of the iodine liberated in the interaction of the compounds with potassium iodide in presence of hydrochloric acid, are based upon the following reactions:

$$As_2O_5 + 4\,HI = As_2O_3 + 2\,H_2O + 2\,I_2,$$
$$Sb_2O_5 + 4\,HI = Sb_2O_3 + 2\,H_2O + 2\,I_2,$$
$$V_2O_5 + 2\,HI = V_2O_4 + H_2O + I_2,$$
$$SeO_2 + 4\,HI = Se + 2\,H_2O + 2\,I_2,$$
$$SeO_3 + 6\,HI = Se + 3\,H_2O + 3\,I_2,$$
$$V_2O_5 + 4\,HI = V_2O_3 + 2\,H_2O + 2\,I_2,$$

and, at extreme concentration,

$$2\,MoO_3 + 4\,HI = 2\,MoO_2I = 2\,H_2O + I_2,$$
$$2\,CeO_2 + 2\,HI = Ce_2O_3 + H_2O + I_2.$$

The Volatilization of Iodine in Acid Solution and the Reoxidation of the Residue by Iodine in Alkaline Solution

Errors due to the action of atmospheric oxygen may often be eliminated if the determination is based upon finding the amount of the reduced product in the residue.

Determination of Iodides by the Action of Arsenic Acid and Reoxidation by Iodine. — The iodine of soluble iodides may be accurately determined by a process which depends upon breaking up the iodide by the action of an arsenate and sulphuric acid, the volatilization of the iodine, and the iodometric * determination of the arsenious acid retained in the residue. The reduction proceeds in the acid solution according to the expression

$$H_3AsO_4 + 2\,HI \rightleftarrows H_3AsO_3 + H_2O + I_2,$$

and is completed by boiling out the iodine. The arsenious acid of the residue is determined, after neutralization, by titration, with iodine which should be exactly equivalent in amount to iodine evolved from the iodide. Under conditions to be described, the presence of as much as 0.5 grm. of sodium chloride does not increase the amount of arsenious oxide in the residue, but does induce a slight loss of arsenious oxide (due to volatilization as arsenious chloride) which is proportionate to the amount of the last and the amount of the chloride. The effect of a bromide is to produce a trifling reduction of the arsenic

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* Gooch and Browning: Methods in Analysis, Gooch, p. 457.

acid without volatility. Due correction of the amount of iodine indicated by the determination of the arsenious oxide in the residue may be made by adding to the indicated amount 0.008 of the product of the weight of iodine by the weight of chlorine in the chloride and subtracting 0.0024 of the weight of bromine in the bromide.

Experimental Process: Determinations of Iodine in an Iodide. — Dissolve in a little water contained in an Erlenmeyer beaker of 300 cm.^{3} capacity, the substance (which should not contain of chloride more than the amount corresponding to 0.5 grm. of sodium chloride, nor of bromide more than corresponds to 0.5 grm. of potassium bromide, nor of iodide much more than the equivalent of 0.5 grm. of potassium iodide), and to the solution add 2 grm. of dihydrogen potassium arsenate dissolved in water, 20 cm.^{3} of a mixture of sulphuric acid and water in equal volumes (the (1 : 1) acid), and enough water to increase the total volume to 100 cm.^{3} or a little more. Introduce a hollow tetrahedron of thin platinum foil to prevent bumping in the boiling, hang in the neck of the flask a trap made of a straight two-bulb drying tube cut short, as shown in Fig. 30, and boil the liquid until the level reaches a mark put upon the flask to indicate a volume of 35 cm.^{3}. When chlorides and bromides are present great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and of setting up reduction of the arsenate by the bromide. On the other hand, though 35 cm.^{3} is an ideal volume, failure to concentrate below 40 cm.^{3} introduces no appreciable error. Cool the liquid remaining, nearly neutralize with alkali hydroxide (ammonia is not equally good). Complete the neutralization with alkali hydrogen carbonate, add an excess of 20 cm.^{3} of the saturated solution of the latter, and titrate the arsenite in solution with N/10 iodine, using starch as the indicator.

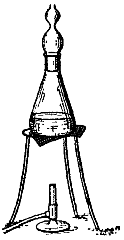

Fig. 30.

From the number of cubic centimeters (n) of the iodine solution used in the titration and the iodine value per cm.^{3} (i), find the weight of iodine liberated from the iodide by means of the formula

$$w = ni.$$

Errors due to the presence of chlorides and bromides may be eliminated by adding (algebraically) to the iodine indicated (which is equal to the amount of iodine used in the process of titration), an amount

$$i' = (0.008 \times \text{wt. Cl} \times \text{wt. I}) - 0.0024 \times \text{wt. Br}.$$

Determination of Arsenic in Arsenic Acid. — The determination of iodine in haloid salts based upon the action of arsenic acid in presence of sulphuric acid, according to the equation

$$H_3AsO_4 + 2\,HI = H_3AsO_3 + H_2O + I_2,$$

the iodine being completely volatilized, but leaving behind in the amount of arsenious acid produced by the action the record of the iodine of the iodide, has been described in the preceding paragraph. In the determination of arsenic in arsenic acid and its salts the reaction is utilized conversely, and potassium iodide in excess, in presence of sulphuric acid, is employed to bring about the reduction of arsenic acid to arsenious acid, which, after neutralization, may be determined by titration with standard iodine.* The conditions of the methods are different, in that in the former the hydriodic acid is entirely broken up by the action of the arsenic acid, with the complete volatilization of the iodine, while in the latter some hydriodic acid remains, retaining iodine and evolving more under the action of the air, until a very low degree of concentration is reached. If the concentration is pushed too far arsenious iodide separates from the sulphuric acid solution and then volatilizes. The small amount of iodine which remains dissolved after the arsenic acid has been fully reduced may, however, be converted to hydriodic acid by the careful addition of very dilute sulphurous acid (approximately N/100), and if cold water is added as soon as the sulphurous acid has bleached the iodine, and the solution immediately neutralized, the return of the iodine color and the reversion of the arsenious acid to arsenic acid are precluded.

Experimental Process: Determination of Arsenic in Arsenic Acid. — Heat in a trapped Erlenmeyer flask (see Fig. 30) the solution containing in a volume of 50 cm.^{3} to 75 cm.^{3} an amount of arsenate not more than the equivalent of 0.4 grm. of arsenic pentoxide, with potassium iodide to an amount about 0.5 grm. in excess of that theoretically required, and 10 cm.^{3} of sulphuric acid (1 : 1). After introducing folded platinum foil to prevent bumping, boil the liquid, taking care that the volume never becomes less than 40 cm.^{3}, until iodine vapor is no longer visible, and bleach the iodine

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* Gooch and Browning: Methods in Analysis, Gooch, p. 291. Gooch and Morris: Ibid., p. 294.

color in the still hot liquid by the cautious addition of very dilute (approximately N/100) sulphurous acid. Should too much sulphurous acid be inadvertently added the error may be corrected by allowing the hot solution to stand in the air until the iodine color returns, when the bleaching may be repeated with more care. At the instant when the bleaching has been accomplished exactly, dilute the solution with cold water, cool quickly, and nearly neutralize with potassium hydroxide. Complete the neutralization with potassium hydrogen carbonate, and add an excess of this reagent amounting to about 20 cm.^{3} of the saturated solution. Titrate the arsenite in the solution with N/10 iodine, using the starch indicator.

From the number of cubic centimeters (n) of iodine used and the iodine value per cm.^{3} (i), calculate the weight of arsenic (w) from the proportion

$$ni : w = I_2 : As = 2 \times 126.92 : 74.96,$$

$$w = \frac{ni \times 74.96}{2 \times 126.92}.$$

Determination of Antimony in Antimonic Acid. — In treating compounds of antimonic acid by a method similar to that just described for the determination of a compound of arsenic acid, it is necessary to take the precaution of preventing the precipitation of antimonic acid from solution upon the addition of sulphuric acid, and tartaric acid accomplishes this effect satisfactorily. Furthermore, the separation and incipient volatilization of antimony iodide takes place at a moderate concentration. Otherwise the process employed in the estimation of arsenic, arsenic acid and its derivatives is applicable to the determination of antimony in antimonic acid and its derivatives, according to the reaction

$$H_3SbO_4 + 2\,HI = H_3SbO_3 + H_2O + I_2.$$

According to procedure developed experimentally an antimonate, in amount not exceeding the equivalent of 0.2 grm. of antimony trioxide, is treated in a trapped 300-cm.^{3} Erlenmeyer flask (see Fig. 30) with tartaric acid (4 grm.) and sulphuric acid to acidity. Thereafter 10 cm.^{3} of sulphuric acid (1 : 1) and 1 grm. of potassium iodide are added. The mixture is boiled, after introducing folded platinum foil to prevent bumping of the liquid. When the liquid has been concentrated to a volume of about 50 cm.^{3} (not less than 45 cm.^{3}) the boiling is stopped, and the color of the iodine is bleached by the cautious addition of sulphurous acid (approximately N/100). The solution is diluted at once, and nearly neutralized with potassium hydroxide. The neutralization is completed with potassium hydrogen carbonate, an excess of this reagent (about 20 cm.^{3} of a saturated solution) is added, and the titration is made with N/10 iodine. This method is also applicable to the determination of antimony and arsenic associated in the higher condition of valence.* It may also be used in the determination of either of these elements after a determination of associated copper by the action of potassium iodide and titration of the liberated iodine, according to the method described on p. 184, provided that citric acid is the acid used in the copper separation and that the tetrathionate formed in the thiosulphate titration is broken up by treatment with bromine before proceeding further with the method.†

Evolution of Chlorine and Absorption by Potassium Iodide: Titration of the Iodine set Free

Hydrochloric acid, which is not susceptible to atmospheric oxidation under the ordinary conditions of action, is to be preferred to hydriodic acid wherever it can be applied in processes in which the halogen evolved in the reaction, incomplete in the cold, is to be taken as the measure of the reducing action upon the substance to be determined. In such processes, the evolved chlorine is made to react with potassium iodide and sets free an equivalent amount of iodine which thus becomes the measure of the substance to be determined.

The Operation. — The operation may be conducted with advantage in the apparatus shown in Fig. 29, on p. 187, and described in the context. According to the generally applicable procedure, the weighed material, in amount not exceeding the equivalent of 50 cm.^{3} of N/10 thiosulphate, is put into the reaction flask. Connection is made, as shown, with the trapped receiver charged with a solution of potassium iodide (3 grm.). The stopper is inserted, hydrochloric acid of suitable concentration is introduced through the stoppered funnel, a current of carbon dioxide is sent through the apparatus (to promote quiet boiling and rapid removal of the liberated chlorine), and the solution in the flask is boiled for a suitable time. The iodine set free in the receiver, ordinarily titrated with N/10

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* Gooch and Gruener: Methods in Analysis, Gooch, pp. 308, 310.

† Heath: Ibid., p. 318.

thiosulphate, is the measure of the substance reacting with the hydrochloric acid.

Examples of this procedure are determinations of manganese dioxide, chlorates, nitrates, and selenates.

Determination of Manganese Dioxide. — Suitable proportions for the analysis of manganese dioxide are 0.2 grm. of this substance with 50 cm.³ of hydrochloric acid (1 : 2). The reaction in the flask proceeds according to the equation

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2,$$

and that in the receiver according to the equation

$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

In this process the chlorine is quickly evolved and the transfer to the receiver, charged with potassium iodide, should be regulated with care.

Determination of Chlorates. — The analysis of a chlorate may be made by procedure similar to that employed in the treatment of manganese dioxide. In consequence of the high oxidizing power of chlorates the amount conveniently handled is, however, comparatively small. With potassium chlorate, for example, the reactions are

$$\begin{aligned} KClO_3 + 6\,HCl &= KCl + 3\,H_2O + 3\,Cl_2, \\ 3\,Cl_2 + 6\,KI &= 6\,KCl + 3\,I_2, \end{aligned}$$

and the amount equivalent to 50 cm.³ of N/10 thiosulphate is approximately 0.1 grm.

Determination of Nitrates. — Manganese chloride in concentrated hydrochloric acid induces the easy decomposition of nitrates with the production of nitrogen dioxide and chlorine, appearing itself at the end of the operation in its original form. At the ordinary temperatures the action is slow, but upon warming a mixture of manganese chloride, hydrochloric acid, and a nitrate, the decomposition of the last begins with the formation of a high chloride of manganese and liberation of nitrogen dioxide:

$$2\,HNO_3 + 3\,MnCl_2 + 6\,HCl = 3\,MnCl_4 + 4\,H_2O + 2\,NO.$$

Ultimately, if the heating is continued, the nitrogen dioxide and chlorine from the higher chloride are evolved and manganous chloride remains:

$$3\,MnCl_4 = 3\,MnCl_2 + 3\,Cl_2.$$

During the process of heating the color of the solution passes from the original characteristic green of manganous chloride in concentrated hydrochloric acid through darker shades to black, and returns by the reverse changes to the original tint. In the presence of concentrated hydrochloric acid the decomposition of the nitrate extends to the last traces, but the addition of a large amount of water will reverse an action already established in strong acid. The reaction serves to detect nitrates (in absence of other oxidizers) when present in fairly small amounts (e.g., one part of potassium nitrate in sixty-thousand parts of water) and may be utilized in the quantitative estimation of nitrates.* In applying the reaction quantitatively, the nitrate to be determined is treated in an atmosphere of carbon dioxide, with a saturated solution of crystallized manganous chloride in concentrated hydrochloric acid, the volatile products of action — chlorine, nitrogen dioxide, and perhaps nitrosyl chloride — are passed into a solution of potassium iodide, and an amount of iodine equivalent to the nitrate originally present is set free:

$$3\,Cl_2 + 6\,KI = 6\,KCl + 3\,I_2,$$

or

$$6\,NOCl + 6\,KI = 6\,KCl + 6\,NO + 3\,I_2.$$

In these reactions $HNO_3 \approx 3\,I$.

The apparatus shown in Fig. 29 will serve for the operation if a trap to exclude air from the absorption trap and receiver is attached outside the trap sealed to the receiver. In conducting the experiment the receiver and traps are charged with a solution of potassium iodide and the receiver stands in a jar of cold water. The nitrate is introduced into the reaction flask, and followed by the solution (10 cm.^{3} for every 0.1 grm. of nitrate) of manganous chloride in concentrated hydrochloric acid. The current of carbon dioxide is started and, after a suitable interval for the removal of air, heat is applied and the

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* Gooch and Gruener: Methods in Analysis, Gooch, p. 213.

distillation is continued until nearly all the liquid has passed over. The iodine in the receiver and trap is titrated as expeditiously as possible by N/10 thiosulphate in order that traces of dissolved nitrogen dioxide may not be reoxidized by the air and again react to liberate more iodine.

Determination of Nitrites. — The process just described for the determination of nitrates is also applicable to the determination of nitrites, with allowance, of course, for the difference in the degree of oxidizing power. In the solution of manganous chloride in concentrated hydrochloric acid the nitrite reacts according to the equation

$$2\,\mathrm{HNO_2} + \mathrm{MnCl_2} + 2\,\mathrm{HCl} = \mathrm{MnCl_4} + 2\,\mathrm{H_2O} + 2\,\mathrm{NO},$$

the manganese chloride breaks up,

$$\mathrm{MnCl_4} = \mathrm{MnCl_2} + \mathrm{Cl_2},$$

and the chlorine sets iodine free from potassium iodide,

$$\mathrm{Cl_2} + 2\,\mathrm{KI} = 2\,\mathrm{KCl} + \mathrm{I_2}.$$

In these reactions $\mathrm{HNO_2} \approx \mathrm{I}$.

Evolution of Bromine and Absorption by Potassium Iodide. Titration of the Iodine set Free

The reaction between potassium bromide, a strong acid, and certain substances capable of liberating bromine from hydrobromic acid has been put to advantageous analytical use. Examples of the utility of the reaction are processes for the determination of vanadates, selenates, and tellurates.

Determination of Vanadates. — The reduction of vanadic acid to the condition represented by vanadium tetroxide by the action of hydrochloric acid and potassium bromide* is ideally simple and complete if the concentration of the bromide is kept reasonably small. If, however, the concentration of hydrobromic acid (or bromide) is too great the reduction is excessive and irregular.†

In the practical operation, the vanadate (0.3 grm. to 0.5 grm.) is put in the reduction flask of the distillation apparatus

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* Holverscheit: Dissertation, Berlin, 1890.

† Gooch and Curtis: Methods in Analysis, Gooch, p. 337.

(see Fig. 29) with potassium bromide (1.5 grm. to 2 grm.), concentrated hydrochloric acid (30 cm.^{3}) is added, and the mixture is boiled in a current of carbon dioxide until the color of the liquid in the flask is a pure blue. Bromine, liberated according to the reaction

$$V_2O_5 + 2\,HBr = V_2O_4 + H_2O + Br_2,$$

is absorbed in the trapped receiver charged with potassium iodide (3 grm. in 300 cm.^{3}) and the liberated iodine,

$$Br_2 + 2\,KI = 2\,KBr + I_2,$$

is titrated with N/10 sodium thiosulphate.

Determination of Selenates. — When acted upon in boiling solution by sulphuric acid and potassium bromide in suitable concentrations,* selenic acid liberates bromine according to the reaction

$$SeO_3 + 2\,HBr = SeO_2 + H_2O + Br_2.$$

When the concentrations of sulphuric acid and the bromide are both low the action is very slow. When the concentration of the bromide is large bromine is retained obstinately in the solution. A fairly high concentration of the sulphuric acid and low concentration of the bromide in excess make the conditions most favorable to the reaction. Under these conditions the bromine is removed rapidly to the distillate leaving a colorless residue which, however, again takes on color if the distillation is prolonged, while elementary selenium makes its appearance in the distillate.

In handling 0.25 grm. or less of selenic acid in an initial volume of 60 cm.^{3} containing 20 cm.^{3} of sulphuric acid (1 : 1) and 1 grm. of potassium bromide the reduction is almost theoretically exact when the distillation is continued until the recoloration of the boiling liquid is barely recognizable.

The apparatus shown in Fig. 29 is convenient for the distillation process. The bromine evolved is absorbed in the solution of potassium iodide contained in the receiver and trap, and the liberated iodine is titrated with N/10 thiosulphate.

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* Gooch and Scoville: Methods in Analysis, Gooch, p. 386.

Determination of Tellurates. — By the action of potassium bromide and sulphuric acid, telluric acid may be reduced to the condition of tellurous acid,

$$TeO_3 + 2\,HBr = TeO_2 + H_2O + Br_2,$$

and estimated by determining the iodine liberated from potassium iodide by the bromine set free in the operation.*

According to this method, the alkali tellurate (equivalent to 0.5 grm. of tellurous oxide, or less) is introduced into the distillation apparatus (see Fig. 29) with 3 grm. of potassium bromide and 10 cm.^{3} of sulphuric acid (1 : 1) in a total volume of 50 cm.^{3} or more. A current of carbon dioxide is passed through the apparatus, and the solution is boiled to set free the bromine, which is absorbed in the cooled solution of potassium iodide in the trapped receiver. The iodine liberated from the iodide by the bromine is titrated with N/10 thiosulphate.

The formation of tellurium tetrabromide in the concentrated acid solution makes it impossible to tell by the color when all the bromine has been distilled, but the experimental evidence goes to show that the boiling of the liquid from a volume of 50 cm.^{3} to a volume of 25 cm.^{3} is sufficient, while concentration from 100 cm.^{3} to 20 cm.^{3} apparently does no harm.

Iodometric Processes Based upon a Preliminary Reduction or Oxidation of the Substance to be Determined

Certain analytical methods demand the reduction of the substance to be determined previous to a titration by iodine. The determination may rest upon *the action of standard iodine upon a reduced product in presence of an excess of a reducer which is inert toward iodine,* or it may depend upon *the action between iodine and the remainder of a known amount of reducer in presence of a reduced product which is inert toward iodine.*

Determination of Vanadates: Preliminary Reduction by Oxalic Acid, Tartaric Acid, or Citric Acid. — Vanadic acid may be reduced in hot solution by oxalic acid, tartaric acid, or citric acid and reoxidized by iodine in alkaline solution.† To

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* Gooch and Howland: Methods in Analysis, Gooch, p. 401.

† Browning and Goodman: Ibid., p. 341.

the solution of a vanadate is added approximately 1 grm. of the organic acid for every 0.1 grm. of vanadium pentoxide in the substance analyzed. The solution is heated to boiling. To the cooled liquid is added about 5 grm. of alkali hydrogen carbonate for every gram of acid used and iodine in slight excess. The mixture is set aside until no further fading of the iodine is noticeable. The excess of iodine is bleached with standard arsenite, starch is added, and the excess of the arsenite is titrated with N/10 iodine. The reduction by oxalic acid takes place in the sense of the expression

$$V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + 2\,CO_2.$$

Vanadium tetroxide is also a product of the reaction with tartaric or citric acids. The reoxidation of the tetroxide by iodine in the presence of the alkali hydrogen carbonate used to take up hydriodic acid takes place in the sense of the expression

$$V_2O_4 + H_2O + I_2 = V_2O_5 + 2\,HI.$$

From the iodine value per cm.^{3} (i) of the iodine used and the total number of cubic centimeters (n), with the iodine equivalent per cm.^{3} of the arsenite (i') and the number of cubic centimeters (n'), the weight of vanadium pentoxide (w) may be found:

$$w = \frac{1 \text{ grm. mol. } V_2O_5\,(ni - n'i')}{2 \times \text{grm. equivalent I}} = \frac{182\,(ni - n'i')}{253.84}.$$

The oxalic acid reduction and the citric acid reduction may be applied in the manner described to the determination of a vanadate in presence of a molybdate or tungstate. The tartaric acid process may be used to determine a vanadate in presence of a tungstate and if the process of reduction be modified by substituting digestion in the cold during twenty-four hours in place of the boiling it will then be applicable in presence of a molybdate as well as a tungstate.

Determination of Bromates. Reduction by Arsenious Acid with Titration of the Excess. — Bromic acid may be reduced by arsenious acid in acid solution,

$$3\,H_3AsO_3 + HBrO_3 = 3\,H_3AsO_4 + HBr,$$

and determined by the action of iodine upon the arsenite formed by neutralization of the residual arsenious acid.* In this process it is sufficient to treat the bromate with a considerable excess of N/10 arsenite, acidify into sulphuric acid [1 : 1] (3 cm.^{3} to 7 cm.^{3}), make up the solution to a volume not exceeding 200 cm.^{3}, boil for ten minutes, neutralize with alkali hydrogen carbonate, and titrate with N/10 iodine.

From the iodine equivalent per cm.^{3} of the arsenite (i) and the number of cubic centimeters employed (n), with the iodine value per cm.^{3} of the iodine (i'), and the number of cubic centimeters (n'), the amount of bromate is given by the proportion

$$ni - n'i' : w = 6\,\mathrm{I} : \mathrm{RBrO_3},$$

$$w = \frac{1 \text{ grm. mol. } \mathrm{RBrO}\ 3\,(ni - n'i')}{6 \times 126.92}.$$

Determination of Chromates: Reduction by Arsenious Acid, with Titration of the Excess. — Chromic acid is reducible by arsenious acid, in presence of hydrochloric acid, in accordance with the expression

$$4\,\mathrm{CrO_3} + 3\,\mathrm{As_2O_3} + n\,\mathrm{As_2O_3} = 2\,\mathrm{Cr_2O_3} + 3\,\mathrm{As_2O_5} + n\,\mathrm{As_2O_3}.$$

According to procedure based upon this reaction † an excess of N/10 arsenite is added to the cold solution of a chromate acidulated with 10 cm.^{3} of dilute hydrochloric acid or sulphuric acid [1 : 3], the total volume being less than 100 cm.^{3}. After a few minutes, when the solution has taken on the bluish green color characteristic of chromic salts, the solution is treated with alkali hydrogen carbonate in excess (about 5 grm.). To the alkaline solution N/10 iodine is added in excess, the mixture is allowed to stand, with frequent shaking, for about half an hour, the residual iodine is taken up with N/10 arsenite and the titration is finished with N/10 iodine in presence of starch.

The long standing is necessary on account of the tendency of precipitated chromic hydroxide to hold arsenious acid and thus delay the oxidation of iodine. The presence of a tartrate before the neutralization will prevent the precipitation but the

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* Gooch and Blake: Methods in Analysis, Gooch, p. 474.

† Browning: Ibid., p. 407.

dark green color then assumed by the solution makes the end reaction of the starch iodide difficult to determine.

In the presence of a ferric salt the determination of the end reaction is also difficult in consequence of the formation of the reddish brown precipitate unless syrupy phosphoric acid before the neutralization, in which case the iron precipitate will be white.* In the reactions of the operation

$$4\,CrO_3 \Leftrightarrow 3\,As_2O_3 \Leftrightarrow 12\,I.$$

From the iodine equivalent per cm.³ of the arsenite (i) and the number of cubic centimeters (n), with the iodine value per cm.³ of the iodine (i') and the number of cubic centimeters (n'), the weight of the chromate (w) may be calculated from the proportion

$$ni - n'i' : w = 12 \times 126.92 : 4 \text{ grm. mol. } M_2CrO_4,$$
$$w = \frac{(ni - n'i')\ (1 \text{ grm. mol. } M_2CrO_4)}{3 \times 126.92}.$$

Determination of Tellurous Oxide by Action of Permanganate and Iodide, with Titration of the Iodine Set Free. — Tellurous oxide in an alkali tellurite may be determined by treating the alkaline solution with standard permanganate until the pink color of the permanganate or the green color of the manganate appears in the meniscus of the liquid, adding potassium iodide with sulphuric acid, and titrating the iodine set free. The free iodine may be titrated by standard thiosulphate† or, after the addition of an excess of alkali bicarbonate, by standard arsenite (also used to fix the standard of the permanganate) to the vanishing point of the iodine color, without starch.‡

The difference between the iodine found and the iodine equivalent of the permanganate, ΔI, measures weight, w, of the tellurous oxide according to the proportion

$$I_2 : TeO_2 = \Delta I : w,$$
$$w = \frac{\Delta I \times 1 \text{ grm. mol. } TeO_2}{2 \times 126.92}.$$

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* Edgar: Methods in Analysis, Gooch, p. 511.

† Norris and Fay: Am. Chem. Jour., **20,** 278.

‡ Gooch and Peters: Methods in Analysis, Gooch, p. 399.

Processes Based upon the Reaction Between Acids and an Iodide-Iodate Mixture

The action of certain strong acids upon the neutral solution containing an iodate and an excess of a metallic iodide results, under suitable conditions of concentration, in the liberation of iodine in definite proportion to the acid:

$$MIO_3 + 5\,MI + 3\,H_2SO_4 = 3\,I_2 + 3\,M_2SO_4 + 3\,H_2O.$$

The action is non-reversible, and the iodine set free may be determined by standard sodium thiosulphate and taken as the measure of the acid.* In dilute solutions, however, the end-point of the reaction may be obscured by the slow and continuous evolution of iodine.†

Determination of Hydrochloric Acid, and Sulphuric Acid. — When hydrochloric acid in amounts not exceeding 0.15 grm. or sulphuric acid not exceeding 0.2 grm. is allowed to act upon a mixture containing 1 grm. of potassium iodide and 0.1666 grm. of potassium iodate in a total volume which does not exceed 100 cm.^{3} the conditions are suitable for the completion of the reaction given above, and the liberated iodine, which may be titrated by sodium thiosulphate, is an exact measure of the acid.‡

From the iodine equivalent per cm.^{3} (i) and the number of cubic centimeters (n) of the thiosulphate, the weight (w) of the acid may be calculated:

$$w = \frac{ni \times 1 \text{ grm. mol. HCl}}{126.92} = \frac{ni \times 1 \text{ grm. mol. } H_2SO_4}{2 \times 126.92}.$$

Boric Acid. — Under certain conditions of dilution at which hydrochloric acid and sulphuric acid will react completely with the iodide-iodate mixture boric acid has no appreciable action upon this reagent. The iodide-iodate mixture may be used, therefore, to remove free hydrochloric acid, or free sulphuric acid, from a solution containing free boric acid, and the iodine

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* Gröger: Zeit. Angew. Chem., 1894, 52.

† Furry: Am. Chem. Jour., 6, 341.

‡ Phelps and Weed: Methods in Analysis, Gooch, p. 60.

thus liberated may be taken up by sodium thiosulphate while the boric acid still remains free.*

When, however, mannite and boric acid are associated the acidic boromannite compound formed is sufficiently strong to liberate from the iodide-iodate mixture an amount of iodine equivalent to the boric acid upon the assumption that the acid reacts in the monobasic form, as metaboric acid.

$$5\,KI + KIO_3 + 6\,HOBO = 3\,I_2 + 6\,KOBO + 3\,H_2O.$$

Experimental Process: Determination of Boric Acid. — In the practical utilization of these reactions for the determination of boric acid or a borate, take in a solution of small volume an amount of the substance not exceeding the equivalent of 0.2 grm. of boric anhydride, add hydrochloric acid (as little as may be), shake to remove any excessive amount of carbon dioxide, and nearly neutralize by sodium hydroxide with the use of litmus paper as an indicator. Adjust the volume of the still distinctly acid solution to the limit of 50 cm.^{3}, and treat with a mixture of potassium iodide (2 grm.) and potassium iodate (0.5 grm.). Bleach the iodine liberated by the free hydrochloric acid with a strong solution of sodium thiosulphate, added drop by drop and thoroughly mixed with the solution, and add N/10 iodine to faint coloration. Add a sufficient amount of mannite to saturate the solution (10 grm. to 15 grm.) and a measured amount of N/5 thiosulphate until the iodine set free by the boromannite compound is bleached, and then 10 cm.^{3} more. Again saturate the solution with mannite, and allow it to stand in a cool place for half an hour, or more. Titrate the excess of thiosulphate with N/10 iodine. The addition of the starch indicator is unnecessary, since half a drop of the N/10 iodine is sufficient to give a strong coloration to solutions of the prescribed volume.

From the number of cubic centimeters (n) and the iodine equivalent per cm.^{3} (i) of the N/5 thiosulphate solution, with the number of cubic centimeters (n') and the iodine value per cm. (i') of the N/10 iodine, calculate the weight (w) of boric anhydride, according to the proportion

$$ni - n'i' : w = I_2 : B_2O_3 = 2 \times 126.92 : 70,$$

$$w = \frac{(ni - n'i')\,70}{2 \times 126.92}.$$

Determination of Acids Liberated in the Hydrolysis of Salts. — Certain salts when put into solution in water tend to undergo hydrolysis with the formation of a basic hydroxide, or

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* Jones: Methods in Analysis, Gooch, p. 210.

basic salt, and a free acid. This action is progressive to an equilibrium and is generally promoted by heat. In the presence of the iodine-iodate mixture, the free acid is taken up, an equivalent amount of iodine being set free, and the hydrolysis advances to completion or to some definite stage short of completion, depending upon the nature of the salt and the concentrations.

Aluminium Sulphate and Aluminium Chloride. — Though only partially hydrolyzed at ordinary temperatures in presence of the iodide-iodate mixture, aluminium sulphate is completely broken up by heating, according to the reaction

$$Al_2(SO_4)_3 + 5\,KI + KIO_3 + 3\,H_2O = 2\,Al(OH)_3 + 3\,K_2SO_4 + 3\,I_2.$$

The behavior of aluminium chloride with the iodide-iodate mixture is similar. Upon the presumption that the aluminium salt is neutral, this reaction affords means for determining aluminium iodometrically; or, it may be applied to the determination of the relation of the acidic ion to the alumina in the salt or unknown constitution in respect to chemical neutrality.*

Other Salts Showing Similar Behavior. — Other salts showing complete hydrolytic decomposition in reaction with the iodide-iodate mixture are chromic sulphate and nickelous sulphate. Ferrous sulphate and cobalt sulphate are similarly hydrolyzed while the hydroxide is oxidized at the expense of the excess of iodate. The hydrolysis of zinc sulphate comes to an end with the formation of an apparently definite basic sulphate.†

Determination of Alkali Hydroxides. — Alkali hydroxides may be estimated by the action of N/10 hydrochloric acid or N/10 sulphuric acid in excess and the determination of that excess may be made by the action of the iodide-iodate mixture (1 grm. KI : 0.166 grm. KIO_3; 50 cm.^{3} of water) and titration

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* Chemically neutral salts of alumina undergo partial hydrolysis in water solution and show an acid reaction with litmus and other similar indicators.

† Moody: Methods in Analysis, Gooch, p. 61.

of the liberated iodine with N/10 thiosulphate added to an initial volume not exceeding 100 cm.^{3}:

$$MOH + (n+1)\,HCl = MCl + H_2O + nHCl,$$
$$6\,nHCl + 5\,nKI + nKIO_3 = 3\,nI_2 + 6\,nKCl + 3\,nH_2O.$$

From the iodine value per cm.^{3} (i) and the number of centimeters (n) of the thiosulphate used, with the iodine equivalent per cm.^{3} (i') and the number of cubic centimeters (n') of the acid, the weight (w) of the alkali hydroxide will be given by the proportion

$$n'i' - ni : w = I : MOH,$$
$$w = \frac{(n'i' - ni)\ 1\ \text{grm. mol. MOH}}{126.92}.$$

Determination of Alkali Carbonates. — Alkali carbonates may be determined by the action of N/10 sulphuric acid in excess, boiling to remove carbon dioxide, determination of the excess of acid by the action of the iodide-iodate mixture (1 grm. K : 0.166 grm. KIO_3) and titration of the free iodine by N/10 thiosulphate in an initial volume not exceeding 100 cm.^{3},

$$M_2CO_3(1 + 3\,n)H_2SO_4 = M_2SO_4 + 3\,nH_2SO_4 + H_2O + CO_2,$$
$$5\,nKI + nKIO_3 + 3\,nH_2SO_4 = 3\,nK_2SO_4 + 3\,nH_2O + 3\,nI_2.$$

From the iodine equivalent per cm.^{3} (i) of the thiosulphate and the number of cm.^{3} (n) used, with the iodine equivalent (i') and the number of cubic centimeters (n') of the acid, the weight w of the alkali carbonate may be calculated by

$$n'i' - ni : w = 2\,I : M_2CO_3,$$
$$w = \frac{(n'i' - ni)\ 1\ \text{grm. mol. } M_2CO_3}{2 \times 126.92}.$$

Processes Dependent upon the Action of Iodine upon Basic Hydroxides to form an Iodide and an Iodate in Mixture

Determination of Basic Hydroxides. — When the solution of an alkali hydroxide is acted upon by iodine at a temperature sufficiently high to decompose the small amount of hypoiodite that might otherwise persist, the final action results in the formation of an exactly neutral mixture of iodide and iodate according to the equation

$$6\,MOH + 3\,I_2 = MIO_3 + 5\,MI + 3\,H_2O.$$

The reaction of iodine with barium hydroxide is similar:

$$6\,Ba(OH)_2 + 6\,I_2 = Ba(IO_3)_2 + 5\,BaI_2 + 6\,H_2O.$$

I. If a known amount of standard iodine is used to bring about the reaction under such conditions that the excess may be kept from volatilization, the determination of the excess by standard arsenite will give, by difference, the amount used up in acting upon the hydroxide,* and thus supply the necessary data for determining the amount of the hydroxide.

The operation is conveniently carried out in a glass stoppered flask trapped like the reaction-bottle of Fig. 28. A suitable measured volume (80 cm.^{3} to 90 cm.^{3}) of N/10 iodine is introduced into the flask and the barium hydroxide is added either from a burette or from a stoppered funnel which is weighed before and after withdrawing the hydroxide. The glass stopper is introduced and the trap is charged with a solution of potassium iodide to prevent the escape of iodine. The solution is heated to the boiling point to break up traces of hypoiodite and is then cooled. The excess of iodine is determined by N/10 arsenite.

From the iodine value per cm.^{3} (i) and the number of cubic centimeters (n) of the standard iodine, with the iodine equivalent per cm.^{3} (i') and the number of cubic centimeters (n') of the standard arsenite, the weight (w) of the hydroxide is given by the proportion

$$ni - n'i' : w = I : MOH = 2\,I : Ba(OH)_2,$$

$$w = \frac{(ni - n'i')\ 1\text{ grm. mol. MOH}}{126.92} = \frac{(ni - n'i')\ 1\text{ grm. mol. Ba(OH)}_2}{2 \times 126.92}.$$

In case it is desired to record the iodine value per cm.^{3} (i'') of the hydroxide solution (for subsequent use in the differential determination of an acid),† this value may be found by taking into consideration also the number of cubic centimeters (n'') of that solution, from the expression

$$i'' = \frac{ni - n'i'}{n''}.$$

II. Instead of determining the amount of the excess of standard iodine, the estimation of the hydroxide may be based

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* Phelps: Methods in Analysis, Gooch, p. 231.

† See p. 207.

upon the expulsion of the excess of iodine, the treatment of the residue of iodide and iodate with sulphuric acid (or hydrochloric acid, in the determination of barium hydroxide) and the titration of the liberated iodine by N/10 thiosulphate.*

From the iodine equivalent per cm. (*i*) and the number of cubic centimeters (*n*) of the thiosulphate used the weight *w* of the hydroxide is given by the proportion

$$ni : w = \mathrm{I} : \mathrm{MOH} = \mathrm{I}_2 : \mathrm{Ba(OH)_2},$$

$$w = \frac{ni \times 1 \text{ grm. mol. MOH}}{126.92} = \frac{ni \times 1 \text{ grm. mol. Ba(OH)}_2}{2 \times 126.92}.$$

and with the added knowledge of the number of cubic centimeters (*n'*) of the hydroxide solution the iodine equivalent per cm.³ (*i'*) of that solution is given by the expression

$$i' = \frac{ni}{n'}.$$

The Differential Determination of Acids.† — The determination of acids which form with alkali hydroxides, or with barium hydroxide, salts which are not susceptible to the hydrolytic action of water, may be determined by neutralizing them with the solution of an alkali hydroxide, or the solution of barium hydroxide, of previously determined iodine value, and then determining the excess of the hydroxide remaining (by one of the methods I or II just described).

Hydrochloric Acid. — Hydrochloric acid may be determined by introducing its solution into an Erlenmeyer flask, adding a measured excess of the alkali hydroxide or barium hydroxide with N/10 iodine in excess, expelling the excess of iodine by boiling, cooling the residue, and then acidulating with hydrochloric acid and titrating with N/10 thiosulphate the iodine liberated from the iodide and iodate.

From the iodine equivalent per cm.³ (*i*) and the number of cubic centimeters (*n*) of the thiosulphate used, with the iodine equivalent per cm.³ (*i'*), and the number of cubic centimeters (*n'*) of the standard hydroxide, the weight *w* of the acid may be found by means of the proportion

$$n'i' - ni : w = \mathrm{I} : \mathrm{HCl},$$

$$w = \frac{n'i' - ni \times 1 \text{ grm. mol. HCl}}{126.92}.$$

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* Walker and Gillespie: Methods in Analysis, Gooch, p. **70.**

† Ibid.

Sulphuric Acid. — Sulphuric acid may be determined by a process precisely similar to that just given for the determination of hydrochloric acid.

The weight (w) will be found by the expression

$$w = \frac{n'i' - ni \times 1 \text{ grm. mol. } H_2SO_4}{2 \times 126.92}.$$

Carbonic Acid. — The carbon dioxide of carbonic acid may be determined by absorbing it in standardized barium hydroxide, thus forming the insoluble barium carbonate, and estimating the excess of the barium hydroxide from the excess of a measured amount of standard iodine made to react with it according to the process previously described (see p. 205).

Processes Based upon the Action of Potassium Iodate in Hydrochloric Acid upon Substances Susceptible to Oxidation

The action between certain substances and a standard iodate in presence of hydrochloric acid (60 per cent) may result in the reduction of a part of the iodic acid to hydriodic acid, the interaction of these acids with liberation of iodine, and the conversion of the free iodine to iodine monochloride. Valuable processes based upon this characteristic action are the determinations of arsenious acid and antimonious acid,*

$$2\,H_3AsO_3 + KIO_3 + 2\,HCl = 2\,H_3AsO_4 + KCl + ICl + H_2O,$$
$$KIO_3 \Bumpeq 2\,H_3AsO_3,$$
$$2\,H_3SbO_3 + KIO_3 + 2\,HCl = 2\,H_3SbO_4 + KCl + ICl + H_2O,$$
$$KIO_3 \Bumpeq 2\,H_3SbO_3;$$

processes for the determination of sulphurous acid and sulphates, thiosulphates, and tetrathionates (the process does not apply to dithionates),†

$$2\,H_2SO_3 + KIO_3 + 2\,HCl = 2\,H_2SO_4 + ICl + KCl + H_2O,$$
$$KIO_3 \Bumpeq 2\,H_2SO_3 \Bumpeq 2\,SO_2,$$
$$Na_2S_2O_3 + 2\,KIO_3 + 2\,HCl = Na_2SO_4 + K_2SO_4 + 2\,ICl + H_2O,$$
$$2\,KIO_3 \Bumpeq Na_2S_2O_3,$$

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* Andrews: Jour. Am. Chem. Soc., **25**, 756 (1908).

† Jamieson: Am. Jour. Sci. (4) **38**, 166 (1914): (4) **39**, 639 (1915).

and a process for the determination of copper in cuprous sulphocyanide which is adapted to the estimation of copper in sulphide ores.*

$$(a)\quad Cu_2(SCN)_2 + 2\,KIO_3 + 4\,HCl = 2\,CuSO_4 + 3\,KCl + 2\,HCN + ICl + I_2 + H_2O,$$

$$(b)\quad 2\,I_2 + KIO_3 + 6\,HCl = KCl + 5\,ICl + 3\,H_2O,$$

or

$$4\,CuSCN + 7\,KIO_3 + 14\,HCl = 4\,CuSO_4 + 7\,KCl + 4\,HCN + 7\,ICl + 5\,H_2O,$$

$$KIO_3 \approx \tfrac{4}{7}\,Cu.$$

Experimental Process: Determination of Sulphurous Acid.—Introduce from a pipette not more than 20 cm.^{3} of a carefully measured solution of sulphurous acid below the surface of 30 cm.^{3} of cooled concentrated hydrochloric acid contained in a 250-cm.^{3} bottle provided with a glass stopper. Add chloroform (6 cm.^{3}) and measure into the solution from a burette standard potassium iodate (about $\frac{1}{60}$ mol.), rapidly and with gentle mixing of the liquids, until the iodine set free at first has largely disappeared. Insert the stopper in the bottle and shake the mixture vigorously. Continue the titration gradually, shaking the mixture thoroughly after each addition of the iodate, until the *violet* color of free iodine vanishes from the *chloroform*. Calculate the amount of sulphuric acid from the expression

$$KIO_3 \approx 2\,H_2SO_3$$

derived above.

Experimental Process:† *Determination of Copper in Ore.*—Treat the copper ore (0.5 grm.) in a 200-cm.^{3} flask with a strong nitric acid (10 cm.^{3}). Boil off the larger part of the liquid from the flask kept in constant motion and inclined to prevent mechanical loss in the process. Cool, add concentrated hydrochloric acid (unless the decomposition of the ore has been already accomplished) and boil until the volume of liquid amounts to about 2 cm.^{3}. Cool, add 12 cm.^{3} of sulphuric acid (1:1), and boil again until fumes of sulphuric acid are evolved copiously. After cooling, add cold water (25 cm.^{3}), heat until the soluble sulphates dissolve, filter, and wash the precipitate thoroughly. Add a few drops of hydrochloric acid and if silver chloride is precipitated filter again.

Neutralize the filtered solution with ammonium hydroxide, add hydrochloric acid (not exceeding 1 per cent by volume of the concentrated acid) and a saturated solution of sulphur dioxide (10 to 15 cm.^{3}). Heat to boiling and add ammonium thiocyanate (1 to 2 grm.) in solution, stirring

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* Wells and Jamieson: Jour. Am. Chem. Soc., **30**, 760 (1908).

† Ibid.

thoroughly. Settle the precipitate (5 to 10 min.), filter on paper and wash thoroughly with hot water.

Transfer the precipitate and paper to a 250-cm.^{3} bottle provided with a glass stopper, add 20 cm.^{3} of water, 30 cm.^{3} of concentrated hydrochloric acid, and 6 cm.^{3} of chloroform. Introduce standard potassium iodate in successive portions from a burette, inserting the stopper and shaking the contents of the bottle vigorously between the additions, until the *violet* color of iodine in the chloroform just disappears.

Calculate the copper from the expression

$$KIO_3 \Bumpeq \tfrac{4}{7}\,Cu$$

derived above.

PRECIPITATION PROCESSES

Processes may frequently be made available in which a known amount of a precipitant in standard solution acts upon a chemically equivalent amount, or at least a definite amount, of substance in solution in such a way that a practically insoluble and inert product is formed. *In precipitation processes, the end-point may be fixed either by noting during the addition of the precipitant the point at which no further precipitation takes place, the point at which a precipitate begins to form, the advent of a new and visible reaction in the solution, or the first indication of the presence of an excess of the precipitant in a series of tests made upon drops removed successively from the solution.*

The End-Point Marked by Absence of Further Precipitation

Determination of Silver by Precipitation as Silver Chloride. — The reaction between a soluble silver salt and a soluble chloride forms the basis of a classical and reliable process for the exact determination of silver in alloys of approximately known composition. The precipitant is sodium chloride and the silver is precipitated from its solution in nitric acid, according to the reaction

$$NaCl + AgNO_3 \rightleftarrows AgCl + NaNaO_3.$$

A solution of pure sodium chloride containing 2.7 grm. in 1 liter (not quite the equivalent of 0.5 grm. of silver) is made and from this a second solution of $\frac{1}{10}$ concentration is made by suitably diluting a portion of the first. The stronger solution is standardized against pure silver. In this process, an amount of silver weighing exactly 0.5 grm. is dissolved by heating in a (200-cm.^{3}) flask with 10 cm.^{3} of nitric acid (sp. gr. 1.2), the free oxides of nitrogen are blown from the flask, and the solution is cooled. After adding exactly 100 cm.^{3} of the stronger salt solution the mixture is shaken until the precipitate is coagulated and settles from a clear supernatant liquid. To this clear liquid is added from a burette 0.5 cm.^{3} of the sodium chloride solution of $\frac{1}{10}$ concentration so that the liquid will run down the sides of the flask and, spreading over the surface of the liquid, make a visible cloud of silver chloride. The liquid is again shaken and settled, and the process of adding 0.5-cm.^{3} portions of the dilute chloride solution, shaking, and settling is repeated until the addition of a portion of 0.5 cm.^{3} of the solution causes no further precipitation. The 100 cm.^{3} of the stronger solution with the measured amount of the weaker solution, less the last 0.5 cm.^{3}, will contain the amount of sodium chloride which corresponds to exactly 0.5 grm. of pure silver. In employing the solutions thus standardized it is necessary, however, in order that the highest degree of accuracy may be attained, to have present in the analytical process, under conditions otherwise precisely similar, the amount of silver which was present in the standardization.

Determination of Tellurous Acid by Precipitation of Tellurous Iodide. — Hydriodic acid and tellurous acid interact with the formation of tellurium tetraiodide, converted by water into an oxyiodide and by excess of alkali iodides to soluble double salts. When potassium iodide is added to a cold solution of tellurous acid containing at least one-fourth of its volume of strong sulphuric acid, no tendency to form a double salt becomes apparent until the potassium iodide amounts to more than enough to convert all the tellurous acid present into tellurous tetraiodide according to the equation

$$H_2TeO_3 + 4\,H_2SO_4 + 4\,KI \rightleftarrows TeI_4 + 4\,KHSO_4 + 3\,H_2O.$$

The tellurium tetraiodide thus formed is extremely insoluble in sulphuric acid of one-fourth strength, though soluble in excess of potassium iodide, and is acted upon by water with formation of tellurium oxyiodide and hydriodic acid. It is produced at first in the condition of a finely divided dark brown precipitate which upon agitation of the liquid gathers in curdy masses and settles, leaving the liquid clear. By taking advantage of this tendency to curd, it is possible to determine without great difficulty the exact point during the gradual addition of potassium iodide when the precipitation of the tellurium iodide is complete.*

Tellurous oxide is dissolved in a very little of a strong solution of potassium hydroxide, and dilute sulphuric acid is added carefully until the tellurous acid which is precipitated upon neutralization of the alkali hydroxide is just redissolved. To this solution, contained in an Erlenmeyer flask, sulphuric acid [1 : 1] is added in such amount that the liquid shall contain, after the subsequent addition of potassium iodide in solution, at least one-fourth of its volume of strong sulphuric acid. The flask is placed upon a pane of window glass supported upon strips of wood about 1 cm. above the level of the table covered with white paper. A solution of approximately decinormal potassium iodide, free from iodate and carefully standardized,† is introduced gradually from a burette into the middle of the Erlenmeyer beaker. As the drops of the potassium iodide touch the liquid the precipitation begins at the center and travels in rings toward the outer walls of the beaker. When the liquid becomes so opaque that a newly formed precipitate is distinguished with difficulty, the beaker is rotated and the curded precipitate permitted to settle; and then the process of titration is continued as before until precipitation ceases. In an Erlenmeyer flask 10 cm. in diameter across the bottom the end of the precipitation is easily determined if the final volume of the liquid, of which one-fourth is sulphuric acid, does not exceed 100 cm.^{3}. In this process,

$$TeO_2 \approx 4\,KI$$

according to the equation given above.

The End-Point Marked by the Beginning of Precipitation

Determination of the Cyanide Ion. — When a solution of silver nitrate is added to an excess of alkali cyanide the pre-

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* Gooch and Morgan: Methods in Analysis, Gooch, p. 398.

† See p. 177.

cipitate of silver cyanide first formed is redissolved by the excess of the soluble cyanide with the formation of a double salt.

$$AgNO_3 + KCN \rightleftarrows AgCN + KNO_3,$$
$$AgCN + KCN \rightleftarrows AgK(CN)_2.$$

Upon further addition of silver nitrate the soluble double cyanide is attacked and silver cyanide is precipitated.

$$AgNO_3 + AgK(CN)_2 \rightleftarrows 2\,AgCN + KNO_3.$$

In applying this reaction to the determination of the cyanide ion in an alkali cyanide, the solution is suitably diluted before the titration, and in the determination of hydrocyanic acid it is first treated with an alkali hydroxide and then diluted. The container is placed upon a background of black glazed paper and the standard silver nitrate is added cautiously, and with constant stirring, until a faint turbidity indicates the end-point of the reaction

$$AgNO_3 + 2\,KCN \rightleftarrows KAg(CN)_2 + KNO_3$$
$$Ag \approx 2\,(CN).$$

The End-Point Marked by a New Reaction

Determination of the Chloride Ion by Precipitation as Silver Chloride, with an Indicator in the Solution. — In determining silver volumetrically by precipitation as silver chloride use is made of the reaction

$$NaCl + AgNO_3 \rightleftarrows AgCl + NaNO_3,$$

sodium chloride in standard solution serving as the precipitant for silver chloride taken in the form of the nitrate. In making use of this reaction for the determination of the chloride ion, the end-point of the main reaction may be indicated by the advent of a secondary reaction, provided the process be carried out in a solution which is either neutral or devoid of free acid excepting acetic acid, the first excess of silver nitrate being indicated by its action upon a small amount of potassium chromate (*Mohr*) or sodium arsenate (*Lunge*) present in the solution. Free acids other than acetic acid in small amount are eliminated by the addition of an alkali acetate, and solutions of colored chlorides of the metals are first treated with an alkali hydroxide or carbonate to remove the metal hydroxide and, after filtration, with acetic acid in slight excess.

$$2\,AgNO_3 + K_2CrO_4 \rightleftarrows Ag_2CrO_4 + 2\,KNO_3.$$

$$2\,AgNO_3 + 3\,K_2CrO_4 + 2\,HOC_2H_3O \rightleftarrows Ag_2CrO_4 + K_2Cr_2O_7 + 2\,KNO_3 + 2\,KOC_2H_3O + H_2O.$$

$$3\,AgNO_3 + NaH_2AsO_4 + 2\,NaOC_2H_3O \rightleftarrows Ag_3AsO_4 + 3\,NaNO_3 + 2\,HOC_2H_3O.$$

Determination of Silver by Precipitation as Silver Thiocyanate, with a Ferric Indicator in the Solution. (*Volhard.*) — The titration of silver nitrate by ammonium thiocyanate or potassium thiocyanate,

$$AgNO_3 + NH_4SCN \leftrightarrows AgSCN + NH_4NO_3,$$

with the aid of a ferric salt to indicate the point when the thiocyanate is no longer engaged in the reaction of precipitation,

$$Fe_2\,(SO_4)_3 + 6\,NH_4SCN \rightleftarrows 2\,Fe\,(SCN)_3 + 3\,(NH_4)_2SO_4,$$

is another process illustrative of the marking of the end-point of the main reaction by the advent of a new reaction.

Experimental Process: Precipitation of Silver as Silver Thiocyanate.—

A. Preparation of the Solutions and the Indicator.

1. Prepare an approximately N/10 solution of silver nitrate by dissolving 17 grm. of that salt in water and making the solution up to 1 liter.
2. Prepare an approximately N/10 solution of ammonium thiocyanate, NH_4SCN, by dissolving 9 grm. of that salt in water and making the solution up to 1 liter.
3. Prepare an indicator by making a cold saturated solution of ferric alum and add to it enough of pure, colorless nitric acid to bleach the brown color of the water solution.

B. Standardization of the Silver Solution.

Determine exactly the standard of the solution of silver nitrate by precipitating the silver as chloride and weighing as such, according to the gravimetric process.

C. Standardization of the Thiocyanate Solution.

Put a measured portion of the standardized silver solution (45 $cm.^3$) in a beaker with an equal amount of water and 1 $cm.^3$ of the ferric indicator. Add a measured amount of the thiocyanate solution from a burette, with constant stirring, until the mixture of precipitate and liquid assumes permanently a blush of red. Calculate the "silver equivalent per cm.^{3}" of the thiocyanate solution.

D. Determination of Silver in a Silver Coin.

Dissolve a carefully weighed ten-cent piece in nitric acid, sp. gr. 1.2; boil the solution, dilute with water, and repeat the boiling (to expel nitrogen oxides). Cool the solution, make up with water to a suitable volume (200 cm.^{3}) in a graduated flask. Draw from a burette a measured portion of this solution (40 cm.^{3}), add the ferric indicator (1 cm.^{3}), and titrate as in the standardization of the silver solution. Calculate the percentage of silver in the coin.

The End-Point Marked by Drop Tests Outside the Solution

Determination of Phosphoric Acid by Precipitation as Uranyl Phosphate, with a Ferrocyanide Indicator Outside the Solution. (*Pincus.*) — When the solution of acid potassium phosphate is treated with uranyl acetate a greenish white precipitate of uranyl phosphate is formed,

$$KH_2PO_4 + UO_2\,(C_2H_3O_2)_2 = KC_2H_3O_2 + HC_2H_3O_2 + UO_2HPO_4.$$

In presence of ammonium salts the precipitate contains ammonium uranyl acetate, $UO_2NH_4PO_4$. As soon as the uranyl acetate is in excess (in the boiling solution) a drop of the solution touched to a drop of potassium ferrocyanide upon a white surface will give a brown coloration which marks the end-point. A solution of uranyl acetate thus standardized against potassium phosphate or calcium phosphate may be utilized for the titration of alkali phosphate or calcium phosphate, respectively, under similar conditions of concentrations.*

GASOMETRIC PROCESSES

Some processes of analysis in which definite gaseous products are evolved in reaction may be made to depend upon the volumetric measurement of the gaseous products. Such processes are classed under the heading of *Gas-Volumetric Analysis.* Processes in which gaseous mixtures are analyzed by *measurement* of the original substances as well as the *gaseous products* of reaction come in the category of methods of *Gas Analysis.*

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 718.

Gases are commonly measured over a liquid in some form of gas burette — a graduated burette provided with a leveling tube so that by adjustment of the liquid in the burette and tube to the same level the pressure under which the gas is measured may be equalized with that of the atmosphere. (Fig. 31.)

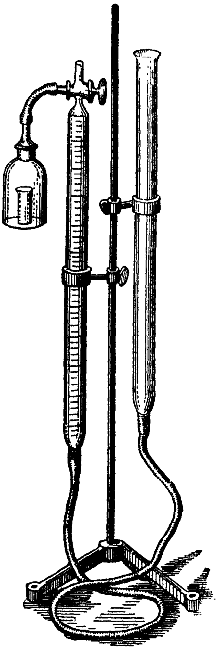
FIG. 31.

In all measurements of gases it is necessary to reduce the volume as measured, under atmospheric pressure and at the atmospheric temperature, to the volume which it would occupy under standard conditions of temperature and pressure, 0 degree and 760 mm. Measured in dry condition the volume ($V_{760}°$) of the gas at 0 degree and 760 mm. may be found from the observed volume (V), the temperature (t), and the barometric height (B) corrected for temperature to what it would be at 0 degree (B) by means of the formula

$$B_0 = \frac{1 + \beta t}{1 + \alpha t} \cdot B,$$

in which α represents the coefficient of expansion of mercury and β the linear coefficient of expansion of glass — the correction amounting to about 1, 2, 3, 4 mm. for temperatures lying in the intervals 5 to 12, 13 to 20, 21 to 28, 29 to 35 degrees, respectively. Then,

$$V_{760}° = \frac{VB_0}{760\,(1 + \frac{1}{273}\,t)} = \frac{VB_0\,(273)}{760\,(273 + t)}.$$

If the measurement is made over water, the vapor tension of water (w) at the observed temperature must be taken into account in determining the pressure (partial) of the gas, and the expression assumes the form

$$V_{760}° = \frac{V\,(B_0 - w)\,273}{760\,(273 + t)}.$$

When many reductions of gas volumes to standard conditions, are to be made, the work may be done mechanically with the aid of a device in which the gas burette and leveling tube are connected with a third tube, the comparison tube, in which air is confined, the amount of which is known under standard conditions. Such an instrument is the Lunge Gas Volumeter shown in Fig. 32. This instrument consists of the gas burette (*B*) (of somewhat more than 100 cm.³ capacity), a comparison tube (*C*), and the leveling tube (*L*), all connected as shown. Air is introduced into the comparison tube (with a drop of water when moist gases are to be measured) and adjusted to the volume which corresponds under the prevailing condition of temperature and pressure to a volume of 100 cm.³ at 0 degree and 760 mm., as determined by the formula given above. That is,

$$V = 100 \cdot \frac{760\,(273 + t^\circ)}{(B_0 - w)\,273}\,.$$

In measuring a gas in the burette (*B*) the tubes are so adjusted, by raising or lowering them, that the level in the comparison tube (*C*) stands at the 100 cm.³ mark, while the levels in the burette (*B*) and the comparison tube (*C*) are the same. Then the indicated volume in the burette will be that of the contained gas at 0 degrees and 760 mm.

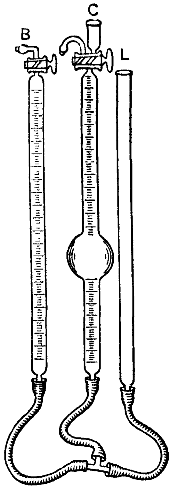

FIG. 32.

Gas-Volumetric Methods

The determination of nitrates by measurement of the nitrogen dioxide (NO) which they are capable of evolving, and the determination of ammonium salts, are representative processes of gas-volumetric analysis.

The Determination of Nitrates. — The main reaction which takes place when a nitrate is acted upon by hydrochloric acid and a ferrous salt is typified by the equation

$$2\,KNO_3 + 8\,HCl + 6\,FeCl_2 = 2\,KCl + 6\,FeCl_3 + 4\,H_2O + 2\,NO.$$

The reaction is, however, accompanied to a small extent, varying with the conditions, by another in which the oxide of nitrogen evolved is the trioxide N_2O_3, but the higher oxide may be reduced to the lower condition by contact with a solution of potassium iodide:

$$2\,KI + H_2O + N_2O_3 = 2\,KOH + I_2 + 2\,NO.$$

The results most nearly in accord with theory of the main reaction are obtained * when the hydrochloric acid is fairly concentrated, the ferrous salt in considerable excess, and the gas swept from the boiling liquid through a solution of potassium iodide to the measuring burette by carbon dioxide and collected over sodium hydroxide.

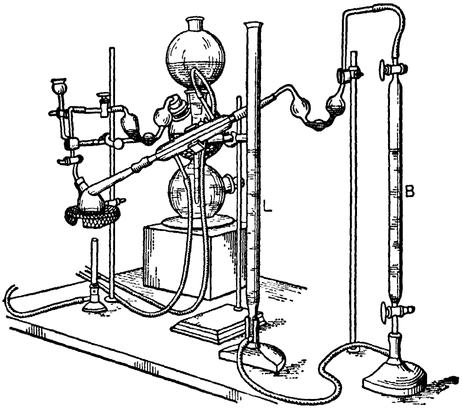

FIG. 33.

A satisfactory apparatus for the operation is shown in Fig. 33. A small tubulated retort, upon the neck of which is fitted a small condenser, serves as the reaction chamber. Into the tubulature of this retort is fitted, by a ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted to stopcocks, as shown in the figure, and so branched as to make it possible to transmit carbon dioxide through the apparatus, or to admit a liquid without introducing air. The condenser is joined to a Will and Varrentrapp bulb containing a solution of potassium iodide, and this is connected by thick vacuum tub-

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* Roberts: Methods in Analysis, Gooch, p. 271.

ing with a Hempel gas burette charged with a strong solution of sodium hydroxide. Carbon dioxide is generated in a Kipp's apparatus by action of boiled hydrochloric acid (charged with cuprous chloride to take up dissolved oxygen) upon boiled marble.

In using this apparatus, the nitrate (about 0.1 grm. of potassium nitrate) is introduced into the retort, generally in the dry condition, carbon dioxide is passed through the apparatus until the gas collected over sodium hydroxide leaves only the minute bubble which the gas from the generator alone has been found to give, and, after shutting off the carbon dioxide and lowering the leveling tube of the Hempel burette, a boiled solution of ferrous chloride in hydrochloric acid is admitted through the funnel tube. The liquid is then slowly heated to boiling and the process continued until the reaction of the ferrous salt upon the nitrate is apparently complete, when the carbon dioxide is again passed through the apparatus, the absorption of this gas being hastened by inclining and shaking the burette at intervals. The volume of the gas residual nitrogen dioxide (NO) is noted under existing barometric and thermometric conditions and the volume under standard conditions, 0 degree and 760 mm., is calculated from the formula

$$V^{\circ}_{760} = \frac{V\,(B_0 - w)\,273}{760\,(273 + t)}.$$

Determination of Nitrogen in Ammonium Salts. — When an ammonium salt is acted upon by a solution containing sodium hydroxide and sodium hypobromite the reaction proceeds in the sense of the following expression

$$\begin{aligned}2\,NH_4Cl + 3\,NaOBr &+ 2\,NaOH \\ &= 2\,NaCl + 2\,NH_4OH + 3\,NaOBr \\ &= 2\,NaCl + 3\,NaBr + 5\,H_2O + N_2.\end{aligned}$$

At 100 degrees the reaction might be completed to the final stage and the nitrogen evolved which represents the entire amount of ammonium salts, but at the atmospheric temperature a small amount of the ammonium hypobromite of the first stage of action remains undecomposed. It is, however, impracticable to apply the reaction at the higher temperature, so that it is best to find empirically the relation between nitrogen evolved and the ammonium salt from which it is evolved under given conditions, and to use that relation instead of the theoretically equivalent proportion in the analysis of the unknown ammonium salt.

The nitrogen may be collected in the Lunge apparatus, shown in Fig. 32, the adjustment of the volume to standard condition being made mechanically as previously described.*

Nitrogen in Organic Substances. — When the products of the combustion of an organic substance mixed with copper oxide are passed over hot copper (to decompose oxides of nitrogen), the nitrogen is left free, and if the operation is so arranged (*Dumas*) that air is excluded while the products are passed on (in carbon dioxide) to the azometer (Fig. 34) charged with potassium hydroxide, the amount of the nitrogen may be determined by the measurement of its volume.†

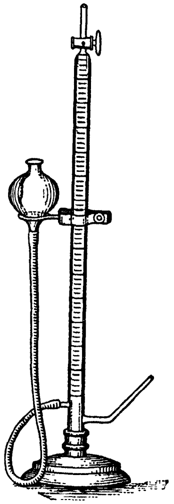

Fig. 34.

Methods of Gas Analysis

The practical analysis of gas mixtures is generally made either (I) by direct treatment with suitable absorbents, the difference between the volumes of the gases before and after treatment measuring, the amount of gas absorbed, or (II) by first submitting the gas mixture to process of chemical treatment (e.g., combustion) and then acting upon the products of reaction with suitable absorbents.

Many forms of apparatus (some of them very intricate) find application in processes of gas analysis.‡ Of these the combination of the "gas burette" and "gas pipette" of Hempel may serve as a simple type. The "gas burette" consists of

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* P. 217. Compare also Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, pp. 387, 822.

† For details, see Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 422.

‡ See Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 729, *et seq.*

a burette (*B*) and a leveling tube (*L*) as shown in Fig. 35. The "gas pipette," also shown (*P*), holds the gas mixture forced in from the measuring tube (by raising the leveling tube) for the action of the absorbent, after which the residual gas is returned to the burette for measurement. In case it is necessary to protect the absorbent from the action of air, the "double pipette" of Fig. 36 the outer bulbs of which hold a water seal is serviceable.

The determination of the oxygen content of air may serve as an example of the simplest of the methods of gas analysis.

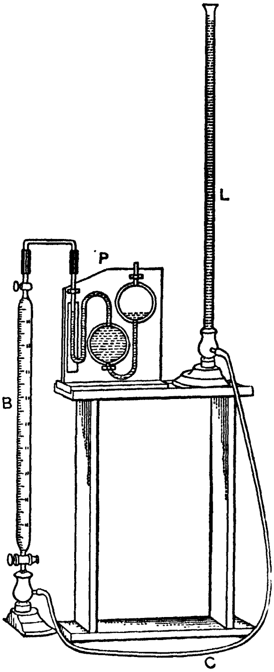

FIG. 35.

The Determination of Oxygen, and of Nitrogen with the Inert Elements, in Air. — The oxygen content of air may be determined approximately by direct absorption in a solution of potassium pyrogallate contained in the double pipette.

In the preparation of the pipette (Fig. 36), enough of an approximately 25 per cent solution of pyrogallic acid is introduced, from a funnel attached by a short rubber connector to the capillary tube, until the first bulb is three-quarters full. This is accomplished by applying alternately gentle suction and pressure by blowing at the outer tube of the fourth bulb to draw in liquid or expel air as may be necessary. Next a solution of potassium hydroxide (sp. gr. 1.27) is similarly introduced until the liquid fills the first bulb and the connecting tube up to the second bulb. Then, allowing air to enter the capillary tube, the solution is drawn into the second bulb until it is two-thirds full, and water is introduced into the fourth bulb. By

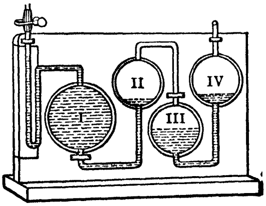

FIG. 36.

gently blowing into the outlet tube the water is made to flow into the third bulb, while the reagent solution fills the first bulb and the capillary, which is then closed with a cap. The gradual absorption of oxygen from the air inclosed and in contact with the reagent draws in more water from the fourth bulb. In the final adjustment the third and fourth bulbs should contain enough water to preserve the seal when the air to be analyzed is forced into the first bulb. With the first bulb and capillary tube filled with the reagent connection is made with the Hempel burette. Air measured under atmospheric conditions of temperature and pressure is forced from the burette into the pipette, kept in contact with the pyrogallate solution (gently agitated with a rotary motion) for three or four minutes, returned to the burette, and measured again under the atmospheric condition. The difference between the volume of the air taken and that of the gas remaining (nitrogen and the inert elements) is the volume of oxygen contained in air measured under similar conditions.

COLORIMETRIC PROCESSES

The fact that the solution of a colored substance shows by transmitted light a depth of color proportionate to the thickness of the layer through which the light is sent, finds application in most processes of colorimetric analysis: a few colorimetric processes depend upon comparisons of colored films produced under similar conditions of reaction.

Two solutions of a substance in the same solvent will have the same concentration per cm.^{3} when equal layers having the same volume transmit the same depth of color. When variation in the concentration of a substance in solution is not accompanied by chemical change (solvation, hydrolysis, ionization) which of itself has effect upon the color of the solution, the concentrations per cm.^{3} of two solutions of the substance in the same solvent which show the same depth of color for different thicknesses of layers through which the light is transmitted, will be inversely as the thicknesses of the layers. In such cases, the concentration per cm.^{3} (c') of an unknown solution may be found, in terms of the concentration per cm.^{3} (c) of a known solution, by determining the thickness of the layers

(l') and (l) respectively, which transmit the same depth of color. Then

$$c' = \frac{lc}{l'}.$$

If variation in concentration is accompanied by chemical change affecting the color, then, in order that the matching of color in layers of equal thickness may indicate a condition of equal concentrations, it is necessary that the layers of equal thickness should also have the same volume. In such cases, the solutions compared must be matched in color by adjusting the volumes (by measured dilution or strengthening of one solution or the other) until the equal transmitting layers are also equal in volume.

Comparison Tubes: Colorimeters. — For making colorimetric comparisons many different forms of apparatus have been employed. For determinations in which equal volumes in equal layers may be matched in color, it is usual to employ sets of tubes of the same size graduated to equal volumes — with flat, polished bottoms, for lengthwise observation (such as the Nessler cylinders which are used in the colorimetric determination of small amounts of ammonia in ammonium salts); or of equal thickness of wall for crosswise observation of a clear liquid above a settled precipitate (such as the tubes used in color tests for carbon in steel). For most purposes, and especially for comparisons of colors of small intensity, an efficient apparatus is a simple and easily constructed colorimeter * consisting of two graduated comparison tubes of equal size, with flat and polished bottoms, and set vertically in perforations in the bottom of a dark box (used as a camera) over a mirror which is illuminated from a white background. If a measured amount of the unknown solution is put into one of the comparison tubes and a portion of the known solution is measured out (best from a burette) into the other tube until the colors match, the amounts contained in the measured por-

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* For other excellent devices see Hillebrand: U. S. Geol. Survey Bulletin, 442, pp. 33–38.

tions of the known and unknown solution should be equal (provided the dilutions are suitable in respect to delicacy of observation and that differences in concentration of the solutions have no chemical effects). Then, dilution of the liquids to equal volumes will not change the matching of the color. Should, however, any appreciable change be observed on dilution, the test may be regarded as preliminary and the data used to point the way to making up the solutions (known and unknown) so that when the colors of equal layers match the volumes (and concentrations) will be practically equal. The amount taken of the substance in the unknown solution will then equal the amount of the substance in the known solution measured.

By the colorimeter comparison of solutions small amounts of manganese [*] may be determined in the form of permanganate; titanium [†] as pertitanic acid; nitrous acid [‡] as tri-amido-azobenzene (Bismarck brown) or as indicated by a mixture of sulphanilic acid and naphthylamine in acetic acid; and gold [§] in red colloidal solution.

The Nephelometer. — Minute amounts of material in opalescent suspension can be determined by measuring the brightness of light reflected on the suspended particles with reference to a similar suspension of known content, by means of the *Richards Nephelometer.* [||] Two test tubes slightly inclined toward one another in a nearly vertical position and arranged so as to be partly shielded by sliding screens from the nearly horizontal rays of a powerful electric light, are observed from above through two thin prisms which bring their images together. When the unknown and minute quantity of a dissolved substance (e.g., silver chloride) is precipitated as a faint opalescence in one tube and a known amount of the dissolved substance is treated in exactly the same way in the other tube,

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[*] Treadwell-Hall: Analytical Methods, 3rd ed., Vol. II, p. 127.

[†] Ibid., pp. 100, 101.

[‡] Ibid., p. 344.

[§] Maxsom: Analytical Methods, Gooch, p. 150.

[||] Richards and Wells: Am. Chem. Jour., **31**, 235.

the light reflected from the one tube may be equalized with that reflected from the other tube by changing the position of the sliding screens. The precipitates, if not too dense, may then be taken as inversely proportionate to the lengths exposed to light. Traces of substances in suspension too minute to be caught by any ordinary filter (such as silver chloride in opalescent suspension) may be thus estimated.

CHAPTER V

SYSTEMATIC ANALYSIS

Separations and Determinations

The Preparation of the Substance. — Substances in gaseous condition or in solution are generally ready for the immediate application of the analytical methods. In some cases, solid substances may also be submitted at once to the determinative process, as in the determination of the water content of a hydrous salt (see p. 34) or in the determination of the carbon dioxide of a carbonate (p. 38); but in most cases the first step in the analysis is the solution or decomposition of the substance by means of a liquid reagent adapted to the character of the substance and the nature of the subsequent operations. Common reagents for this purpose are water (e.g., in the solution of copper sulphate — see p. 51), nitric acid (e.g., in the attack upon a nickel-copper coin — p. 53), hydrochloric acid (e.g., in the evolution of carbon dioxide from calcite — p. 40; or in the decomposition of hematite — p. 144), *aqua regia* for gold or platinum, or hydrofluoric acid for silica and certain silicates. Sometimes a substance which is refractory to acids or ordinary liquid reagents may be first attacked by fusion with a suitable flux as a preliminary to processes of solution — e.g., the fusion of silicates with sodium carbonate (see p. 94), and of pyrites with sodium carbonate and peroxide (see p. 78).

It should not be forgotten that in case the substance contains organic material which may interfere with later analytical operations — e.g., tartaric acid, citric acid, or other organic matter (sugar, paraffin, etc.) in large amount — this, in general, must be removed by a suitable solvent (water, alcohol, ether, etc.) or destroyed by ignition or by the action of an oxidizing agent (e.g., nitric acid or the mixture of that acid with strong sulphuric acid) before proceeding with the attempt to determine the inorganic constituents; but the procedure must be so chosen that it will not occasion the loss of the constituent to be determined or affect its subsequent determination unfavorably.

Qualitative Tests. — In most cases it is desirable that a thorough qualitative examination should precede the quantitative analysis, at least so far as to make it sure that nothing is present which may interfere with the accuracy of the proposed procedure. For example, the analysis of a preparation of a crystallized hydrous copper sulphate, for the purpose of establishing the proportionate composition in respect to copper, the sulphate-ion, and water, will naturally be preceded by a qualitative examination at least sufficient to show the absence of substances which if present might interfere with the analytical process — e.g., the electrolytic determination of copper, the precipitation of the sulphate-ion by barium chloride and weighing as barium sulphate, the determination of water by loss of a portion of the crystallized substance on fusion with sodium paratungstate (pp. 51, 76, 36).

On the other hand, when the qualitative analysis is to be exhaustive and complete so far as may be practicable, as in the more elaborate of silicate rocks or of iron ores, the preliminary qualitative examination of the material whose composition is known in a general way may be superfluous inasmuch as the quantitative methods to be used will be more searching than the qualitative procedure.

The Choice of Methods. — The conditions to be met and the difficulties to be overcome vary as widely as the composition of substances. The determination of certain selected constituents of a substance may be a comparatively simple matter and one easily attained by direct and special methods. Such, for example, are determinations of iron in iron ores (p. 144), sulphur in pyrites (p. 78), or phosphorus in iron (p. 148). On the other hand, the complete analysis of a complex substance may prove to be a very intricate matter involving separations and determinations in sequence as well as direct methods for the determination of certain special constituents. In the determination of basic ions the specifically determinative processes are frequently preceded by systematic processes of separation which involve the use of the general reagents employed in qualitative analysis for the grouping of ions of reaction according to certain characteristic properties. In the determination of acidic ions group reagents (excepting silver nitrate for the chlorine-ion, the bromine-ion, and the iodine-ion) have very little application, such determinations being generally made by direct and special methods, which, however, often involve the preliminary separation of interfering substances.

Grouping of Basic Ions. — The broad classification of basic ions according to their behavior in respect to hydrogen sulphide in acid solution, to an alkali sulphide, and to ammonium hydroxide, is useful in quantitative analyses, as in qualitative analysis, and the following grouping of the basic ions is a convenient one.

Group I. — Basic ions whose compounds, soluble in water or in dilute nitric acid, are acted upon by dilute hydrochloric acid with the formation of *insoluble chlorides.* (These ions may also be precipitated as sulphides under suitable conditions.)

Group II. — Basic ions which do not yield chlorides insoluble in water or in dilute nitric acid, but whose compounds soluble in water and in presence of dilute hydrochloric acid are acted upon by hydrogen sulphide with the formation of *insoluble sulphides.*

Group III. — Basic ions which do not yield insoluble chlorides or insoluble sulphides in presence of dilute hydrochloric acid, but whose compounds are acted upon by *ammonium hydroxide* with the formation of *hydroxides* (or *phosphates* if phosphoric acid be present) insoluble in a faint excess of the precipitant and in presence of ammonium salts, and whose *acetates* are hydrolyzed when heated in dilute solution, with the formation of insoluble *basic acetates* or *hydroxides.*

Group IV. — Basic ions which do not form insoluble chlorides or sulphides in presence of dilute hydrochloric acid, insoluble hydroxides in presence of ammonium salts, or insoluble basic acetates, but whose compounds are acted upon by *ammonium sulphide* with the formation of *insoluble sulphides.*

Group V. — Basic ions which do not yield insoluble chlorides or sulphides in presence of dilute hydrochloric acid, or hydroxides in presence of ammonium salts, or basic acetates, but whose compounds are acted upon by *ammonium carbonate* in presence of ammonium salts in dilute water solution or by highly concentrated ammonium carbonate in alcoholic solution (magnesium) with the formation of *insoluble carbonates.*

Typical Forms Precipitated by the Group Reagents Applied in the Order Indicated

Group I.	*Group II.*		*Group III.*	*Group IV.*	*Group V.*	*Group VI.*
Precipitant HCl.	Precipitant H_2S in acid solution, after the separation of Group I.		Precipitant NH_4OH in presence of NH_4Cl, after separation of Groups I and II and removal of H_2S.	Precipitant $(NH_4)_2S$, after separation of Groups I-III.	Precipitant $(NH_4)_2CO_3$, after separation of Groups I-IV.	Not precipitable by the group reagents of Groups I-V.
$AgCl$ Hg_2Cl_2 $PbCl_2$* $TlCl$*	HgS PbS Bi_3S_3 CuS CdS $\left.\begin{matrix}Tl_2S\dagger\\ Ru\\ Rh\\ Pd\\ Os\end{matrix}\right\}S_n$	Insol. in $(NH_4)_2S$ $+S$	$Al\ (OH)_3$ $Fe\ (OH)_3$ $Cr\ (OH)_3$ $Gl\ (OH)_2$ $Ti\ (OH)_4$ $Zr\ (OH)_4$ $Th\ (OH)_4$ $Ce\ (OH)_3$ $Sc\ (OH)_3$ $La\ (OH)_3$ $Pr\ (OH)_3$ $Nd\ (OH)_3$ $Sm\ (OH)_3$ $Eu\ (OH)_3$ $Gd\ (OH)_3$ $Tb\ (OH)_3$ $Y\ (OH)_3$ $Dy\ (OH)_3$ $Ho\ (OH)_3$ $Er\ (OH)_3$ $Tm\ (OH)_3$ $Yb\ (OH)_3$ $Lu\ (OH)_3$ $Ga\ (OH)_3$ $In\ (OH)_3$ $Tl\ (OH)_3$ $(NH_4)_2U_2O_7$ NH_4VO_3‡	FeS NiS CoS MnS ZnS (UO_2S)	$BaCO_3$ $SrCO$ $CaCO_3$ $\left\{\begin{matrix}(NH_4)_2CO_3\cdot\\ MgCO_3\cdot\\ 4H_2O\end{matrix}\right.$§	Soluble salts of Li Na K Rb Cs NH_4
	PtS_2 Au_2S_{0-3}	Partly sol. in $(NH_4)_2S$ $+S$				
	Ir_2S_3 As_2S_3 As_2S_5 Sb_2S_3 Sb_2S_5 SnS SnS_2 GeS Mo_2S_{2-3} Te, TeS_2 Se	Sol. in $(NH_4)_2S$ $+S$				

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* Precipitated under favorable conditions of concentration, always incompletely.

† Precipitation incomplete in presence of the stronger acids.

‡ In a solution saturated with NH_4Cl.

§ In a concentrated alcoholic solution of $(NH_4)_2CO_3$.

Group VI. — Basic ions which do not yield insoluble chlorides or sulphides in presence of dilute hydrochloric acid, insoluble hydroxides precipitated by ammonium hydroxide in presence of ammonium salts, insoluble sulphides precipitated by ammonium sulphide, or insoluble carbonates precipitated by ammonium carbonate in aqueous or alcoholic solution.

These groups may be separated by the application of the group reagents in sequence and the forms of combination in which they appear are shown in the preceding table.

Representative Methods of Separation

In general, the separation and the determination of both basic ions and acidic ions may be accomplished in quantitative analyses more conveniently by the application of special methods rather than by the orderly use of group reagents and subsequent separations of the members of a group.

The Analysis of Brass

Three of the ordinary constituents of brass (copper, with lead and tin in small amounts) are precipitable by hydrogen sulphide in acid solution, one (iron) is precipitable by ammonium hydroxide, and two (zinc and traces of nickel) are precipitable by ammonium sulphide. Instead, however, of first precipitating copper, tin, and lead together from a suitably prepared solution and afterward separating them, it is preferable to remove the tin first, by special treatment, then the lead by another special treatment, and then the copper alone by means of the hydrogen sulphide in acid solution. Similarly, instead of precipitating the zinc and nickel together by ammonium sulphide and then separating them, it is better to adjust the sulphide precipitation in such a way that the zinc only may be first precipitated and the nickel recovered from the filtrate after the precipitation of the zinc.

Experimental Process: Determination of Copper, Zinc, Tin, Lead, Iron, and Nickel in Brass. — (1) *Solution of the Metal.* Treat in porcelain dish, covered with a watch-glass, a portion (0.5 grm.) of the metal with cold nitric acid (sp. gr. 1.2; 20 cm.^{3}), warming as the violence of the action allows, and finally evaporating the solution to dryness. Moisten the dry residue with nitric acid, dissolve the soluble portion in hot water (50 $cm.^3$), filter off the insoluble residue upon ashless paper, washing with hot water containing ammonium nitrate (1 per cent). The filtrate contains nearly all of the copper, zinc, lead, iron and nickel as nitrates. The residue is chiefly metastannic acid contaminated with traces of the metals other than tin.

(2) *Treatment of the Residue of Impure Metastannic Acid.* Ignite the precipitate and filter in porcelain and weigh as *impure stannic oxide.* Fuse the impure oxide with a mixture of sodium carbonate and sulphur in equal parts (six times the weight of the oxide) in the covered crucible until the flame of sulphur which burns at the junction of cover and crucible is no longer visible, and then cool. Treat the contents of the crucible with hot water and should any gritty residue remain separate it by filtration, fuse it with more of the carbonate-sulphur mixture, and again treat with hot water. To the solution add sodium sulphite until brown sodium polysulphide is changed to the pale yellow monosulphide and filter off any precipitate (metallic sulphides excepting tin sulphide) and dissolve it in nitric acid, adding this solution to the filtrate from the impure metastannic acid. To the sodium sulphide solution, containing the tin in solution as sulphostannate, add acetic acid to acidity, settle the precipitated stannic sulphide, filter, wash with a solution of ammonium nitrate (1 per cent), ignite the precipitate and filter (cautiously at first, and then very strongly) well exposed to the air, cool, add a little ammonium carbonate (to aid in destroying any tin sulphate) and reignite. Weigh the residue as *stannic oxide*, SnO_2, and calculate the corresponding amount of *tin.*

(3) *Treatment of the Filtrate from the Impure Metastannic Acid and Determination of Lead Sulphate.* Treat the filtrate from the metastannic acid, to which has been added the nitric acid solution of the sulphides left insoluble on extracting with water the product of the carbonate-sulphur fusion, with sulphuric acid (3 $cm.^3$) and evaporate on the water-bath and over the radiator until all nitric acid has been removed and the dense fumes of sulphuric acid appear. Add water (50 $cm.^3$) then alcohol (20 $cm.^3$), stir thoroughly, filter off the precipitate upon asbestos in the perforated crucible, ignite gently, and weigh as *lead sulphate*, $PbSO_4$, and calculate the corresponding amount of *lead.*

(4) *Treatment of the Filtrate from Lead Sulphate and Determination of Copper.* Evaporate the filtrate from the precipitated lead sulphate to remove the alcohol, add water (100 $cm.^3$), heat the solution to boiling and pass in hydrogen sulphide maintaining the current while the liquid cools. Filter off the precipitated cupric sulphide, washing with 2 per cent sulphuric acid. Set aside the filtrate containing the iron, zinc, and nickel as sulphates. Wash the precipitate from the filter as well as may be into a beaker and dissolve it with nitric acid. Ignite the paper and adhering,

precipitate and dissolve the residual copper oxide in nitric acid, adding this solution to the solution of the main portion of the precipitate. Filter the solution of copper nitrate, add sulphuric acid (2 $cm.^3$), evaporate to the fuming point of sulphuric acid, cool, dilute to a volume of 50 $cm.^3$ and electrolyze. (See pp. 49, 51.) Weigh the deposit of *metallic copper.*

Instead of determining the copper electrolytically, it may be precipitated, collected on asbestos, and weighed as cuprous sulphocyanate*; or the cupric sulphide may be ignited with sulphur in hydrogen, by Rose's method, and weighed as cuprous sulphide, Cu_2S. (See p. 105.)

(5) *Treatment of the Filtrate from Cupric Sulphide and Determination of Ferric Oxide.* Boil the filtrate from the precipitated cupric sulphide to remove hydrogen sulphide, oxidize the ferrous sulphide by means of bromine water, and add ammonium hydroxide until the solution smells strongly of ammonia. Filter off and wash the precipitated ferric hydroxide, setting the filtrate aside. Dissolve the precipitate in hydrochloric acid and reprecipitate with ammonium hydroxide (to remove any included zinc compound). Filter off and wash the precipitate, adding the filtrate to the filtrate from the former precipitate of ferric hydroxide. Ignite the precipitate and weigh as *ferric oxide,* Fe_2O_3. Calculate the corresponding amount of *iron.*

(6) *Treatment of the Filtrates from Ferric Hydroxide and Determination of Zinc Oxide.* Evaporate the filtrate from the ferric hydroxide, acidify carefully with hydrochloric acid and then add an excess of the acid equivalent to 10 $cm.^3$ of the N/10 acid (0.0365 grm.) to every 100 $cm.^3$ of liquid. Heat the solution to 60 or 70 degrees, saturate it with hydrogen sulphide, and set it aside until the zinc sulphide has settled. Filter off the precipitate, washing with a 2 per cent solution of ammonium sulphate, and set the filtrate aside. Dissolve the precipitate in hydrochloric acid, evaporate the solution (in a large platinum crucible) to remove the excess of acid, dissolve the residue of zinc chloride in water, add mercuric oxide in large excess, evaporate the liquid, ignite the residue, and weigh as *zinc oxide,* ZnO. Calculate the corresponding amount of *zinc.*

(7) *Treatment of the Filtrate from Zinc Sulphide and Determination of Nickel.* Boil the filtrate from the zinc sulphide to expel hydrogen sulphide, add to the hot solution a 1 per cent alcoholic solution of dimethyl glyoxime $(CH_3)_2C_2(NOH)_2$ (taking care that the alcohol shall make only a small proportion of the total amount of liquid — never more than half — to avoid solubility of the nickel precipitate) and ammonium hydroxide in faint excess. Filter on asbestos in the perforated crucible, wash with hot water, dry at 110 to 120 degrees, and weigh as *nickel dimethyl glyoxime,* $(CH_3)_2C_2(NO)_2Ni \cdot (CH_3)_2C_2(NOH)_2$, containing 20.31 per cent of nickel. Calculate the amount of the *nickel.*

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* For details, see Van Name: Methods in Analysis, Gooch, p. 108.

(8) State the results of the analysis in the following form.

ANALYSIS OF BRASS

Weight taken of brass.	Weight found.					
	SnO_2.	$PbSO_4$.	Cu.	Fe_2O_3.	ZnO.	$(CH_3)_2C_2(NO)_2Ni\cdot(CH_3)_2C_2(NOH)_2$
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.

PERCENTAGE COMPOSITION

Copper...............

Zinc.................

Tin..................

Lead.................

Iron.................

Nickel...............

The Analysis of Limestone

The chief constituent of limestone, calcium carbonate, is readily attacked by hydrochloric acid, as are some of the other constituents; but few limestones are so pure that this treatment will effect complete solution or even complete decomposition. The residue of the treatment may consist of quartz, silicates, pyrites, or other refractory materials, and carbonaceous matter may also be found in the residue. The thorough analysis of limestone implies the use of a very elaborate system of procedures and the determination of many constituents,* but for many purposes, in fact for most technical work, the examination may be confined to the determination of the silica, alumina (with phosphoric pentoxide and titanium dioxide), ferric oxide (and, perhaps, ferrous oxide), calcium oxide, magnesium oxide, carbon dioxide, and water. The determination of these substances will serve as another illustration of the application of some representative procedures in systematic analysis.

Experimental Process: Determination of CaO, MgO, FeO, Fe_2O_3, $Al_2O_3 + P_2O_5$, SiO_2, CO_2, *Insoluble Siliceous Matter, and Loss on Ignition.* — Powder

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* Hillebrand: Bulletin 422, U. S. Geol. Survey, p. 212.

the material, dry at 100 degrees (or use the well air-dried material, determining the hygroscopic water in a small portion (1 grm.–5 grm.) and calculate determinations to the basis of the condition of the material dried at 100 degrees). Weigh out exactly for analysis several portions *A, B, C, D, E.*

A. The Determination of Loss on Ignition. Weigh a portion of the material in a weighed platinum crucible. Ignite to constant weight, gently at first, and finally at the highest heat of the blowpipe. Record the *loss on ignition* which may be the resultant of several factors — loss of water, loss of carbon dioxide, possible loss by oxidation of carbonaceous matter to volatile carbon dioxide, and possible gain in weight by oxidation of ferrous iron to the ferric condition. In the case of a limestone devoid of carbonaceous matter, ferrous compounds and sulphides, the loss on ignition will probably represent fairly well the sum total of water and carbon dioxide. By subtracting from the percentage of loss on ignition, the percentage of carbon dioxide present (and to be calculated from the subsequent determination, *B*), an approximative determination of the percentage of *water* may be obtained.

B. The Determination of Carbon Dioxide. Weigh a portion of the material (1 grm.) and treat it with hydrochloric acid in an apparatus — e.g., the Kreider apparatus — suitable for the determination of carbon dioxide by loss (see p. 40). Calculate the percentage of *carbon dioxide.*

C. The Determination of Ferric Oxide. Put a weighed portion of the material (1 grm.) in a small beaker, add HCl (10 cm.^{3}), cover with a watch-glass, digest and warm until the acid appears to have no further action. When the ore contains organic matter, add a pinch of potassium chlorate and digest until effervescence ceases. Wash off the watch-glass, evaporate the liquid, treat the dry residue with a little hydrochloric acid (5 cm.^{3}), dilute with an equal amount of water, filter and wash upon a small filter, allowing the liquid to run into a small flask (50 cm.^{3} to 75 cm.^{3}). If this treatment of the ore leaves any of the original material undecomposed, ignite filter and residue in a platinum crucible, treat the residue with sulphuric acid (4 to 5 drops) and hydrofluoric acid (5 cm.^{3}), evaporate carefully to the fuming point of the sulphuric acid, cool, dilute with water, and add to the contents of flask. Reduce by zinc (see p. 144) the ferric salt in solution, hanging a funnel in the neck of the flask to prevent loss by spattering. When the color indicates complete reduction add 15 cm.^{3} of sulphuric acid. When all the zinc is dissolved, pour the contents of the flask into a liter of cold water, and titrate with $KMnO_4$ of known standard. From this amount of *total iron* thus found, calculate the corresponding percentage of ferric oxide. In case no ferrous compound is present in the original material this percentage will represent the *ferric oxide.* If, however, a compound of iron in the ferrous condition is subsequently found, in *D*, the percentage of ferric oxide corresponding to the total iron must be diminished by that corresponding to the ferrous oxide in order to find the amount originally present of *ferric oxide.*

D. The Determination of Ferrous Oxide. Put a weighed portion of the material (1 grm.) in a flask (150 cm.^{3}), fill the flask with CO_2, add HCl (10 cm.^{3}), insert a two-hole stopper provided with inlet and outlet holes, pass a current of CO_2 through the flask, and warm until the acid appears to have no further action. Cool and dilute the contents of the flask with cold, freshly boiled water. Filter quickly through a thin felt of asbestos in the filtering crucible, wash the felt, add to the filtrate and washings 15 cm.^{3} of (1 : 1) sulphuric acid, dilute the solution with boiled and cooled water to the volume of 1 liter, and titrate with potassium permanganate.

Remove the asbestos and residue to a roomy solid platinum crucible, washing out the filtering crucible with the minimum amount of water, add H_2SO_4 (4 to 5 drops), add HFl (5 cm.^{3}), fill the crucible with CO_2, put the cover in place, heat the contents to gentle boiling (in order to keep the crucible full of steam), immerse crucible and contents in cold water, add 5 grm. of calcium chloride,* 1 grm. of manganous chloride (see pp. 140) and 15 cm.^{3} of sulphuric acid (1 : 1), and titrate with standard $KMnO_4$.

Add together the percentages of ferrous oxide found in the two processes of titration and take the sum as indicating the *ferrous oxide.*

E. The Determination of Insoluble Siliceous Matter, Silica, Alumina, Calcium, and Magnesium. (1) Put a weighed portion of the material (1 grm.) in a small dish of platinum, fused quartz, or (less desirably) porcelain, add water (25 cm.^{3}), cover with a watch-glass, and then cautiously add hydrochloric acid, finally warming gently to complete the action of the acid and to expel dissolved carbon dioxide while the dish is still covered. Add bromine water until it gives its color to the solution (to oxidize ferrous iron), evaporate the solution to dryness, and desiccate at 110 degrees. Treat the residue with hydrochloric acid (1 : 5), warm and digest on the water-bath for some minutes. Filter on a small ashless filter, wash carefully with hot water and preserve the filter and residue. Evaporate the filtrate to dryness, desiccate, extract with dilute hydrochloric acid, filter, wash carefully the supplementary residue of silica. Preserve the filtrate for further treatment. Ignite together in platinum the residues of both evaporations, and weigh as *Insoluble Siliceous Matter.*

(2) Fuse the insoluble siliceous matter with at least six times its weight of sodium carbonate, cool, treat the mass with hydrochloric acid in excess, evaporate the solution to dryness, desiccate at 110 degrees, digest the residue with hydrochloric acid (1 : 5), filter, and wash carefully with hot water. Preserve the filter with the precipitated silica upon it.

Evaporate the filtrate from the precipitated silica to dryness, desiccate

* To form an insoluble fluoride which is inert toward permanganate, so that the end reaction may be definite.

at 110 degrees, and digest the residue with dilute hydrochloric acid as before. Filter off the supplementary residue of silica and wash carefully.

Add the filtrate to the filtrate from the insoluble siliceous matter of (1).

Ignite together the first residue of silica and the supplementary residue of silica obtained in the evaporation of the filtrate, finishing with the full heat of the burner or blast-lamp. Moisten the residue with sulphuric acid, heat gently until visible fuming ceases, and then ignite for a minute at low red heat. Weigh as *impure silica.*

Treat the impure silica with hydrofluoric acid and a few drops of sulphuric acid, evaporate off the free acid over a radiator, finally ignite to low redness for a minute, and weigh. Take the loss of weight of the impure silica in this process as the weight of *silica.*

Fuse with sodium carbonate the material left in the crucible after the treatment with hydrofluoric acid and sulphuric acid, which may consist of sodium sulphate with sulphates and oxides of the basic elements retained in the insoluble siliceous matter when the limestone was acted upon by hydrochloric acid, and add the solution to the filtrate from the insoluble siliceous matter of (1).

(3) To the filtrate from the insoluble siliceous matter of (1), to which has been added the hydrochloric solution of the basic elements left in the hydrofluoric acid treatment of the silica of (2), add hydrogen dioxide (unless manganese is absent) and ammonium hydroxide in slight excess. Heat the liquid to boiling, filter, and wash with hot water.

Preserve the filtrate for further treatment. Dissolve the precipitate off the filter in hot hydrochloric acid (1 : 1), wash the filter with hot water and finally with dilute ammonia. Neutralize the acid in the filtrate by ammonium hydroxide, adding a slight excess of the last (and hydrogen dioxide if manganese is present), filter off the precipitate upon the original filter, and wash. Add the filtrate to the former filtrate from the precipitate by ammonium hydroxide.

Dry the precipitate and filter, ignite thoroughly, and weigh. The residue should consist of ferric oxide, corresponding to the *total iron* found in *C*, and alumina (with manganese oxide (Mn_3O_4), phosphoric pentoxide (P_2O_5), and titanium oxide (TiO_2), in case manganese, phosphorus and titanium were constituents of the limestone). The difference between the percentage weight of this residue and the percentage weight of ferric oxide corresponding to the *total iron* will therefore represent the percentage of *alumina* (with, possibly, oxides of manganese, phosphorus, and titanium).

(4) To the combined filtrates from the precipitations by ammonium hydroxide add hydrochloric acid to very faint acidity. Heat to boiling and add slowly a solution of oxalic acid (1 grm.), neutralize the acid and finally make the solution ammoniacal by the very gradual addition, with constant stirring, of 1 per cent ammonium hydroxide. Digest at least an hour (over-night if the amount of calcium is very small). Filter and wash,

after complete settling, and set the filtrate aside for further treatment. Dissolve the precipitate of calcium oxalate (which may now include magnesium oxalate) in hot (1 : 1) hydrochloric acid, add oxalic acid, make the solution ammoniacal, digest, filter and wash this second precipitate of calcium oxalate as in the former precipitation.

Add the filtrate to the filtrate from the first oxalate precipitation.

Dry the precipitate and paper, ignite (finally with the blast-lamp), and weigh as *calcium oxide.*

(5) Evaporate the combined filtrates from the oxalate precipitations to a volume of about 300 $cm.^3$ and neutralize carefully with hydrochloric acid. Add hydrogen sodium ammonium phosphate (30 $cm.^3$ of the saturated solution), boil for five minutes, cool, add ammonium hydroxide until the solution smells of ammonia acid, then add 10 $cm.^3$ more of the concentrated ammonium hydroxide. Digest until the precipitate becomes crystalline. Filter off the precipitated ammonium magnesium phosphate upon asbestos in the perforated crucible, heat gently until ammonia no longer escapes, ignite at bright red heat and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Calculate the corresponding percentage of *magnesium oxide.*

(6) State the results of the analysis in the following form.

STATEMENT OF ANALYSIS

		Grm.	Per cent
Weight taken			
Weight found	SiO_2		
	Al_2O_3, etc.		
	Fe_2O_3		
	FeO		
	MgO		
	CaO		
	CO_2		
	H_2O (approx.)		
	Summation		

The Analysis of Silicates

The simple analysis of a silicate,* involving the determination of water, silica, aluminium, iron, calcium and magnesium, follows very closely the plan of the analysis of limestone, as described above, provided the silicate is decomposable by hydrochloric acid. Generally, however, the decomposition of the silicate

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* For full information in respect to the analysis of silicate rocks, see Hillebrand: Bulletin 422 of the U. S. Geological Survey.

is best accomplished by fusion with sodium carbonate. The melt is then cooled, decomposed by hydrochloric acid, and subjected to the processes described for the successive separations and determinations in the analysis of the *insoluble siliceous residue* of the limestone.

The determinations of the alkali elements and of fluorine are made by special treatment of separate portions of the material for analysis.

Determination of Alkali Elements. — The alkali elements, not precipitable by ordinary group reagents, may be converted to weighable form and determined after the separation of other basic elements. Potassium and sodium may be conveniently weighed as chloride, sulphate or pyrosulphate.* From a mixture of potassium chloride and sodium chloride, potassium may be precipitated as potassium chlorplatinate or as potassium perchlorate (both insoluble in alcohol) and determined gravimetrically, or the potassium may be determined volumetrically by a process involving the precipitation of potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6 \cdot H_2O$, and the oxidation of this product by standard potassium permanganate, this process being especially applicable to the determination of potassium in soils, fertilizers, and animal fluids.†

When the weight of a mixture of potassium chloride and sodium chloride is known, the difference between that weight and the weight of potassium chloride found experimentally, by one of the methods mentioned, measures the sodium chloride. If the potassium is removed from such a mixture by precipitation as potassium perchlorate, by means of perchloric acid‡ or aniline perchlorate§ in alcoholic solution (97 per cent), the sodium may be precipitated as chloride by saturating the alcoholic filtrate (97 per cent) with gaseous hydrogen chloride, and the sodium chloride thus precipitated may be determined by

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* Browning: Methods in Analysis, Gooch, p. 79.

† Drushel: Methods in Analysis, Gooch, p. 93.

‡ Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 50. Kreider: Methods in Analysis, Gooch, p. 88.

§ D. U. Hill: Am. Jour. Sci., **40**, 75 (1915).

collecting it on asbestos in the perforated crucible, washing with alcohol (97 per cent), drying at about 110 degrees and weighing as such.*

The determination of potassium and sodium in silicates involves first of all the decomposition of the silicates, and this may be brought about according to the nature of the case, by the action of hydrochloric acid, by hydrofluoric acid and sulphuric acid (*Berzelius*), or by ignition in mixture with calcium carbonate and ammonium chloride (*J. Lawrence Smith*). The last method is of wide application and very direct in consequence of the fact that when the residue of the ignition is extracted with water the silica and all basic elements other than the alkali elements and calcium are precipitated by the calcium hydroxide produced in the process. The determination of potassium and sodium in feldspar will illustrate the method.†

Experimental Process: Determination of Potassium and Sodium in Feldspar. — *Process of Decomposition.* Weigh out a portion of the finely ground material (0.5 grm.), put it into a roomy platinum crucible, mix it carefully with an equal weight of pure sublimed ammonium chloride, add eight times its weight (4 grm.) of calcium carbonate (prepared by precipitation with ammonium carbonate and of determined purity), and mix the whole with great care. Heat the covered crucible over a low flame so regulated that the ammonium chloride will be decomposed without volatilizing as such, while calcium chloride (the active agent in the attack upon the silicate) is formed and ammonia is set free. When the evolution of ammonia has ceased, raise the temperature and ignite for an hour in such fashion that only the lower half of the crucible (conveniently held in an ignition-plate ‡) is heated to low redness. Cool, transfer the fritted mass (using water if necessary) to a dish (preferably platinum), digest with water (75 cm.^{3}) kept hot, pulverize with a pestle any large particles, settle the insoluble residue, decant upon a filter the clear solution now containing chlorides of the alkali elements and calcium, and wash the residue thoroughly by decantation and afterwards upon the filter.

Removal of Calcium. — To the filtrate, heated to boiling, add ammonium carbonate and ammonium hydroxide, filter the solution of alkali chlorides from the precipitated calcium carbonate and set the filtrate aside. Dis-

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* D. U. Hill. Am. Jour. Sci., **40,** 75 (1915).

† For the determination of lithium associated with potassium and sodium, see Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 53.

‡ See footnote on p. 78.

solve the precipitate in hydrochloric acid and reprecipitate with ammonium carbonate and ammonium hydroxide, filtering and washing to recover any alkali chloride which may have been included in the former precipitation. Evaporate the combined filtrates, dry the residue thoroughly at 110 degrees and remove ammonium chloride by cautious ignition. Dissolve the residue in a little water, and remove residual traces of calcium by treatment of the solution with ammonium oxalate and ammonium hydroxide, standing over night, filtering, and washing.

Recovery of Alkali Chlorides. — Evaporate the filtrate in a dish or large crucible of platinum, dry the residue carefully and ignite gently to remove the ammonium salts. Moisten the residue with hydrochloric acid (to recover as chloride any alkali salt changed to carbonate in the ignition), ignite gently and weigh the *alkali chlorides.*

Separation and Determination of Potassium. — Dissolve the alkali chlorides in a little water, add in water-solution a moderate (calculated) excess of chlorplatinic acid, H_2PtCl_6, and evaporate the solution on the water-bath until the residue will solidify when allowed to cool. To the cooled residue add a little absolute alcohol, disintegrate the solid mass by means of a stirring rod with rounded end, filter off the precipitate upon asbestos in a weighed filtering crucible, wash with alcohol until the washings are colorless, dry in an air-bath at 140 degrees, and weigh as potassium chlorplatinate, K_2PtCl_6.* Calculate the *potassium oxide* in the silicate.

Determination of Sodium. — Calculate the amount of potassium chloride which is equivalent to the potassium chlorplatinate weighed. Deduct this amount from the weight (previously found) of the alkali chlorides, to obtain by difference (if no other alkali chloride is present) the weight of sodium chloride, from which may be found the corresponding weight of *sodium oxide.*

Determination of Fluorine. — Fluorine contained in a silicate, or in a fluoride mixed with silica, may frequently be expelled in the form of silicon fluoride by the action of concentrated

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* Instead of collecting the potassium chlorplatinate upon asbestos, it may be filtered off and washed upon a paper filter, dissolved in hot water into a platinum dish or crucible, recovered by evaporation of the solution dry at 140 degrees and weighed. In the evaporation of this solution in pure water, however, the potassium chlorplatinate undergoes a slight hydrolysis with the formation of a product of decomposition, $KHPtCl_5OH$, which contains a smaller proportion of potassium than that in potassium chlorplatinate, K_2PtCl_6. Experience shows that the error due to hydrolytic decomposition of the chlorplatinate approximates very closely 0.04 per cent of its weight.

sulphuric acid. When such is the case, the determination of the fluorine may be made by collecting the silicon fluoride in a suitable absorption apparatus and weighing as such (*Fresenius*); or the determination may depend either upon the formation of potassium fluosilicate and free hydrochloric acid by the action of the silicon fluoride upon a 50 per cent alcoholic solution of potassium chloride and the acidimetric determination of the free acid (*Penfield*)* or upon the absorption of silicon fluoride in water and the direct titration of the fluosilicic acid, produced by hydrolysis, with sodium hydroxide (*Hileman*).†

Fluorine contained in a silicate not decomposable by sulphuric acid may be converted to soluble sodium fluoride by fusion of the silicate with sodium carbonate. A refractory fluoride may be attacked similarly if mixed with silica which greatly facilitates the decomposition. Water extracts from the product of fusion soluble sodium fluoride with sodium silicate and sodium carbonate and, after the nearly complete neutralization of the solution by means of hydrochloric acid, the larger part of the silica may be precipitated by prolonged action of ammonium carbonate, nearly all the remainder of the silica may be precipitated by zinc hydroxide in ammoniacal solution (*Berzelius*) and boiling until the free ammonia is expelled.‡ The filtrate from the precipitated zinc oxide, basic carbonate, and silicate contains the sodium fluoride which by reaction with calcium chloride will yield the nearly insoluble calcium fluoride. Precipitated by itself, calcium fluoride is slimy and filterable only with the greatest difficulty, but if the precaution is taken to have present in the solution of the fluoride a little sodium carbonate, before making the precipitation with calcium chloride, the mixed precipitate of carbonate and fluoride thrown down from a hot solution may be filtered off and washed. After drying and igniting the precipitate, the calcium carbonate and calcium oxide of the residue are converted to the soluble acetate by

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 470.

† Methods in Analysis, Gooch, p. 436.

‡ For details, see Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, pp. 471, 481.

treatment with dilute acetic acid, and the excess of acid is removed by evaporation. The dry residue is treated with water and the insoluble precipitate (now compact and washable) is transferred to a paper filter, washed, dried, ignited and weighed as calcium fluoride. The weight of the residue must, however, be corrected for possible contamination with silica by cautious treatment with concentrated sulphuric acid, removal of the excess of acid by evaporation, ignition and weighing as calcium sulphate,

$$CaSO_4 \approx CaF_2.$$

Analysis of Substances Yielding Ammonia

Ammonium Salts. — Ammonium chloride in solution and ammonium salts of acids made volatile by hydrochloric acid may be converted to weighable form by treatment with hydrochloric acid (to prevent hydrolytic decomposition of the chloride and loss of volatile ammonia), evaporation of the solvent and drying of the residue at 110 degrees. Ammonium chloride in solution containing a little hydrochloric acid may also be determined by treatment with chlorplatinic acid, evaporation of the solution to dryness, extraction of the residue with absolute alcohol, collection of the precipitate upon asbestos in the filtering crucible, drying at 130 degrees, and either weighing the ammonium chlorplatinate $(NH_4)_2PtCl_6$, as such or weighing the residue of platinum after igniting very cautiously.

All ammonium salts in solution are decomposed by sodium hydroxide, potassium hydroxide, or calcium hydroxide, and the ammonia thus set free may be volatilized from the boiling solution and absorbed in acid.* If the retaining acid is hydrochloric acid, the ammonium chloride thus formed may be recovered by evaporation of the solution and determined gravimetrically by one of the methods described above. If the absorption of the free ammonia is effected by a measured amount of standard acid, the excess of acid may be determined by titration with standard alkali, with methyl orange (not phenolphthalein) as the indicator, and the difference between the acid

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 59.

taken and that found in the titration will be the measure of the ammonia.

The ammonia liberated by the action of sodium hydroxide upon minute amounts of ammonium salts in solution, such as occur in drinking water, may be collected in an aqueous distillate and determined colorimetrically by use of "Nessler's reagent." *

Organic Compounds. — Ammonia produced from nitrogenous (organic) compounds by oxidation with potassium permanganate in presence of concentrated sulphuric acid and liberated by subsequent treatment with sodium hydroxide (*Kjeldahl*) † may be thus determined and made the measure of the *organic nitrogen.*

Indirect Analysis

The relation of the equivalent weights of the substances involved when two compounds constituting a mixture are changed chemically, with the formation of definite products of reaction, makes it possible to determine by calculation the amounts of the original compounds when (I) the weight of the mixture is known and the combined weights of the products can be determined or when (II) the two original compounds are susceptible to two different reactions each of which yields determinable products. In such cases, it is possible to express the relations in two equations involving two unknown quantities.

The indirect determination of chlorides and bromides constituting a mixture of known weight and the indirect determination of nitrates and nitrites in solution (in absence of interfering substances) will serve to illustrate these *indirect methods.*

Chlorides and Bromides. ‡ — From a solution containing soluble chlorides and bromides, the chlorine and bromine may be precipitated, by silver nitrate, in the form of silver chloride and silver bromide. If the mixture of silver chloride and silver bromide is weighed and the amount of the combined silver

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* Treadwell-Hall: Analytical Chemistry, 3rd ed., Vol. II, p. 60.

† Ibid., p. 62.

‡ Gooch and Fairbanks: Methods in Analysis, Gooch, p. 459.

determined, by electrolytic reduction and weighing, the data are at hand for the indirect determination of the amounts of chlorine and bromine originally present in the mixture of soluble chlorides and bromides. From the relations between the weight of the mixed silver salts (a), the weight of the silver (b), the ratio of the equivalent of silver to that of silver chloride ($107.88 \div 142.34 = 0.7526$), and the ratio of the equivalent of silver to that of silver bromide ($107.88 \div 187.80 = 0.5744$), may be derived two equations defining the amount of silver chloride (x) and the amount of silver bromide (y) in the mixed silver salts:

$$x + y = a,$$
$$0.7526\,x + 0.5744\,y = b,$$

whence,

$$x = 5.6118\,b - 3.2233\,a,$$
$$y = 4.2233\,a - 5.6118\,b,$$

and

$$\text{chlorine} = \frac{35.46}{143.34}x = 0.2474\,x,$$
$$\text{bromine} = \frac{79.92}{187.80}y = 0.4255\,y.$$

*Experimental Process: Indirect Determination of Chlorine and Bromine.** — Dissolve a weighed portion (0.5 grm.) of a known mixture of sodium chloride and potassium bromide in water (300 cm.^{3}), add a few drops of nitric acid and then, gradually and with constant stirring, a solution of silver nitrate until no further precipitation takes place. Heat the liquid to boiling and set the whole aside to cool in the dark. When the precipitate has settled, collect it in a weighed filtering crucible provided with a layer of asbestos upon which rests a perforated platinum disk covering the asbestos and in contact with the wall of the crucible, so that the disk and the crucible may be made parts of an electrical circuit. Wash the precipitate with water containing a few drops of nitric acid and then with a little pure water, dry at about 150 degrees, weigh and determine the weight of the mixed silver salts.

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* For direct determinations of chlorine and bromine in halide salts, see Gooch and Blumenthal: Am. Jour. Sci., **35**, 54. Blumenthal: Ibid., **35**, 93. Gooch and Cole: Ibid., **37**, 257. For a direct determination of chlorine, bromine and iodine similarly associated, see Cole: Ibid., **38**, 265.

Set the capped crucible upon cold metal and fuse the silver salts with a blow-pipe flame directed upon the mass from above. Cover the junction between cap and crucible with a rubber band, nearly fill the crucible with a 10 per cent solution of oxalic acid in 25 per cent alcohol, and pass an electric current (0.5 amp.) through the solution, between a platinum anode dipping in the liquid and the crucible used as the cathode. When the reduction of the silver salts is judged to be complete, set the crucible (after removing the band and the cap) in the holding funnel of the filtering flask, wash well with water, ignite the residue at very low red heat, weigh, and determine the weight of the residue. Repeat the operation of electrolyzing and weighing until constancy of weight shows that the reduction of the silver salts to silver is complete.

Calculate, by the method indicated above, the weight of sodium chloride and the weight of potassium bromide in the original mixture.

Nitrates and Nitrites. — When nitrates and nitrites in solution are acted upon by manganous chloride in presence of concentrated hydrochloric acid the following reactions take place:

$$\begin{aligned} 2\,\overset{\text{I}}{\mathrm{M}}\mathrm{NO_3} + 8\,\mathrm{HCl} + n\,\mathrm{MnCl_2} &= 2\,\overset{\text{I}}{\mathrm{M}}\mathrm{Cl} + 4\,\mathrm{H_2O} + 2\,\mathrm{NO} \\ &\quad + 3\,\mathrm{Cl_2} + n\,\mathrm{MnCl_2}, \end{aligned}$$

$$\begin{aligned} 2\,\overset{\text{I}}{\mathrm{M}}\mathrm{NO_2} + 4\,\mathrm{HCl} + n\,\mathrm{MnCl_2} &= 2\,\overset{\text{I}}{\mathrm{M}}\mathrm{Cl} + 2\,\mathrm{H_2O} + 2\,\mathrm{NO} \\ &\quad + \mathrm{Cl_2} + n\,\mathrm{MnCl_2}. \end{aligned}$$

The chlorine evolved in these reactions may be absorbed in potassium iodide (see pp. 194, 196), while the nitrogen oxide is passed on for measurement over a solution of sodium hydroxide (see p. 218). The weight of iodine set free by the chlorine may be determined titrimetrically and the weight of nitrogen oxide may be calculated from the measured volume of that gas. From the relations between the weight of nitrogen oxide (a), the weight of iodine (b), the equivalent weights of nitrogen oxide, nitric acid ($\mathrm{NO} \Bumpeq \mathrm{HNO_3}$) and nitrous acid ($\mathrm{NO} \Bumpeq \mathrm{HNO_2}$), and the equivalent weights of iodine, nitric acid ($3\,\mathrm{I} \Bumpeq \mathrm{HNO_3}$) and nitrous acid ($\mathrm{I} \Bumpeq \mathrm{HNO_2}$), may be derived two equations defining the unknown amounts of nitric acid (x) and of nitrous acid (y) corresponding to the nitrate and nitrite in the original solution:*

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* Roberts: Methods in Analysis, Gooch, p. 272.

$$\frac{\mathrm{NO}}{\mathrm{HNO_3}}x + \frac{\mathrm{NO}}{\mathrm{HNO_2}}y = a, \quad \text{or} \quad \frac{30.01}{63.02}x + \frac{30.01}{47.02}y = a,$$

$$\frac{3\,\mathrm{I}}{\mathrm{HNO_3}}x + \frac{\mathrm{I}}{\mathrm{HNO_2}}y = b, \quad \text{or} \quad \frac{380.76}{63.02}x + \frac{126.92}{47.02}y = b,$$

whence,

$$x = 0.248\,b - 1.049\,a,$$
$$y = 2.35\,a - 0.185\,b.$$

The amounts of corresponding nitrates and nitrites are, of course, easily found from the values for nitric acid and nitrous acid thus determined.

From the form of the expressions defining the values of the unknown quantities in the examples given, it is obvious that, while the accuracy of an indirect method of analysis depends upon the choice of reactions, the experimental error is always more or less magnified in the process of computation. In general, a reliable direct method is preferable to an indirect method of determination.

INTERNATIONAL ATOMIC WEIGHTS, 1914

O=16			O=16		
Aluminium........	Al	27.1	Molybdenum.......	Mo	96.0
Antimony.........	Sb	120.2	Neodymium........	Nd	144.3
Argon............	A	39.9	Neon...............	Ne	20.0
Arsenic...........	As	74.96	Nickel..............	Ni	58.68
Barium...........	Ba	137.37	Nitrogen...........	N	14.01
Bismuth..........	Bi	208.0	Osmium............	Os	190.9
Boron............	B	11.0	Oxygen............	O	16.00
Bromine..........	Br	79.92	Palladium..........	Pd	106.7
Cadmium.........	Cd	112.40	Phosphorus.........	P	31.4
Cæsium	Cs	132.81	Platinum...........	Pt	195.2
Calcium..........	Ca	40.09	Potassium..........	K	39.10
Carbon...........	C	12.00	Proseodymium......	Pr	140.6
Cerium...........	Ce	140.25	Radium............	Ra	226.4
Chlorine..........	Cl	35.46	Rhodium...........	Rh	102.9
Chromium	Cr	52.0	Rubidium..........	Rb	85.45
Cobalt............	Co	58.97	Ruthenium.........	Ru	101.7
Columbium..			Samarium..........	Sm	150.4
Copper			..	Sc	44.1
Dysp				Se	79.2
Erb					28.3
Eu					107.88
Fluo ne.					23.00
Gadoliniu					7.63
Gallium...					.07
Germanium..					.5
Glucinum......					.5
Gold...........					.2
Helium...........					
Hydrogen.....					
Indium.......					
Iodine......					
Iridium...					
Iron.......					
Krypton..					
Lanthanun					
Lead......					
Lutecium....					
Magnesium..					
Manganese...					
Mercury........					

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