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A LABORATORY OUTLINE
OF
SMITH'S COLLEGE CHEMISTRY

By JAMES KENDALL

SMITH'S COLLEGE CHEMISTRY

REVISED EDITION

739 + xii pp. With 179 Figures and 16 Plates

SMITH'S INORGANIC CHEMISTRY

1030 + xxv pp. With 234 Figures and 18 Plates

NEW YORK, THE CENTURY CO.

A LABORATORY OUTLINE

OF

SMITH'S COLLEGE CHEMISTRY

THIRD REVISED EDITION

By

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G. BELL & SONS, LTD.
LONDON

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PREFACE

This Laboratory Outline has been arranged to parallel, by simple and suggestive experiments, the subject matter presented in the latest revisions of Alexander Smith's *College Chemistry* and *Inorganic Chemistry*. The directions for each experiment are given in sufficient detail to enable the book to be used by students who are taking chemistry for the first time.

It is understood that no class will find it possible to perform all the experiments contained in the *Outline*. The interests of the teacher, the sex of the pupils, the local industries, and other factors will assist to determine the placing of greater emphasis on some experiments and the exclusion of others. The subdivision into small paragraphs will make omissions easy. The choice will depend upon the preferences of the instructor and upon the purpose for which the course is being given.

A difficulty which occasionally arises—the demand of an exceptionally "fast worker," or of a good student who has covered most of the regular laboratory work previously, for additional material—has been met in this revision by the inclusion of a number of references to suitable experiments described in detail in the *Journal of Chemical Education*. It is particularly important that such students should be encouraged at an early stage in their career to develop a research spirit, instead of being driven into a distaste for chemistry through vain repetition, and the trouble involved in assisting them to carry out these extra assignments will be more than compensated, in most cases, by the stimulating effect which successful execution will produce not only upon the individual worker, but upon the class in general.

All modern laboratory manuals contain quantitative experiments. If the laboratory in which the students using this outline are accommodated lacks the simple balances, or the burettes, which quantitative work requires, these experiments must be omitted. In such cases, however, the teacher should discuss in detail, in the

class-room, data such as these experiments would yield, and show how the conclusions demanded in the *Outline* can be reached.

Every effort must be made to prevent the mere mechanical performance of the directions given, without thought about the chemical principles involved. The questions asked in the *Outline* are intended to call attention to the chemical significance of the work. The experiment will teach nothing, unless the pupil is required to answer these questions in his or her laboratory notes.

The exact method to be followed by the class in recording the results of laboratory work is, of course, a matter which is best left to the discretion of the individual instructor. The large size of laboratory sections in most colleges at the present time, however, necessitates that the time spent by assistants in the correction of laboratory records be reduced to a minimum. The plan described in Note 1 of the General Instructions at the beginning of the *Outline* is consequently recommended to the attention of instructors, since it has been found by personal experience to be one which is both economical and efficient. The increase in page size of this volume over that of preceding laboratory manuals in the Alexander Smith series is expressly intended to facilitate the employment of this plan. The chief objection that may be raised against it — namely, that the student should acquire experience in writing connected statements of his laboratory work — may be met by assigning Home-Study Questions upon the more important and involved points.

At the end of each week the class should be examined and the experiments that have been performed should be discussed in the class-room. The teacher may thus make certain that the object of each exercise has been fully appreciated and that the significance of the results obtained has been clearly understood. In the course of this discussion, particular emphasis should be placed upon the practical applications of many of the experiments.

JAMES KENDALL.

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A LABORATORY OUTLINE OF SMITH'S COLLEGE CHEMISTRY

CHAPTER I

GENERAL INSTRUCTIONS

Read the "Regulations" posted in the laboratory. Read also, attentively, the following notes:

Note 1. Each student must secure a supply of loose-leaf note paper in ruled sheets approximately 9 inches long and 5 inches wide, upon which a concise record of all **observations** and **deductions** resulting from his experimental work is to be made. Upon the top of each sheet the student's name and desk number, with the name of his laboratory assistant and any other necessary information, are first written. The remainder of the sheet is then fitted into the *Outline* over the blank interleaf opposite the directions to the exercise which is being performed, and a piece of carbon paper is inserted between the loose sheet and the blank page. The answers to all specific questions in the text, all observations and conclusions therefrom, together with the results of weighings, etc., in quantitative experiments, are written down **immediately** (also, of course, legibly) on the loose sheet as the student proceeds through the experiment. Only the briefest remarks are called for, and no attempt should be made to work up a continuous narrative or to enter into any detailed discussion. At the end of the laboratory period, the loose-leaf copy of the student's notes is handed to his assistant for inspection and correction, the duplicate record on the interleaf being retained for his own use. (See also the Preface to this *Outline,* p. vi.)

Note 2. Whenever an **interrogation point** or a direct **question** appears, a corresponding observation or answer should appear in

the student's notes. The "(?)" indicates something to be observed and recorded.

Note 3. The very numerous **questions** asked in the course of this outline are intended to be answered, not by speculation, but by careful observation and reasoning based on the results of this. Very often the student will find it necessary to devise and carry out further experiments of his own before a satisfactory answer is obtained. When any difficulty occurs, the student should endeavor by reflection and study to solve it himself before consulting an instructor.

Note 4. In many cases the work outlined could not in itself furnish the basis for an answer, and fuller investigation of the point would require work beyond the time or ability at the disposal of the beginner. Such questions are distinguished by references to Smith-Kendall's *College Chemistry* (*Third Revised Edition*) or *Inorganic Chemistry*, the page where the necessary information may be obtained being indicated in bold type between square brackets. Where the reference is to *College Chemistry*, the page number is prefixed by **C**, while in the case of references to *Inorganic Chemistry* the prefix **I** is employed. The text-book actually used in the classroom should always be at hand in the laboratory for reference purposes, but should be consulted, however, only after the experiments have been made and the notes written up as far as possible. Cross-references to other experiments in this laboratory outline are also frequently given.

Note 5. When a chemical change has been observed the **equation** should always be given in the notes, but an equation alone is seldom a sufficient record.

Note 6. Where the word [Instructions] appears, consult the instructor before going further.

Note 7. In quantitative experiments, marked [Quant.], use the finer balance; in all other cases the rough scales in the laboratory.

Note 8. The expression [Storeroom] indicates that the necessary apparatus is not included in the individual outfits.

Note 9. When the word [Hood] appears, the operation is **not** to be conducted in the open laboratory. The apparatus is to be placed at once near the desk-ventilator, or transferred to the hood.

Note 10. Where exact quantities are not indicated, **very small amounts** of solutions (1 c.c. or less) should be taken. This advice

is given, partly to secure saving of material, but chiefly to avoid the waste of time which working with large quantities always entails.

Note 11. To obtain the necessary chemical substances, if the chemicals are not furnished in "kits" to each student, do **not** carry the bottles from the side-shelf to the desk. Bring a clean test-tube for liquids and a watch-glass for solids. For the latter, a piece of paper, provided near the side-shelf, may also be used. When too much of any reagent has been taken, do not return it to the bottle.

Note 12. The **chemicals**, if on a side-shelf, are divided into two sets, each arranged alphabetically according to the scientific names. The first set consists of solids in small bottles, the second of liquids. The bottles and their places are numbered consecutively to facilitate accurate replacement, and scrupulous care must be taken not to disarrange them. Read the labels attentively, as there are frequently several kinds of the same substance (*e.g.*, pure, commercial, dilute, concentrated, and normal).

All **materials** are supplied through the storeroom service. Do not therefore take side-shelf bottles, when found empty, to the instructor, but to the storekeeper for refilling.

Note 13. The expression [From Instructor], however, indicates one of a few special substances for which the student must apply to an instructor.

Note 14. The **bottles on the desk**, if there are any, contain certain substances which are frequently used. These substances will not be found on the side-shelf.

Note 15. When any **acid** gets upon the clothing, apply ammonium hydroxide solution at once.

Note 16. **Burns**, whether caused by contact with hot objects, by acids, or by corrosive liquids like bromine, are rubbed gently with a paste of sodium-hydrogen carbonate and water. All burns, save the slightest, must afterwards be dressed with an aqueous solution of boric acid (half-saturated) to prevent infection. Obtain the assistance of an instructor.

Cuts must be washed in running water and dressed with boric acid as above, or with lanolin containing 2 per cent of boric acid.

Note 17. All students **work independently**, except where coöperation is expressly directed.

CHAPTER II

MANIPULATION

The Outfit of Apparatus. As articles missing or found imperfect when the course is completed will be charged for, check the outfit of apparatus carefully by comparison with the list. To do this, put all the articles on the top of the desk and make a mark on the margin of the list opposite to the names of such as you are able to identify, at the same time returning the article to the cupboard or drawer. With the assistance of an instructor, the remaining, unfamiliar articles can then be checked also.

1. Instructions

a. Read the general directions and notes preceding this chapter very carefully, and do not fail to observe them.

b. The number of blast-lamps and balances being limited, the whole class cannot perform the experiments in this chapter simultaneously in the order given. The order is, in any case, a matter of indifference. Two students from the group under each assistant will begin with glass-working (3) or weighing (5 and 6 **a–d**). The other students will meanwhile perform 2, 4, and 6 **f** at the desks.

2. Bunsen Burner

a. Attach the Bunsen burner by means of rubber tubing to a gas connection, close the air-holes at the base, and light. In lighting a Bunsen burner, turn on the gas first, and then bring a lighted match over the tube of the burner (?). Now open the air-holes gradually and note the effect upon the flame (?). Sometimes the flame descends and burns noisily at the bottom of the tube. This back-fire happens when too much air is admitted. Shut off the gas at once, close the air-holes partially, turn the gas on again, and relight.

b. Close the air-holes again completely, and hold a porcelain dish in the flame. What is deposited on the dish? When using the

burner for heating purposes, always regulate the air supply so as to get a noiseless, non-luminous flame.

c. Unscrew the tube of the Bunsen burner, turn on the gas, and light it (?). Turn off the gas and replace the tube. Make a drawing of the vertical section of the burner through the feed pipe [C 463; I 652].

d. Is any gas entering or escaping from the holes at the base? To answer this, light a splint, blow the flame out, and hold the smoking end close to the holes (?).

Hold the lighted burner up and blow a sudden puff of air towards one of the holes (?). What is the effect of increasing the supply of air?

e. Determine the structure of the luminous, and also of the non-luminous flame. Which parts in each case are relatively hotter, and which cooler? This may be ascertained by holding a dead match across each flame, first close to the bottom (?), and then near the top, withdrawing it in each case just as soon as it begins to char and then examining the wood (?). Make a sketch showing the real form of the flame (?). Where should you hold an object in the non-luminous flame, in order to get the greatest heating effect? Insert one end of a narrow glass tube into the inner cone, and ascertain whether any unburnt gas ascends through the tube (?).

Which region is deficient in oxygen and which has an excess? The former is called the reducing, the latter the oxidizing region.

f. Place in a watch-glass [Note 11, p. 3] a small quantity of borax* (sodium tetraborate). Heat your platinum wire, which has been inserted into the fused end of a glass rod, and immerse the glowing end of the wire in the borax. Use the wire in straight condition, without any loop. Now, hold the wire in the flame, observe the behavior of the borax, and explain [C 531; I 668. See Note 4, p. 2] (?). The bead must be small to avoid its dropping off.

g. Bring the hot borax bead in contact with a minute particle of manganese dioxide [Notes 11 and 12], heat in the flame near the outer edge until the particle has dissolved, and observe the color of the bead when cold (?). If the bead is opaque, too much

* In this *Outline* the common or popular names are often used intentionally. The systematic names must, in such cases, be found by the student by use of the Index in *College Chemistry* or *Inorganic Chemistry*.

of the dioxide has been taken: melt the bead, throw it off, and start again.

h. Cut off the gas supply until the flame is about 6 cm. in height. Close the air-holes until a luminous point appears at the apex of the inner cone, and hold the bead containing the manganese dioxide steadily in this luminous (reducing) portion. Before withdrawing the bead, lower it into the inner cone of unburnt gases to cool. Observe the color of the bead (?).

i. Reheat the bead in the oxidizing part of the flame (?).

3. Glass-Working

a. Glass Rod. Make a transverse notch about 15 cm. (6 inches) from the end of a glass rod. To do this, hold the rod on the table and draw the edge of the triangle file once firmly and smoothly across it. Now, break the rod at this point by holding it so that the point of the thumbs are together on the side opposite to the notch, and pressing forward with the thumbs so as to bend the rod away from the mark. Cut two other pieces of the same length.

To remove the sharp, often jagged edges, hold the ends of the rods in the Bunsen flame, turning them slowly until the edges are rounded (fire-polished). Observe the color of the flame (?). To what is this color due [C 568; I 720]? Do not lay the hot rods on the table, but balance them across the test-tube rack or on an iron ring until cold. Why does heating the rods remove the sharp edges?

b. Glass Tubing, Drawing Out. Cut, exactly as in **a**, from a piece of narrow glass tubing a portion 15 cm. long. Hold the center of this piece of tubing in the Bunsen flame, turning it slowly (?), until it becomes soft. Hold and turn it, as a whole, carefully, so as not to bend or twist it. When it is quite soft, remove it from the flame, and draw the two ends slowly apart (Fig. 1). If the result is satisfactory, reserve to make a nozzle as directed in Exercise 4 **b**.

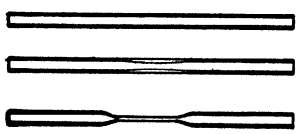


FIG. 1.

c. Glass Tubing, Bending. To **bend glass tubing**, never use the ordinary Bunsen flame (why?). Place the wing-top on the

burner, and use the resulting flat luminous flame of fish-tail form. Hold a piece of tubing 15 cm. long in the flame so that as long a portion as possible is heated, and rotate it steadily so as to heat all sides alike. Do not allow the tube to bend or twist. When the glass is quite soft, withdraw the tube and bend it to form a right angle, giving an L-tube (Fig. 2). The bend must be gradual and smooth, not sharp or crumpled. Bend another similar piece to form an obtuse angle. Fire-polish the edges (for this, use the non-luminous flame), but do not heat too long, otherwise the bore will be diminished.



Fig. 2.

Hold a piece of tubing in the Bunsen flame, without rotating the tube, and bend it while it is in the flame (?). Compare the bend with one made in the proper way (Fig. 2) and account for the difference (?).

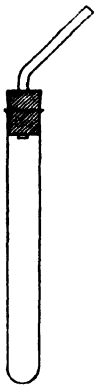
d. If time is available, perform the following experiments:

(1) Cut a small piece off the wide soft glass tubing and make a test-tube of it.

Wide tubing may be cut by making a deep scratch completely round the tube and starting the crack by touching with the red-hot end of a glass rod. Other methods may be shown by the instructor.

In the case of test-tubes, and other tubes of wide bore in which corks are to be inserted, the mouth must be strengthened and rendered fit for receiving the cork. To accomplish this, heat the edge in the flame and spread it slightly, but uniformly, by rotating in it a pointed piece of charcoal, or by turning outward the softened edge with the reverse end of a file.

In making test-tubes and in connecting pieces of tubing, distend the softened parts by blowing immediately before allowing to cool, otherwise cracks are likely to appear (?).


Fig. 3.

(2) Make a test-tube of hard (?) [C 529; I 665] glass.

Fit a bored rubber stopper into the hard glass test-tube. Remove the stopper, and push the shorter end of an obtuse-angled tube through the hole (Fig. 3). In inserting tubes in stoppers, always grasp the tube near the end to be inserted, for if force is applied at the far end of a long tube, the tube is apt to snap. Do not use much force — moisten the tube and the hole and rotate the tube while pushing it gently through (don't hurry). Allow the tube to project not

over 1 mm. on the inside. Replace the stopper in the test-tube and test for air-tightness. To do this, place the end of the tube in the mouth, suck out some of the air, and note whether the tip of the tongue seems to adhere to the tube. Remove the test-tube, and repeat (?). What caused the tongue to adhere in the first instance?

(3) Connect two pieces of narrow tubing to make a longer piece.

(4) Make a T-tube by connecting two pieces of narrow glass tubing at right angles to each other.

Reference for additional work. Laboratory Instruction in Glass Blowing; Baker, Journal of Chemical Education, vol. 9, p. 203, 1932.

4. Construction of a Wash-Bottle

a. Select a good cork which will fit the mouth of the largest flask and soften it in a cork-softener or by rolling it under the foot upon the floor while pressure is cautiously applied. Bore two parallel holes with the cork-borer, and smooth them by means of a rat-tail file. The **cork borer** is usually made of brass, and the edge is easily turned. Do not hold the cork against the table while boring, as the edge of the tool may be ruined. Hold the cork in the hand (or better, against a block of *soft* wood) and bore from the narrow end, with care, exactly parallel to the axis. If the cork and borer are rotated round their axes and the edge is fresh, very little force will be required. Clear the core of cork out of the cork-borer, after use, by means of the iron rod. The borer is purposely chosen so as to be smaller than the tubing. Its use thus permits the enlarging and smoothing of the hole made in the cork with the rat-tail file until a perfectly fitting bore has been made.

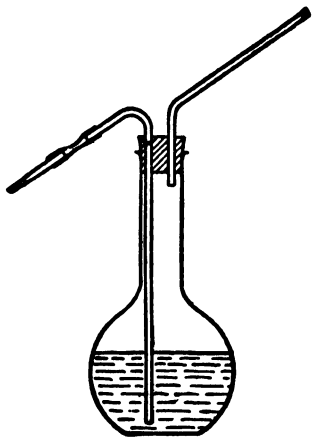


Fig. 4.

b. Bend two pieces of glass tubing as indicated in Fig. 4, fire-polish their edges and insert them in the openings in the cork. Make the nozzle by softening a piece of glass tubing in the Bunsen flame, drawing the two ends apart after removal from the flame (Fig. 1), cutting in the center with the file, and fire-polishing the rough ends. Connect the nozzle by means of a short

piece of rubber tubing. Test the apparatus to see that it is air-tight, as below.

c. Place in the flask enough water to cover the lower end of the longer tube and transfer the rubber connection to the shorter glass tube and close it with a clamp. Now, blow through the longer tube so that a few bubbles of air pass into the flask. If the apparatus is air-tight the water will rise in this tube when the mouth is withdrawn and will remain in an elevated position (?). If the water gradually sinks to its former level, the apparatus is not air-tight. Examination of the holes in the cork may show defects, which can be remedied only by boring a fresh cork more carefully. A two-hole rubber stopper may be substituted for the cork, if desired.

Before use, every piece of closed apparatus employed in all succeeding experiments must be **tested for air-tightness**, and rendered perfectly air-tight. Do not on any account employ paraffin or sealing-wax to patch defective places in a cork; use a fresh one.

Distilled water is to be used for making solutions and for rinsing glassware (why?). Common water is to be employed for all other purposes. Always keep your wash-bottle filled with distilled water and have it ready on your desk for use in later experiments.

d. Use of the Wash-Bottle. There are two ways in which the wash-bottle is commonly employed in laboratory work. In the first place, a fine jet of water may be expelled from the nozzle by blowing into the bottle through the short tube on the right (the mouth-piece). This is especially useful for washing precipitates and in filtration generally. Secondly, the bottle may be held upside down, whereupon a stream of water flows out through the mouth-piece directly into any piece of apparatus which it is desired to wash out or fill.

Why should the tube to which the nozzle is attached extend almost to the bottom of the bottle? Why should the mouth-piece reach only just beyond the stopper?

5. Use of the Simple Balance

a. By turning the screw attachment in front of balance case, release the beam and pans, allowing the beam to swing. Observe the excursions made by the pointer. Divide by two the total divisions covered by the pointer in one full swing, and count off

from either end of the swing the divisions which this number designates, thus finding the position of the true zero point. The beam must swing freely during the observation: the zero is never to be read with the beam at rest.

This observed zero point may lie a little to the right or to the left of the marked zero. Note down its distance, in scale divisions, from the marked zero. If it lies to the right, prefix to the number of divisions the minus (—) sign; if to the left, the plus (+) sign. The zero of any one balance changes, and must be redetermined every time a weighing is made.

b. Place a 10 g. weight in each pan, and determine the zero as before. Add the 0.01 g. weight to the right-hand pan, and find the reading about which the pointer now oscillates. The difference in reading between this point and the last determined zero point gives the deflection due to the 0.01 g. weight. It may be used for estimating weights less than 0.01 g. Thus, suppose the 0.01 g. weight causes a deflection of 5 divisions to the left (+ 5). When some body is being weighed, if the deflection is + 1, then ⅕ of the 0.01 g., or 0.002 g., must be subtracted from the sum of the weights.

Great care must be taken in the **use of the balance and weights.** The pans of the former must be let down upon their supports when not in use and every time weights or other objects are to be added or removed. All objects to be placed upon the pans must previously be carefully cleaned and dried. Solids are placed upon a watch-glass or upon a piece of glazed paper, and never directly upon the pans. The weights must be lifted from their case by means of forceps, never by the fingers. They are usually placed on the right-hand pan, the objects to be weighed on the left.

In reckoning results, count first by the places vacant in the box, and check by counting the weights themselves. This will enable you to avoid the commonest error in weighing, namely, miscounting the weights. Finally record the weights in the note-book, and never upon loose sheets of paper, as loss of the latter will necessitate a repetition of the entire experiment.

c. Determine the weight of one or more of the following articles in your equipment: a watch-glass, an evaporating dish, a beaker. Record the weight in each case, and state the probable degree of error, with reasons.

6. Capacities of Vessels. Weighing and Density

a. Fit a burette (Fig. 5) with a short piece of rubber tubing and glass nozzle (see Exercise 4 b). The withdrawal of liquid from the

burette is regulated by a pinch clamp upon this rubber connection.

b. Support the burette upon a ring-stand by means of a clamp. Now fill the burette with distilled water, drawing off a portion to insure the complete removal of air from the rubber tubing and nozzle. The last bubble of air may be removed by turning the nozzle upward while the water is allowed to flow. Read the height of water by observing the lower side of the meniscus, or curved surface of the liquid (Fig. 6). Keep the eye as nearly as possible at the level of this surface while taking the reading (?), and estimate to tenths of a division.



FIG. 6.

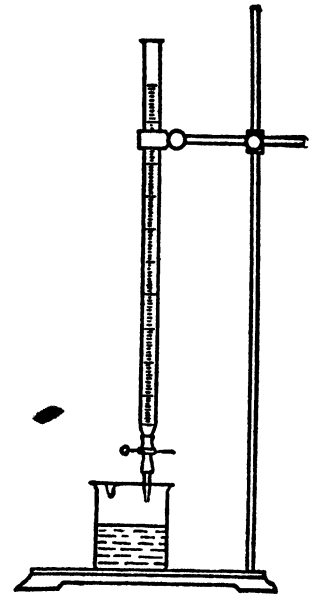


FIG. 5.

c. Clean and dry a small beaker carefully, weigh it on the balance to the nearest decigram (0.1 g.) and record the weight. In doing this, follow faithfully any additional directions as to the proper use of a balance given you by your instructor, and write down these directions in detail in your book for future reference.

Allow 10–20 c.c. of the distilled water to run from the burette into the beaker, read the new level of the water, and ascertain the volume taken by subtracting the readings. Weigh the beaker again and ascertain the weight of the water by subtraction. Take the temperature of the water by means of the thermometer. Calculate from your figures the weight of 1 c.c. of the water. The result is the density of water at the recorded temperature.

d. Weigh an evaporating dish (dry) on the balance to the nearest decigram (0.1 g.) and record the weight.

Place in the dish about 10 g. of pieces of roll sulphur (no particles or dust of sulphur), and weigh once more. Record the weight. The difference (?) is the exact weight of the sulphur actually taken.

Place in the graduated cylinder exactly 20 c.c. of water. Incline the cylinder and allow the sulphur gently to slide into the water in the cylinder. Read and record the total volume. The increase (?) is the volume of the sulphur. Calculate from your data the weight of 1 c.c. of sulphur (?). This is the density of the sulphur.

e. Record the specific properties of sulphur which you have observed, namely: color (?), crystalline or not (?), brittle or malleable (?), density (?), soluble in water or not (?).

Is measuring volume by burette or by cylinder more accurate and why?

f. Measure by means of the cylinder, roughly, the volumes of water your flasks and beakers hold, and record the figures. Fill the vessels to a convenient height for use, and not to the brim.

7. Density Determinations and Experimental Errors

a. In Exercise 6 c you determined the **density of water** by means of your burette. Is your result an exact value, or is it only a rough approximation? Refer to the temperature of the water recorded in your notes, and now compare your experimental result with that indicated by the curve* in Fig. 7. Suppose that your error in each reading of the meniscus in the burette might amount to 0.03 c.c., could that account for the whole difference between your value and the accepted one? What other errors might occur in the course of the experiment, and what are their respective magnitudes? Are you sure that your burette is correctly graduated?

It is no use doing a quantitative experiment unless you know to what extent you can trust your results. Errors may be divided into three classes: (*a*) **errors of apparatus** (such as an incorrect burette or a faulty balance), (*b*) **errors of manipulation** (such as reading the meniscus wrong through looking at an angle), and (*c*) **errors of method** (such as the impossibility of reading a burette more accurately than 0.01 c.c.). The first class of errors you can diminish by standardizing or refining your apparatus, the second by working carefully and gaining the necessary technique, the third by modifying the method.

b. Suppose you wanted to obtain a really accurate value for the **density of benzene** at 25°. It would be futile to use the burette method. You employ instead a *pycnometer*, of the form illustrated

*Note carefully that in this curve the *volume occupied by* 1 *gram of water* is plotted against *temperature*. How can you transform these *specific volume* values to *densities*?

in Fig. 8. After cleaning, drying and weighing the pycnometer, fill it with distilled water, suspend it in a bath regulated to constant temperature at 25° and then by means of a piece of filter-paper at *A* draw the meniscus down on the other side exactly to the mark *B*. Removing the pycnometer from the bath, carefully

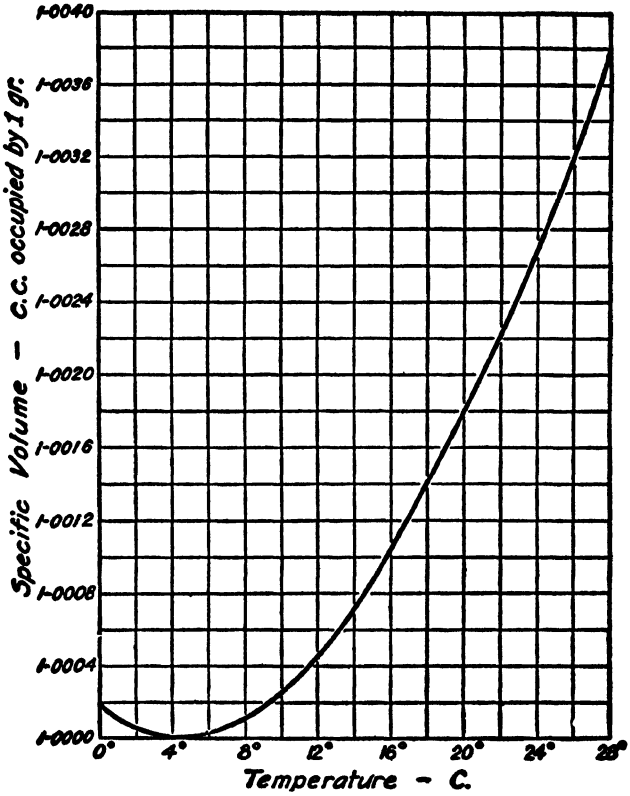


FIG. 7. Change of Volume of Water with Temperature.

dry its outside surface, and reweigh it. After that repeat the determination, using benzene instead of water. Subtracting the weight of the empty pycnometer from the two subsequent weights gives the weights of water and of benzene respectively required to fill the instrument to the mark *B* at 25°. The ratio of these weights, wt. of benzene/wt. of water, is the *specific gravity* of benzene referred to water at 25°. To get the *absolute density* (grams

in 1 c.c.) of benzene at 25°, multiply the specific gravity, as obtained above, by the density of water at that temperature (0.9971, see Fig. 7).

c. If the substance you have to investigate is a **solid insoluble in water**, such as chalk (calcium carbonate [**C** 573; **I** 725], *not* blackboard crayon, which is mainly calcium sulphate [**C** 577; **I** 731]), you use a pycnometer of a different type, shown in Fig. 9. As before, find the weight of this (*a*) when empty, and (*b*) when filled with water to the mark *C*. Next powder up some of the solid very finely in a mortar, introduce a few c.c. of the powder into the empty and

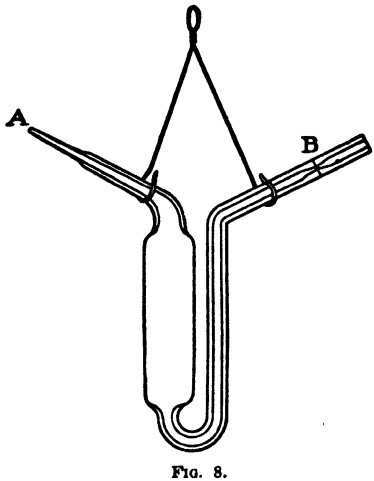


Fig. 8.

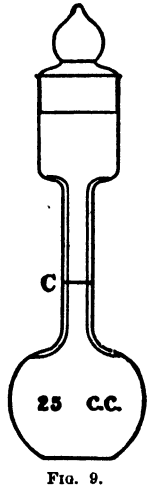


Fig. 9.

dry pycnometer, and weigh again, (*c*). Finally, add water to this, agitate to remove all air-bubbles, adjust to the mark at constant temperature, and reweigh, (*d*). Suppose your results were as follows:

(*a*)	Wt. of pycnometer empty		= 10.035 g.
(*b*)	" " "	+ water	= 30.100 g.
(*c*)	" " "	+ chalk	= 25.210 g.
(*d*)	" " "	+ chalk + water	= 39.680 g.

How can you derive the **density of chalk** from the above data? Subtracting (*a*) from (*b*) tells you that the pycnometer holds 20.065 g. of water. Subtracting (*a*) from (*c*) tells you that 15.175 g. of chalk were used in the determination. Subtracting (*c*)

from (*d*) shows that the pycnometer will hold only 14.470 g. of water when this amount of chalk is present. 15.175 g. of chalk, therefore, *displace* or *occupy the same space* as 20.065 — 14.470 = 5.595 g. of water. The specific gravity of chalk is consequently 15.175/5.595, or 2.712. If all the fillings were done at 25°, the density of chalk would be 2.712 × 0.9971, or 2.704.

The final result, you will notice, stops at the third place of decimals, although by actual multiplication of the two previous values we could obtain a much more formidable answer. **One of the most important things for you to know in all quantitative work and in all numerical problems is when to stop figuring. Never take any calculation beyond your probable limits of error.**

How can you tell when to stop? To simplify matters, let us assume that you do not want to ascertain more than the order of magnitude of your inaccuracy. Suppose we return to the experiment on chalk described above. You were obviously weighing to the nearest 0.005 of a gram. Your probable error in the difference between any two weighings therefore approximates this weight as a limit. To get the sp. gr. of the chalk, you found the quotient of two such differences, 15.175 and 5.595 g. The percentage error will be greater in the smaller of these values, namely about one-tenth of one per cent. Unless any other error involved in your work is proportionately greater,* this is the limit to which you are entitled to take your final answer. You do not, therefore, write down the sp. gr. as 2.7122, since this would infer that your value was accurate to less than 1 part in 20,000! Neither do you stop at 2.71, since that would not be giving yourself a square deal for the trouble you have taken in the experimental work.

One place beyond the last figure of which you are absolutely certain is always ample. When you multiply or divide two values, the lower limit of accuracy prevails.

* For very accurate work, correction must be made for the weight of air displaced in each observation, and the degree of accuracy to which the meniscus can be adjusted in the pycnometer must also be established.

CHAPTER III

CHARACTERISTICS OF CHEMICAL CHANGE

8. Mixtures and Compounds

a. The Properties of Iron. Place about 0.5 c.c. of iron powder on a piece of paper. Examine it (?). Draw one pole of a magnet across the lower surface of the paper, noting the behavior of the iron (?).

Transfer half the iron to a dry test-tube, add 2 c.c. of carbon disulphide [CARE! Inflammable! Do not handle near a flame], and shake. Fold a filter-paper once, and then again at right angles to the straight edge. Open the paper as a cone, with a triple layer of paper on one side and a single layer on the other, and place it in a glass funnel (Fig. 10). Place the funnel in one ring of the iron stand, place the watch-glass below the end of the stem, and pour the contents of the test-tube on to the paper. When the liquid has run through, open up the paper, so that the remaining liquid may evaporate. Place the watch-glass in a draft, away from all flames, where its contents may evaporate also. While evaporation is going on, proceed with the operations described in the following paragraphs. When the paper and watch-glass are dry, examine the residue on the paper (?) and draw the pole of the magnet across the lower surface of the paper (?). Examine the watch-glass (?). Is iron soluble in carbon disulphide (?).



Fig. 10.

Place the other half of the iron in a test-tube, add a few drops of hydrochloric acid (?) and note the odor [C 711; I 981] or absence of odor.

Record the properties of iron, namely: color (?), effect of magnet (?), solubility in carbon disulphide (?), effect of hydrochloric acid (?) and odor of the evolved gas (?).

b. The Properties of Sulphur. Pulverize some sulphur in the mortar, and repeat **a**, using about 1 c.c. of sulphur instead of the iron. Record the properties of sulphur, additional to those already recorded in Exercise 6 **e**, namely: effect of magnet (?), soluble in carbon disulphide or not (?), shape of crystals (sketch ?), effect of hydrochloric acid (?) and odor or not (?).

c. On a piece of paper weigh out 3 g. of pulverized sulphur and 5.5 g. of iron powder. Mix the powders as well as possible. Can the particles of each substance still be recognized or not? Pass the magnet underneath the paper (?). Place half the mixture in a test-tube, add 3–4 c.c. of carbon disulphide, shake, and filter into the watch-glass. When the liquid has evaporated, examine the residues on the paper and in the watch-glass (?). Why does the result show that the material was a mixture and not a chemical compound?

d. Place the remainder of the mixture from **c** in a dry test-tube, hold the test-tube by means of a test-tube holder or a piece of folded paper, and heat it gently in the Bunsen flame until all action has ceased (?). When the test-tube is cold, place the lower end in the mortar, cover with a towel, and use the pestle to strike through the towel so as to break the test-tube (?). Continue in this way until the material which was in the tube, separated as far as possible from attached fragments of glass, can be placed in another test-tube. Add 2 c.c. of carbon disulphide, filter, and allow the filtrate to evaporate as before. Examine the material on the filter to ascertain whether it is iron (?). If it is in the least affected by the magnet, too little sulphur was used. Does the filtrate yield all the sulphur used (?), or any sulphur? Place the material on the filter in a test-tube, add a few drops of hydrochloric acid (odor? [C 314; I 464]). Did either iron or sulphur give this odor?

Record the properties of the new substance, ferrous sulphide, namely: color (?), effect of magnet (?), solubility in carbon disulphide (?), effect of hydrochloric acid (?) and odor of the evolved gas (?). What was the effect of heating the mixture? Is the product an element or a compound, or a mixture? Write a condensed statement [C 12; I 14] for the reaction.

What variety of chemical change is illustrated in this experiment? What evidence of a chemical change is afforded besides the formation of a new substance?

e. Gunpowder. Gunpowder is made from saltpeter (potassium nitrate), roll sulphur, and charcoal. Take specimens of these three substances, and examine them with respect to properties which can be used for recognition and separation, such as appearance and solubility in various solvents. Try the solubility of each in distilled water and in carbon disulphide, using in the latter case thoroughly dried (why?) test-tubes. Do not judge of solubility by the eye, but filter the mixture, catch a few drops of the liquid on a watch-glass, allow to evaporate, and see whether there is any greater stain on the glass than the pure solvent would itself have left. The taste (?) of the saltpeter is a characteristic property.

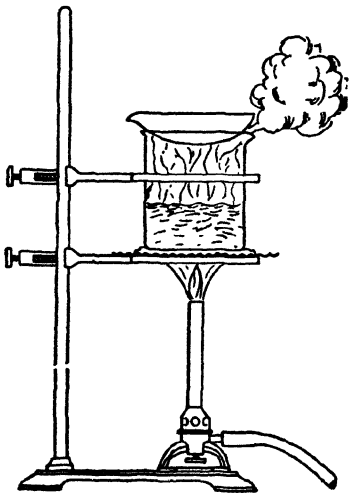


FIG. 11.

Now place about 1 g. of gunpowder in a large test-tube and add 5–10 c.c. of water. Shake well (after closing the test-tube with the thumb), warm gently, and filter. Evaporate the filtrate upon a water bath or over a beaker of boiling water (Fig. 11). Describe and name the residue (?). Dry (why?) the filter paper and its black contents over a radiator or in a drying oven. Shake the dried product with cold carbon disulphide in a dry test-tube, filter, and allow the filtrate to evaporate [HOOD] spontaneously (?). What remains upon the paper?

Did any chemical change occur during the manufacture of gunpowder? Are the three substances components or constituents of gunpowder? Is the latter a mixture or a compound?

Why are the ingredients of gunpowder pulverized so finely and mixed so intimately?

9. Changes in Metals Heated in Air

a. Take about 5 meters of copper wire (No. 30), wind it into a coil around a pencil, and place the coil in the porcelain crucible, which has previously been weighed (uncovered). Weigh the whole on the balance, recording the weights as in **5 b.** Place the crucible

(uncovered) in the pipe-stem triangle (Fig. 12) and heat, at first gently and then with the full Bunsen flame, for fifteen minutes. Now lower the flame to permit the crucible to cool gradually, and finally remove it. Weigh the crucible when cold (?). To what is the difference in weight due?

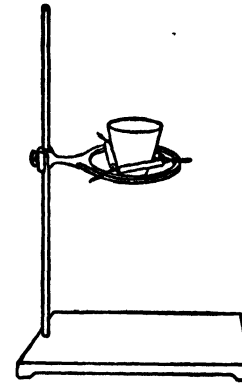


Fig. 12.

Examine the coil (?), and bend the remains of the wire (?). Name the product, and make a condensed statement of the change. Record the specific properties of the copper and of the product, namely: color (?), appearance (lustrous or otherwise?), pliability or brittleness (?) of each.

Why is the result of this experiment not reliable quantitatively? Devise improvements in the method of carrying out the experiment which would enable you to obtain a quantitative result [C 28; I 44].

What happens when copper is heated in the absence of air or oxygen? Devise a means of proving that the presence of air or oxygen is necessary for any chemical change to occur.

b. Fold up about 10 cm. square of tin-foil and place it in the porcelain crucible. Weigh the whole on the balance and proceed as in **a.** Stir the tin occasionally with a short piece of iron wire, but be careful to keep all the material in the crucible. Describe what you observe (?).

Name the product (?) and make a condensed statement of the change. Record the specific properties of the tin and of the product, namely, color (?), appearance (?), pliability (?) of each, and melting point of tin [C 541; I 679] (?).

Is the result of this experiment quantitatively reliable? If not, why not? Suggest methods of improvement.

c. Slow Oxidation of Metals. Devise a way of showing that air loses a part of its substance (not, *e.g.*, that the iron gets heavier, but that the air diminishes in amount) when moist iron powder rusts, and try it. Submit your arrangement to the instructor for criticism before using it.

10. Composition and Formula of Nickel Sulphide

a. Weigh a crucible (without cover) to the nearest centigram. Place *about* 2 g. of reduced nickel (do not attempt to take this amount exactly) in the crucible and weigh again. Put about 2 g. of sulphur in the crucible, stir the contents, and place the crucible on the pipe-stem triangle. Set the cover on the crucible, and heat gently so long as sulphur vapor burns [HOOD] at the chink between the crucible and cover. Heat strongly for 1–2 minutes. Then hold the flame against the upper portion of the crucible, so that every part receives a thorough heating. Allow the crucible to cool. When it is cold (not before) remove the cover and weigh. Tabulate the results as follows:

Wt. of crucible + nickel	g.
Wt. of crucible empty	g.
Wt. of nickel taken	g.
Wt. of crucible + nickel sulphide	g.
Wt. of crucible + nickel	g.
Wt. of sulphur combined	g.
Wt. of crucible + nickel sulphide	g
Wt. of crucible empty	g
Wt. of nickel sulphide	g.

b. Calculate the percentage composition:

$$\text{Per cent sulphur} = \frac{\text{wt. of sulphur} \times 100}{\text{wt. of nickel sulphide}} = ?$$

$$\text{Per cent nickel} = \frac{\text{wt. of nickel} \times 100}{\text{wt. of nickel sulphide}} = ?$$

c. Find the empirical formula of nickel sulphide. To do this, first obtain the atomic weights of nickel and sulphur from the table [C and I, inside back cover].

$$\text{Wt. of sulphur} \div \text{at. wt. of sulphur} = ? \text{ (factor 1)}$$
$$\text{Wt. of nickel} \div \text{at. wt. of nickel} = ? \text{ (factor 2)}$$

The combining proportion of sulphur to nickel found in the experiment is therefore:

$$\frac{\text{S} \times \text{factor 1}}{\text{Ni} \times \text{factor 2}}$$

Divide above and below by the smaller of the two factors (?). What is the formula?

d. Make the equation for the union of sulphur and nickel to form nickel sulphide.

Reference for additional work. The Combining Ratio of Copper and Sulphur; Stone, Journal of Chemical Education, 5, 1129, 1928.

11. Composition and Formula of an Oxide of a Metal

On account of the difficulties attending the making, the collecting, or the weighing of most oxides formed by direct union, the following indirect method is suggested. It consists in converting a known weight of a metal into the nitrate of the metal by the action of nitric acid, and obtaining the oxide by decomposition of this salt. Make no equations for these actions.

a. Composition of an Oxide of Tin. Weigh the crucible (without cover) (?). Place in it *about* 1 g. of tin-foil (do not try to take exactly 1 g.) and weigh again (?). Record the weights in tabular form (see below). Place the crucible on the pipe-stem triangle [HOOD] and add 5 c.c. of concentrated nitric acid. In doing this, pour the acid over every part of the metal. Hold the burner in the hand and warm the crucible with a very small flame, stopping for a moment if there is a tendency for any particles to be spattered out of the vessel. When the contents are dry, use a larger flame and heat for ten minutes. Weigh when cold (?).

The nitric acid oxidizes the tin. A brown gas (nitrogen tetroxide [C 414; I 584]) and water are given off during the process. Be careful not to get any of the issuing gases into the lungs (?).

Wt. of crucible + tin	g.
Wt. of crucible, empty	g.
Wt. of tin taken	g.
Wt. of crucible + oxide of tin	g.
Wt. of crucible + tin	g.
Wt. of oxygen	g.
Wt. of crucible + oxide of tin	g.
Wt. of crucible, empty	g.
Wt. of oxide of tin	g.

Calculate from your results the percentage composition of the oxide of tin.

Find the atomic weight of tin in the table [C and I, inside back cover] and calculate the formula of the oxide.

b. Composition of an Oxide of Iron. Weigh an evaporating dish of medium size, place in it about 1 g. (12 inches) of pure iron wire, and weigh again. Cover the dish with a watch-glass, convex side downward, and add 10 c.c. of pure dilute nitric acid [HOOD]. Set the dish, covered, on a water bath (see Fig. 11, p. 18) until the iron has dissolved, adding a few drops of concentrated nitric acid if any of the wire remains unattacked (Instructions). Then rinse any material on the cover-glass carefully into the dish with the help of your wash-bottle and evaporate the solution to dryness. When the residue is dry, place the dish on a clay triangle supported on the ring-stand and heat carefully with a burner held in the hand as long as any red fumes are given off. During this process, and especially at first, great care and patience must be exercised, as too rapid heating may cause solid particles of the product to be thrown from the vessel. If any crackling noise is observed, remove the burner at once. When, after final strong heating of every part of the material, red fumes or other evidence of continued change can no longer be perceived, allow the dish and contents (?) to cool, and then weigh. To make sure that the decomposition was complete, heat once more, cool, and weigh again. This precaution is always necessary in experiments of this nature.

The difference of the weights of the metal and of the oxide gives the weight of oxygen combined with the known weight of iron.

Assuming the atomic weights of iron and of oxygen to be 55.84 and 16, respectively, calculate from your data the formula of the oxide of iron. What is the name of this oxide? What other oxides of iron are known?

Calculate the percentage composition of the oxide of iron represented by your formula and compare this percentage with the actual composition you obtain from your work.

12. Law of Definite Proportions *

a. Clean and dry two evaporating dishes, taking care to remove paper labels which may be pasted upon them. Weigh each dish

* Before beginning, always endeavor to ascertain the object of each experiment. By this means confused work and much waste of time will often be avoided, and significant facts to be observed and recorded will not escape

[Quant., balance], and record the results as shown below. Place in each some sodium bicarbonate (baking soda), in the one about 1 g. and in the other about 2 g., and weigh again. Treat both alike, as follows: Dissolve the solid in pure dilute hydrochloric acid, adding little by little and covering with a watch-glass between successive additions to avoid loss by spurting. When the solid has wholly dissolved, wash the watch-glass over the dish, and evaporate [Hood] the contents of the latter on the water bath, or on a beaker of boiling water (Fig. 11). (Avoid loss of time by borrowing a second Bunsen burner and gas tubing temporarily from the storeroom.) Allow the dishes to become perfectly cold, and weigh. To make sure that the drying was complete, heat once more for half an hour and, when cold, weigh again. This precaution is taken in all experiments of this kind. The product is common salt.

	Dish No. 1.	Dish No. 2.
Wt. of dish + sodium bicarbonate		
Wt. of dish (empty)		
Wt. of sodium bicarbonate		
Wt. of dish + salt		
Wt. of dish (empty)		
Wt. of salt		
Ratio (x)		

b. Calculate the proportion of bicarbonate taken to salt produced thus:

$$\text{Wt. of bicarbonate: Wt. of salt} :: 1 : x.$$

Compare the two values of x found from the two differing quantities of the bicarbonate and interpret.

What physical property of hydrochloric acid permits use of an excess of the acid without damage to the result? What form of statement of the law of definite proportions is verified directly by this experiment?

Reference for additional work. An Experiment to Illustrate the Law of Multiple Proportions; Bailar, Journal of Chemical Education, 6, 1759, 1929.

notice. Consider, first, carefully the title, as it will usually indicate the object of the exercise. If the title is not at once fully understood, look up the topic in a reference book before going further. Here, if in doubt, refer to **C 26; I 42.**

CHAPTER IV

OXYGEN

13. Oxygen — Preliminary Experiments

a. Place about 1 c.c. of mercuric oxide (properties ?) in a dry hard glass test-tube, and fasten the tube in an inclined position in the clamp on the iron stand. Heat at first gently and then strongly with the Bunsen flame. Introduce a wooden splint, glowing at one end, into the tube until the spark almost reaches the oxide (?). What gas is liberated? What physical and chemical properties do you observe the gas to have? After removing from the flame, examine the residue on the side of the tube (?). How did it get there? Name the variety of chemical change illustrated [C 20; I 22].

Beginning with this chapter, include in your notes **balanced equations** [C 60; I 79] for all the chemical changes you observe. When no change is observed, do not attempt to give an equation until otherwise instructed. In the present experiments the formulæ of the materials used will have to be sought in the text-book. The formulæ of the products will also be sought in the book after the physical properties of the product and the evolution or non-evolution of oxygen have been noted and an indication of what to seek for has thus been obtained.

b. Repeat **a**, using 1 c.c. of silicon dioxide (sand), and answer the same questions.

c. Repeat **a**, using 1 c.c. of potassium chlorate (properties ?), and answer the same questions.

d. Repeat **a**, using 1 c.c. of manganese dioxide (properties ?), having previously dried this by warming it in the porcelain crucible.* Answer the same questions.

e. Place in a dry test-tube about 0.5 c.c. of sodium peroxide.

*Be sure to dry your sample of manganese dioxide before heating it strongly, since most commercial samples contain an appreciable quantity of water, and the condensation of drops on the side is liable to crack the tube. Unless you have a very good blast-lamp, you will probably be unable to note any evolution of oxygen from this substance [C 68; I 88].

Detach the nozzle from your wash-bottle (Exercise 4 b), fill it with water, hold your finger over the open end, and release for a moment to add one or two drops of water to the peroxide (?). Test this gas with a glowing splinter of wood (?). Afterwards, dip a piece of red litmus paper in the residual liquid (?). A blue color indicates the presence of an alkali [C 135; I 181].

14. Oxygen — Preparation and Properties

a. Take 4 g. of finely-powdered potassium chlorate. Mix it thoroughly on paper with 2 g. of manganese dioxide. (To avoid accidents, the latter should be carefully heated in an open dish, with stirring, to free it from carbonaceous matter before use.*) Place about one-tenth of the mixture in a dry test-tube, heat it, and test the gas with a glowing splinter of wood (?).

How does the temperature at which this mixture gives off oxygen compare with the temperature at which each substance would yield oxygen if heated alone (Exercise 13)? Why is the manganese dioxide used? What is a substance which behaves in this way called?

Devise a way of showing that the manganese dioxide, used as in **a**, remains unchanged after the action, and that it is the potassium chlorate that loses its oxygen, and try it (?). Consult the instructor in regard to the details of your plan before executing it.

b. Place the remainder of the mixture made up for **a** in the hard glass test-tube provided with a stopper and glass tube (Exercise 3 d), and test for air-tightness. Moisten the end of a piece of narrow rubber tubing (12 in. long) and slip it over the end of the tube. Clamp the tube in a horizontal position (Fig. 13). Fill the pneumatic trough with water so as to cover the shelf or other support. Fill 3 wide-mouth bottles with water, cover them with glass plates, and invert them, one on the shelf, and the other two in the trough. Use a small Bunsen flame to heat the tube and collect the first bubbles of gas in a test-tube filled with water and inverted over the exit of the rubber tube. Test this gas with a glowing splinter (?). What is this gas, and where did it come from? Now

*Ferric oxide may be conveniently substituted for manganese dioxide as a catalyst in this experiment. It is more efficient, it does not need to be dried in advance, and its distinctive color is a safeguard against accidents. A careless student might easily use powdered charcoal instead of manganese dioxide, and the results would be very distressing (?).

fill the bottles one by one, covering each when full with a glass plate, and setting it mouth upwards on the table. During the operation, regulate the flame with great care so that the gas comes off in a steady, but not too rapid stream of bubbles. If the gas begins to come too fast, move the flame promptly to another part of the material and lower it slightly. The glass must not become hot enough to tinge the Bunsen flame yellow. Do not remove the flame, however, at any time, without first taking the rubber tube out of the water (Why?). After the third bottle is filled, remove

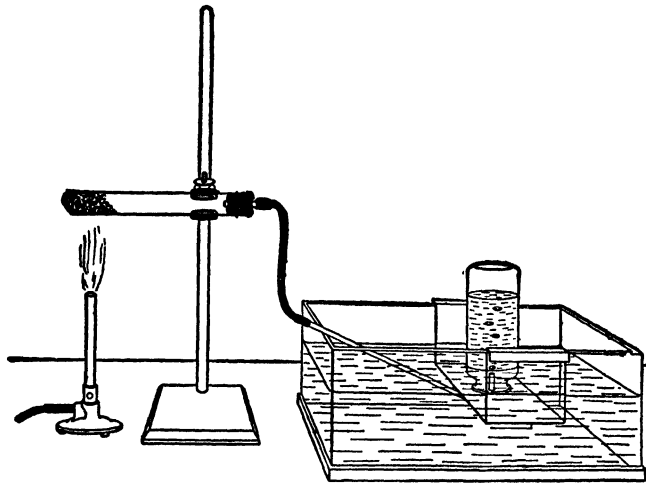


FIG. 18.

the rubber tube from the water, let the test-tube cool and then fill it with water and set it aside.

c. Place in the deflagrating spoon a little sulphur. Heat the sulphur until it catches fire. Observe the flame for a moment (?). Then lower the spoon into one bottle of oxygen (?), keeping the bottle as far as possible covered with the glass plate. How does the flame differ from that in air, and why? Is it finally extinguished? If so, why? Cautiously note the odor of the gas in the bottle. Then add a little water to the bottle, close the mouth with the plate and shake (?). Test the water with blue litmus paper or solution [**C 99; I 135**] (?). Make lists of such physical and chemical properties of the product as you have observed (?).

d. Empty the spoon (burning off any sulphur left upon it), let it cool, and place on it a little red phosphorus. Set fire to the latter, observe the flame (?) and lower the spoon into the second bottle as before (?).

Proceed now as in **c**. Test with blue litmus (?). Why does the product form a smoke, instead of remaining in the spoon?

If yellow phosphorus is used, it must always be cut under water and handled with forceps. Great care must be taken not to touch it with the hand, as it catches fire easily, and causes very severe burns. Red phosphorus is safer, and should be employed if available.

Before using the spoon in **e**, heat it strongly in the Bunsen flame to burn up all the phosphorus.

e. Lay a splinter of charcoal in the bowl of the deflagrating spoon, hold in the Bunsen flame until the charcoal begins to glow, and lower the spoon into the third bottle as before (?).

Proceed now as in **c**. Is any decided result obtained with litmus [C 443; I 624]? Add some limewater (calcium hydroxide) and shake again [C 443; I 625] (?).

f. Record the physical properties of oxygen: color (?), odor (?), solubility in water (?). Record the chemical properties: glowing splint (?), sulphur (?), phosphorus (?), charcoal (?). What is the difference between a chemical and a physical property?

Write balanced equations for the reactions that occur in **a**, **c**, **d**, and **e**.

g. Repeat **a**, substituting other oxides for manganese dioxide, in order to obtain an approximate indication as to the relative efficiency of each as a catalyst for the decomposition of potassium chlorate. Suggested oxides for this experiment are ferric oxide, chromic oxide, aluminium oxide, cupric oxide and silicon dioxide.

Is oxygen the only gas evolved when potassium chlorate is heated in the presence of the above oxides, or can you detect any other gaseous product? What properties of this second product enable you to distinguish it from oxygen (refer to Exercise 40)?

15. Weight of a Liter of Oxygen*

a. Place 6 g. of pulverized manganese dioxide (or ferric oxide, see footnote to preceding exercise) in a porcelain crucible (un-

*This experiment may be deferred, if desired, so as to form an immediate practical introduction to Exercise 26.

covered) and heat it with the full Bunsen flame for 5–6 minutes to drive off all moisture (see Exercise 13 **d**). During this time, stir it occasionally with an iron wire.

While this is going on, insert an obtuse-angled tube in a one-hole rubber stopper which fits into a hard glass test-tube (as in Fig. 3, Exercise 3 **d**). Fill a 2-liter bottle with water, invert it in the pneumatic trough, and arrange the apparatus as in Fig. 13, Exercise 14.

Take 7 g. of dry, pulverized potassium chlorate and, when the manganese dioxide has cooled, mix the two substances thoroughly on a sheet of paper. Place the mixture in the hard glass test-tube. Weigh on the balance the test-tube and contents to the nearest centigram and record the result according to the table on p. 29 (?). Replace the stopper in the test-tube, and test for air-tightness (see Exercise 3 **d**).

b. Heat the contents of the test-tube, beginning at the end next to the stopper (be careful not to burn the stopper (?)), and collect all the gas in the bottle. Regulate the heating so that you can at all times count the bubbles. Continue heating until gas ceases to come off, and then remove the rubber tube from the water and allow the test-tube to cool.

Lower the bottle of gas in the trough until, when the eye is on a level with the water, the latter is seen to be at the same height inside and outside. To accomplish this and the next operation, it may be necessary to incline the bottle slightly, taking great care not to let any bubbles of gas escape. While the bottle is in this position, close it with a cork or glass plate and set it mouth upwards upon the table. Read and record the temperature of the water (?) and also the barometric pressure (?). If, at this point, there is not time to complete the experiment, the test-tube may be corked tightly and put away (upright) along with the 2-liter bottle and its contents.

c. Weigh on the balance the test-tube and contents, and record the weight (?). To measure the volume of gas collected in the bottle, fill the 500 c.c. graduated cylinder to the top of the graduation, note down the volume of water, and pour the latter into the bottle. Repeat until the bottle is filled level with the mouth, and record in the table the total volume of water used.

Wt. of test-tube and contents before heating	g.
Wt. of test-tube and contents after heating	g.
Wt. of Oxygen	g.
Volume of Oxygen	c.c.
Temperature	C.
Barometric Pressure	mm.
Tension of aqueous vapor **[Appendix I, p. 191]**	mm.
Barometric pressure, corrected [C 86; I 118]	mm.

d. Reduce the observed volume of oxygen from the observed temperature and pressure to 0° and 760 mm. **[C 85; I 112-6]**.

e. From this reduced volume, and the weight, calculate the weight of 1 c.c. (the density) of oxygen.

$$\frac{\text{Wt. of oxygen}}{\text{vol. at 0° and 760 mm.}} = x = \text{wt. of 1 c.c.} = \text{density.}$$

In this experiment, the following points are of particular importance. (*a*) Dry your manganese dioxide or ferric oxide carefully before you mix it with the potassium chlorate; otherwise when you weigh the mixture you will weigh some water as well, and the loss of weight on heating will not be due entirely to evolution of oxygen. (*b*) Use a hard glass test-tube; one of soft glass will fuse and spoil the experiment. (*c*) Make absolutely sure the apparatus is air-tight, using the method recommended in the text. If there is a leak, it will probably be between the test-tube and its cork, since the weight of the rubber tube introduces a strain at this point. Try to arrange matters so that your cork, without being in any sense too small, fits well into the test-tube. (*d*) Heat very cautiously at first or the oxygen evolved will contain small particles ("smoke") of potassium chlorate. Why will this spoil results? (*e*) Be careful not to have a suck-back of water from the trough into the test-tube at any stage of the experiment. How can you avoid this? (*f*) Do not lose any gas from the bottle in equalizing the levels inside and outside. Why is this step necessary?

What errors can you locate in this experiment, as you have carried it out? Subdivide them into errors of apparatus, manipulation and method, as directed in Exercise 7 **a**, and estimate the approximate magnitude of each. What is the probable error in your final result? How would you modify your experimental procedure so as to diminish this error?

Reference for additional work. An Experiment to show the Catalytic Action of Manganese Dioxide on the Decomposition of Potassium Chloride and the Measurement of the Products of the Reaction; Mackenzie, Journal of Chemical Education, 9, 1111, 1932.

CHAPTER V

HYDROGEN. VALENCE

16. Hydrogen — Preliminary Experiments

a. Place in separate test-tubes a few small pieces of each of the metals: iron (nails), zinc (granulated), tin (granulated), copper (shavings), aluminium (wire), magnesium (ribbon). Pour from the graduated cylinder 25 c.c. of pure concentrated hydrochloric acid [C 99; I 135] into a small beaker, add an equal volume of water, and mix. Add 5 c.c. of this diluted acid to the contents of each tube.

Observe each case critically, and tabulate the results. Is there bubbling? If not, then warm gently (?). If the eye detects the formation of a gas or vapor, smell the contents of the tube (?). For comparison, take 5 c.c. of the acid by itself in a test-tube, smell it (?), warm and smell again (?). If heating seems to produce a gas, remember that it may be the acid, or steam, and not hydrogen. The formation of hydrogen may be inferred from continued bubbling when heat is not being furnished, and may be proved by the slight explosion which follows when a light is brought to the mouth of the tube. If the gas is coming slowly, hinder its escape into the air by partially closing the mouth of the tube and let it accumulate before applying the light.

Number the metals in your notes in the order of their apparent activity (most active = No. 1). Do the bubbles appear on the side of the glass tube or on the metal? Why do they appear on one and not on the other? Record the properties of hydrogen you have observed: Gas, liquid or solid (?), soluble in water or not (?), colored (?), odor or not (?), unites with oxygen from the air or not (?) and if so when cold or hot (?).

b. Add some zinc dust, made into a paste with water, to another 5 c.c. of the diluted acid (?). To what is the difference, if any, between the apparent activity of zinc dust and granulated zinc due? After the action has ceased, filter the solution and evaporate

1 c.c. of it on a watch-glass to dryness as follows [Hood] (?). Place the watch-glass on a beaker half filled with water, set the beaker on the wire gauze and boil the water (Fig. 11, p. 18). If the water in the beaker runs too low, because of evaporation, the vessel may crack. Add more hot water, if necessary. What is the solid left on the watch-glass by evaporation?

c. Place one small piece of *pure* zinc into each of two test-tubes and add 5 c.c. of the diluted acid to both tubes. If little or no action takes place in the cold, try upon one tube the effect of heating (?). Try the effect of putting a platinum wire in contact with the zinc in the second tube (?). Notice where the hydrogen appears to come from, and explain [**C 100; I 137**]. Withdraw the platinum wire, add two drops of cupric sulphate solution and shake until the blue color is removed from the solution (?). Is the zinc still silvery? What is the substance upon the zinc [**C 228; I 330**], and what effect does it produce upon the apparent activity of this metal? Explain (?).

d. The same metals displace hydrogen from all acids. To illustrate, place a few pieces of zinc (gran.) in each of two test-tubes and add to one 5 c.c. of dilute sulphuric acid (?) and to the other 5 c.c. of acetic acid (?).

e. Now compare (?) the behavior of concentrated sulphuric acid with that of the diluted acid used in **d**, by placing some zinc (gran.) in a test-tube and adding enough of the concentrated acid barely to cover the metal (?). After noticing the effect in the cold (?), apply heat (?). Odor (?). What products are formed [**C 336; I 137**]?

f. Fill a test-tube with distilled water, and invert it in a large beaker half filled with water. Place a small piece of calcium * in the water and hold the test-tube over it (?). After the action has ceased, apply a light to the gas in the tube (?). Examine the water in the beaker (?) and test it with red litmus paper (?).

Write balanced equations for the reactions that occur in **a, d, e** and **f.**

If Exercise **16 a** could be carried out under standard conditions, you would obtain reactions varying in speed according to the position of the metal in the activity series [**C 107; I 146**]. But standard conditions are

*Calcium (metal) is most easily broken into small pieces by fixing it in a vise and using a chisel and hammer.

difficult to arrange, and your results will be affected by such factors as (*a*) the rate at which the acid can remove surface oxides, (*b*) the state of division of the metal, and (*c*) the nature of the impurities in the metal. For a more detailed discussion of this last effect, see [C 671; I 921].

The hydrogen obtained from zinc and *dilute* sulphuric acid in 16 d may not be odorless, owing to non-metallic impurities in the zinc (compare Exercise 8 a). Do not allow this, however, to cause you to miss the different and very characteristic odor encountered in 16 e, where *concentrated* sulphuric acid is used.

Evidently the nature and the concentration of the acid are just as important in regulating the rate of hydrogen evolution as the nature of the metal. You will see exactly why this is so later [C 215, 249; I 307, 366].

Exercise the greatest care in all experiments involving hydrogen. Never, under any circumstances, attempt to light a jet of the gas until you have made absolutely sure that all air has been swept out of your apparatus. To be positive upon this point, you must have obtained a sample in a test-tube which burns quite quietly (Exercise 17). If you have any doubt at all, consult your laboratory assistant. *An explosion during a hydrogen preparation is a sign of criminal carelessness,* and you will get no sympathy however badly you may be hurt.

17. Hydrogen — Preparation and Properties

a. Fit a 90 c.c. gas-generating bottle with a 2-hole stopper, a thistle-tube, and an L-tube (Fig. 14). Slip a narrow rubber tube over the end of the last, and attach to it a glass delivery tube. Place in the bottle about 20 g. of zinc (gran.). Test the apparatus to see whether it is air-tight. To do this, pour into the bottle through the thistle-tube enough water to cover the zinc. The lower end of the thistle-tube must also be under the water. Now blow through the rubber tube a little air, so as to force the water up the stem of the thistle-tube, and immediately compress the rubber tube with the thumb and forefinger. If the water does not remain stationary, but gradually falls, there is a leak which must be remedied [Instructor].

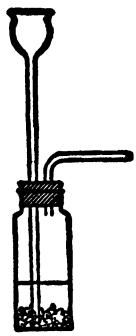


Fig. 14.

Add concentrated sulphuric acid slowly through the thistle-tube until brisk bubbling sets in. Do not add more than one-fourth of the volume of the water already in the bottle. Place the end of the delivery tube in the trough. Collect a test-tube full of gas. Close the tube with the thumb and carry it mouth downwards to a distant flame. (Under no circumstances bring a flame near the generator!) Re-

move the thumb and, still holding the tube mouth downwards, sĕt fire to the gas. Repeat this test until a sample is obtained which burns quietly. Why does it not do so at first? Do not at any time attempt to light the gas at the exit tube until a quietly-burning sample is obtained (?).

b. Collect over water two bottles of the gas. Cover the first with a glass plate and set it mouth downwards on the table (?). Light a taper, raise this bottle (still mouth downwards), insert the burning taper (?) almost to the bottom of the bottle (?) and then withdraw it slowly (?). What happens to the gas? What happens to the taper on insertion and on withdrawal? Explain.

c. Set the other bottle mouth upwards on the table and leave it open for one minute. Then bring a lighted taper to the mouth (?). Explain.

d. Fill a test-tube over water with the gas. Bring this tube, mouth downwards, mouth to mouth with a test-tube filled with air, and keep them in this position for 3 minutes. Then apply a light first to the lower (?) and then to the upper tube (?). What fact about the molecules of gases is shown by this experiment?

e. Remove the glass delivery tube, and connect a glass nozzle with the exit tube of the generating flask. Press the mouth of the nozzle close against the side of a cold, dry beaker. If moisture is deposited from the unlighted gas (what is its source?), fill a **U**-tube with calcium chloride [**C** 121-2; **I** 141] and connect it between the exit tube and the nozzle. Does the gas now deposit moisture upon a beaker? If not, ascertain very carefully that the issuing gas is not explosive (see test in **a**), and set fire to it. What is the color of the flame? Does the color change, and, if so, why? Hold a cold, dry, inverted beaker over the flame. What is deposited on the beaker? Why did we use dried hydrogen for this experiment? Keep the apparatus in operation for Experiment **18**, unless a Kipp's apparatus is available or hydrogen is furnished in the laboratory.

Turn off the gas supplying the Bunsen burner, remove the burner, and push a glass nozzle tightly into the end of the gas tubing. Turn on a gentle stream of gas and set fire to it. Hold a cold, dry beaker over this flame (?). What inference in regard to illuminating-gas do you draw?

f. Record the observed physical properties of hydrogen, namely:

color (?), odor (?), density compared with air (?); also any chemical properties observed (?).

g. Another Method of Obtaining Hydrogen. Fit a test-tube with a one-hole cork and delivery tube (Fig. 5). Pulverize about 2 g. of sodium hydroxide, mix it intimately in the mortar with about 3 g. of zinc dust, and place the mixture in the test-tube. Insert the cork and delivery tube, test the apparatus for air-tightness (Exercise 3 **d**) and clamp the tube in a horizontal position (why?). Heat the mixture and collect the gas (?) over water (Fig. 13) in a test-tube. If the tube should crack [CAUTION] cease heating at once. To learn whether the gas is combustible, when the test-tube is full of the gas, close the mouth with the thumb and carry the tube, mouth downward, to a flame (?).

Assuming that the residue in the tube is sodium zincate [**C 104; I 140**], write a balanced equation for the reaction.

18. Reduction by Means of Hydrogen

a. [Two students working together.] Fit a hard glass tube, 25–30 cm. long and open at both ends, with perforated corks and short glass tubes (Fig. 15). Support it on the ring-stand by means of a clamp grasping it close to one end. Dry 1–2 g. of ferric oxide by heating in a porcelain crucible. Put the oxide into the porcelain boat and place the latter in the hard glass tube near the end remote from the clamp (why?), but not so near that the subsequent heating will char the cork. Insert the corks with their tubes. Connect the tube nearest to the boat with a Kipp's apparatus and drying bottle (Fig. 25, Exercise 68 **a**) delivering dry hydrogen, or with the laboratory supply of the gas, or with the apparatus furnishing dry hydrogen used in 17 **e**.

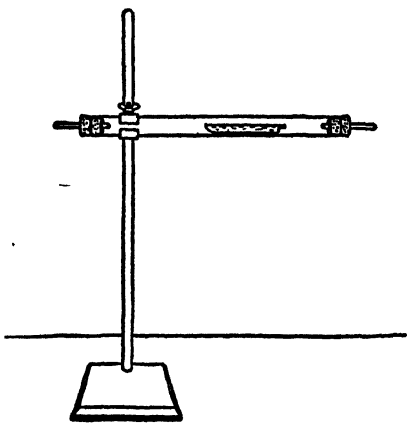


FIG. 15.

b. Test the issuing gas to see that it is not explosive (see 17 **a**)

and repeat the test every time the apparatus is opened. Now heat the boat and contents, at first gently by waving the flame under the tube, and later strongly until the material is red-hot. Observe the effect upon the ferric oxide [C 106; I 147] (?). Does anything condense in the cooler end of the tube?

What is the action of steam upon heated iron [C 98; I 134]?

c. Repeat the above experiment, using freshly heated aluminium oxide in place of ferric oxide, and otherwise following the directions exactly (?). If no effect is noticed after an oxide has been at a red heat for three minutes, absence of action may be inferred. How do you account for the result obtained with aluminium oxide? Which oxides are reducible by hydrogen [C 107; I 147]?

19. Composition of a Chloride

a. [Quant.] Weigh an evaporating-dish of medium size, place in it about 2 g. of pure zinc, and weigh again (?). Tabulate the results as shown below. Add a little diluted (1 water : 2 acid) pure, concentrated hydrochloric acid and cover with a watch-glass, convex side downward. If the action is very slow, the tip of a platinum wire may be placed in contact with the zinc [C 100; I 137]. Maintain a brisk action by further additions of concentrated hydrochloric acid in very small amounts at a time. Final excess of the acid should be avoided, as time will be lost in the subsequent evaporation. When the metal is completely dissolved, rinse the cover-glass and platinum wire carefully into the porcelain dish and remove them. Allow the solution to evaporate as far as possible on the water bath or on a beaker of boiling water [Hood]. Now place the dish on the ring-stand, and, using a small Bunsen flame, allow the syrup-like solution to evaporate slowly to dryness. Then heat the white mass to the point at which it has completely melted and no further. The best way to achieve this with the minimum rise in temperature is to let the Bunsen flame play on the surface from above. Overheating must be avoided, because the product is volatile, giving white fumes, at high temperatures. The moment the dish has so far cooled that the hand can be borne upon the bottom, wipe the dish carefully and weigh it. The substance absorbs moisture greedily from the atmosphere, hence expedition is required in cooling and weighing if accurate results are to

be obtained. To insure accuracy, the melting, cooling, and weighing should be repeated, and the lower result taken as correct.

Wt. of dish + zinc..... g.
Wt. of dish, empty..... g.
Wt. of zinc..... g.
Wt. of dish + zinc chloride..... g.
Wt. of dish + zinc..... g.
Wt. of chlorine..... g.

b. From your results, calculate the equivalent weight of zinc, *i.e.*, the weight combining with 35.46 parts of chlorine (?).

Assuming the atomic weights of zinc (65.37) and of chlorine (35.46), calculate from your results the formula of zinc chloride.

Express the whole action of hydrochloric acid on zinc in symbols by making the equation in accordance with these conclusions. Which of the factors in the equation have you determined experimentally, and which not? What law do we use in assuming that the undetermined factors are correct?

20. Valence of a Metal by Displacement

a. Weigh (balance) to the nearest centigram exactly 2 meters of magnesium ribbon (?). Calculate what length will weigh exactly 0.2 g. and cut off this length for use. (These strips may be cut previously by instructor or assistant to save time.) Record all data as shown under **d.** Roll the ribbon into a spiral coil somewhat smaller than the inside diameter of the mouth of the 250 c.c. bottle.

Place in the trough about 5 cm. depth of water. Measure into the bottle 30 c.c. of hydrochloric acid (conc.), and fill it up to the brim with water. Cover it with a glass plate and invert it in the trough, leaving the glass plate in the trough with the bottle inverted upon it. If any air gets into the bottle, lift out the bottle with the plate firmly pressed against the mouth, fill it up with water and try again. Wash your hands immediately, if you have to immerse them in the dilute acid at any stage of the experiment.

Place the spiral of magnesium ribbon in the trough and slip the mouth of the bottle over it, setting the bottle down firmly on the bottom of the trough. Now tilt the bottle as little as possible, and slide a piece of thin copper wire under one rim (?).

b. When the magnesium has all disappeared and evolution of

hydrogen has ceased, adjust the bottle in the trough (adding water, if necessary) until, on looking horizontally, with the eye at the level of the water, the levels inside and outside are seen to be the same. Incline the bottle, if necessary, to accomplish this. While the bottle is in this position, cover the mouth with a glass plate (or insert a cork), and set the bottle with its contents mouth upwards upon the table.

Read the temperature of the water (?). Ascertain also the height of the barometer (?).

If there is not time to proceed with the operations directed below, the bottle and its contents may be set aside until the following period.

c. The weight of this hydrogen is to be found, not by weighing it directly, but by measuring its volume, and using the fact that 22.4 liters of the dry hydrogen at 0° and 760 mm. weigh 2 g. (see **d**).

d. Use a graduated cylinder (500 c.c.) to fill the bottle once more to the top with water, noting carefully the volume of water required (?).

The hydrogen was mixed with water vapor. Find the tension of the aqueous vapor at the temperature recorded in **a** [Appendix I] (?) and subtract this from the barometric height (?).

Reduce the volume of hydrogen, from the observed temperature and barometric pressure as just corrected, to 0° and 760 mm. (?).

Calculate the weight of this hydrogen. 22.4 liters weigh 2 g.

Weight of metal taken	**g.**
Volume of hydrogen obtained	c.c.
Temperature	°
Barometric height	mm.
Tension of aqueous vapor	mm.
Pressure of hydrogen, corrected	mm.
Volume of hydrogen at 0° and 760 mm.	c.c.
Weight of this hydrogen	**g.**

e. The atomic weight of magnesium is 24.3. State just what experimental fact this sentence represents (?).

f. The weight of hydrogen found in **d** was that displaced by the weight of magnesium taken in **a**. Calculate from these data the weight of hydrogen which would be displaced by one atomic weight (24.3 g.) of magnesium (?). What is the nearest whole

number of atomic weights of hydrogen (1 g.) contained in this weight of hydrogen? This whole number is the valence of magnesium. Mg therefore displaces xH. Supply the value you have found for x (?).

g. How many formula weights of hydrochloric acid (HCl) are required to furnish this amount of hydrogen? Now make the complete equation, supplying the values you have found for x, y and z:

$$Mg + yHCl \rightarrow MgCl_z + \tfrac{1}{2}xH_2.$$

Why do you write $\frac{1}{2}xH_2$ in this equation, rather than xH? You did not measure the weight of Cl_z, or determine the value of z. What law of chemistry enables you to supply this value without measurement?

h. Some members of the class may be instructed to use aluminium wire, following otherwise all the directions given for magnesium. The final results obtained from the two metals should be contrasted and explained in the classroom.

CHAPTER VI

WATER. ATOMIC AND MOLECULAR WEIGHTS

21. Water — Physical Properties

a. Put on a clean watch-glass 3–4 drops of distilled water, place the watch-glass on a 100 c.c. beaker half filled with water, and set the beaker on the wire gauze and boil (see Fig. 11, Exercise 8 **e**). Put on a second clean watch-glass 3–4 drops of tap-water and evaporate in the same way. Compare the two watch-glasses when dry (?). Do the specimens of water contain any non-volatile impurities?

b. Distillation. Bend a 30 cm. piece of glass tubing twice at right angles (see Fig. 16) and fire-polish the ends. Connect with it, by means of a short piece of rubber tubing, a second glass tube also about 30 cm. long. Set up a flask and a test-tube immersed in cold water in a large beaker as in Fig. 16. Place in the flask about 100 c.c. of water, some marble chips (to prevent "bumping"), and a few drops of potassium permanganate solution. Boil the water and examine the distillate (in the test-tube).

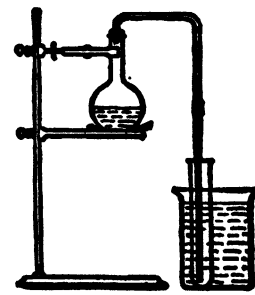


FIG. 16.

In what way has the water been purified by the distillation? Is potassium permanganate volatile under these conditions? If it had been, would distillation have purified the water?

c. Add one drop of phenolphthalein solution to some tap-water (?). Add one drop of ammonium hydroxide solution to some tap-water, and then add one drop of phenolphthalein (?).

d. Using a glass rod, add *a single drop* of ammonium hydroxide solution to 100 c.c. of tap-water. Clean and use the same apparatus as in **b**, place this water in the flask, and distill as before. In each of six clean test-tubes place, from a glass rod, one drop

of phenolphthalein solution, and use these test-tubes one after another to catch the distillate. Change the test-tube when 10 c.c. of liquid has come over until the six have been used. While changing, remove the flame and uncork the flask each time. If the water in the beaker becomes warm, change it for cold water.

What evidence is there that ammonia passes over with the steam? Which portion of the distillate contained the most ammonia and which the least? Cool the residue in the flask in running water, pour 10 c.c. of it into a clean test-tube and add one drop of phenolphthalein (?). Can water be purified from a volatile impurity?

It should be noted that glass of poor quality is appreciably soluble in boiling water, and the resultant solution gives a reaction with phenolphthalein [C 526; I 662]. It is not probable, however, that this complication will cause you to obtain a positive test with your residue on addition of the indicator. Any decided coloration is much more likely to be due to your adding far too large a quantity of ammonium hydroxide at the start. The action of water on glass, nevertheless, may be made evident in a very short time by *increasing the surface*. Take a little glass wool in a test-tube, shake up with distilled water, and test with phenolphthalein. What do you observe?

e. Devise *two* methods for purifying water from clay suspended in it, and submit to your instructor for approval. Which would be the easier method of purification for water containing clay as an impurity? Would this method apply if salt were also present?

f. Name the common states in which water exists (?). How many states of water are known altogether [C 125; I 170]?

22. Union with Oxides

a. Place a pinch of cupric oxide in a test-tube and wash it by shaking with a little distilled water and pouring off the liquid. Add more water and shake again. Test this latter solution with litmus paper (?). At the same time test a sample of the water with litmus paper and compare the tints. Repeat with calcium oxide (?), barium oxide (?).

b. Recall the behavior of acid-forming oxides examined in 14. Some oxides do not interact readily with water (which?). These oxides which do interact may be divided, according to the natures of the products they give, into two classes. What are those classes,

and which oxides belong to each? What are the two classes of elements whose oxides belong to the two groups, respectively [C 135; I 181]?

23. Hydrates

a. Place a clear crystal of washing soda on a watch-glass and set it aside. At the beginning of the next laboratory period, examine it and record any changes you observe (?).

b. Place a clear crystal of washing soda in a dry test-tube and heat the crystal gently (?). What condenses on the walls of the tube? Explain the result of a [C 137; I 183].

c. Place in different dry test-tubes about 1 c.c. each of potassium chlorate, aluminium sulphate, potassium sulphate, barium chloride, and gypsum (calcium sulphate). Clamp one tube in a horizontal position, to prevent any condensed water from running back and causing the tube to crack, and heat the substance in it with the tip of a small flame until no further change occurs (?). Repeat with each tube. Record the results in tabular form as follows:

Substance Heated	What Change	Amount of Condensed Water	Appearance of Final Residue	Substance was a Hydrate or not

The amount of the water condensed may be "great," "small," or "a trace." Do not, however, let the appearance of a *trace* of moisture deceive you into reporting a hydrate. Even an empty "dry" test-tube will show a slight film of condensed vapor on its cooler part, when heated in the flame. Every powder which has been exposed to the air at all will give *some* moisture (see Exercise 13 **d** and *adsorption* [C 488; I 770]). You must, therefore, before recording any result, decide whether the amount of water obtained is significant.

Are all crystalline substances hydrates? Illustrate. Write an equation for the change in each case in which water was given off.

d. Take about 1 c.c. of copper sulphate (blue-stone) crystals. Note their color (?). Pulverize them finely in the mortar and note the color again (?). Explain.

Place the powder in a dry test-tube, clamp the latter in a horizontal position, heat the substance as in **c** and tabulate the results as before.

Leave the tube in the clamp until it is cold, and then set it upright (?). If there is not enough water condensed to permit some to run down to the solid residue, add two drops (?). Note the color. What substance is formed? Feel the bottom of the test-tube. What evidence is there of a chemical change?

Write an equation, showing the action to be reversible [C 136; I 182]. Record its color under the formula of each substance.

e. Take in a test-tube about 5 c.c. of commercial, concentrated sulphuric acid, place in it a crystal of blue vitriol and let the materials stand for an hour, or more (?) [C 219; I 316]. Now heat the contents of the tube to the boiling-point of the acid [HOOD], holding the test-tube in a test-tube holder, keeping it far from the clothing, and taking care that none of the contents spirt out upon the hands or face [CAUTION: Sulphuric acid burns are very painful. Note 6, p. 2]. After the contents of the tube have settled, pour off the clear liquid into another tube. On the following day, examine the little, shining particles on the sides of the tube. What is their color and condition? Of what are they composed [C 625; I 860]?

Are the compounds (such as cupric sulphate) which, in presence of water, yield crystalline hydrates, amorphous or crystalline in its absence? What is the true significance of the crystalline condition [C 42; I 64]?

f. Take a clean match and, after dipping it in a solution of cobalt chloride, write upon a piece of white paper. After the writing is dry, warm the paper gently by waving it above a Bunsen flame (?). Now, breathe repeatedly upon the writing (?). Write equations for the actions that have occurred [C 718; I 988].

24. Quantitative Measurement of Water of Hydration

a. Clean and dry the porcelain crucible and weigh it to the nearest centigram (0.01 g.). Then place in it *about* 2 g. of pulverized gypsum (do not try to take this exact amount) and weigh again as before. Record the weights in tabular form as shown below.

Support the crucible (open) on the pipe-stem triangle, placed on the ring of the iron stand (Fig. 12, Exercise 9), so that the bottom of the crucible is a short distance above the inner cone of the Bunsen flame. Lower the flame and heat at first very gently

to avoid loss of any particles by sudden splitting of the crystals. Later use the full flame.

After 15 minutes' heating, allow the crucible to cool and weigh to the nearest centigram. Replace the crucible on the triangle, heat again for 5 minutes, allow to cool and weigh again. If the weight is less than before, heat once more, and repeat until two successive weighings are identical, *i.e.*, "heat to constant weight."

Wt. of crucible + gypsum	g.
Wt. of crucible empty	g.
Wt. of gypsum taken	g.
Wt. of crucible + gypsum	g.
Wt. after last heating	g.
Wt. of water of hydration	g.

$$\text{Per cent of water} = \frac{\text{wt. of water} \times 100}{\text{wt. of gypsum}} = ?.$$

When the percentage obtained by all who have done the experiment are compared, what law of chemistry is found to be illustrated? Record the average of the values found by all for the percentage.

b. Some members of the class may be directed to use barium chloride crystals, following otherwise all the directions given for gypsum.

c. From the data obtained in **a** or **b**, calculate the formula of the hydrate used. Proceed as follows:

Wt. of water ÷ Formula wt. $= x$. $(H_2O = 18)$

Wt. of residue ÷ Formula wt. $= y$. $(CaSO_4 = 136)$

$$\frac{\text{Wt. of water}}{\text{Wt. of calcium sulphate}} = \frac{x(H_2O)}{y(CaSO_4)}.$$

Divide both x and y by the smaller factor. This will give (within experimental error) the smallest whole numbers which are in the same ratio. Then substitute these whole numbers for x and y in $yCaSO_4,xH_2O$.

In **b**, the formula is $yBaCl_2,xH_2O$, and the values of x and y are found in the same way.

25. Density of Air

a. Fit a round-bottomed 300 c.c. flask [Storeroom] with a rubber stopper through which passes a short glass tube. To the latter attach a short rubber tube with an open screw clip [Storeroom]. Place 40 to 50 c.c. of water in the flask, and boil the water vigorously for about ten minutes to expel the air from the flask. Lower the flame, close the clip, and then *at once* remove the flame.

Wt. of flask and water + air	g.
Wt. of flask and water	g.
Wt. of air	g.
Vol. of flask (total)	c.c.
Vol. of water (remaining)	c.c.
Vol. of air	c.c.
Barometric height (corr.)	mm.
Tension of aqueous vapor	mm.
Pressure of air, corrected	mm.
Temperature	°

Wipe the flask, and weigh it when cold (?). Open the clip slowly to admit air, and weigh again (?). Record the weights (see above). The increase is the weight of the air which entered. To learn its volume, measure in the graduated cylinder the volume of the water remaining (?), and then the total volume required to fill the flask to the bottom of the stopper (?). Record also the temperature (?) and barometric pressure (corr.) (?) and subtract from the latter the tension of the aqueous vapor in the flask (Appendix I).

Reduce the volume of the air from the observed temperature and barometric pressure (as corrected), to 0° and 760 mm. [C 85; I 112–6].

From the weight of the air, and its volume at 0° and 760 mm., calculate the density (wt. of 1 c.c.) of the air (?), and also the weights of 1 liter (?), and of 22.4 liters (?).

b. By admitting other gases, instead of air, this method may be used for measuring the densities of gases which are insoluble in water. Name several gases to which this method could be applied (?).

By calculating from the results the weights of 22.4 liters, the molecular weights of such gases are obtained.

26. Atomic and Molecular Weights

a. From the data obtained in Exercise 15, calculate the weight at 0° and 760 mm. of 22.4 liters (the molecular weight) of oxygen. Compare the molecular weight found with the atomic weight of oxygen (?). How many atoms of oxygen are there in one molecule of the element?

b. The weights of one G.M.V. (22.4 liters at 0° and 760 mm.) of several compounds of carbon are as follows:

	Weight 22.4 l.	*Weight carbon*	*Weight hydrogen*	*Weight oxygen*	*Formula*
Carbon monoxide	28.00	12.0	....	16	....
Carbon dioxide	44.00	12.0	....	32	....
Methane	16.032	12.0	4.032	....	....
Ethylene	28.032	24.0	4.032	....	....
Glycerine (vapor)	92.064	36.0	8.064	48	....

What value should you select for the atomic weight of carbon [C 153; I 199]? Assuming the atomic weights to be, for hydrogen H = 1.008, for oxygen O = 16, and for carbon C = ?, write the formula for each of the five compounds.

c. The density (wt. of 1 c.c. at 0° and 760 mm.) of ethylene chloride is 0.00433 g., what is the molecular weight [C 149; I 209]?

d. Using the weights of 22.4 l. given above, find the weights of 1 c.c. (the densities) of methane and carbon dioxide.

e. How do the densities of the five substances mentioned in **b** compare with that of air [C 199; I 282]?

27. Atomic Weight of a Metal

a. [Quant.] Take two pieces of pure lead of different sizes, about 0.4 g. and 0.6 g. respectively. Clean and dry two evaporating dishes, and weigh each with care. Place one piece of lead in each and weigh again. Be careful in your notes and in your handling to distinguish the dishes from one another.

Dilute 7 c.c. of pure, concentrated nitric acid with 14 c.c. of water in the graduated cylinder and add to the lead in each dish 10 c.c. of the diluted acid. Cover each dish with a watch-glass, convex side downward, and set upon the water bath. An extra Bunsen burner [Storeroom] and two beakers containing water may be used as baths, as in Fig. 11 [Hood]. A match inserted between

the dish and the beaker permits escape of the steam and prevents the possible upsetting of the dish by the vapor. When the action is over, and the lead has entirely disappeared, rinse the lower surface of each watch-glass into the dish by means of a little water from the wash-bottle. Then add to the contents of each 5 c.c. of pure dilute hydrochloric acid. This causes the precipitation of a compound of lead and chlorine whose weight is next to be determined. To accomplish this, the water and other substances present (except the lead chloride) being all volatile, the mixture is dried by evaporation on a water bath. When the contents of the dishes are dry, moisten the contents of each with 2 c.c. of pure, concentrated hydrochloric acid and dry once more. Now transfer the dishes, one at a time, to the clay triangle supported on the ring-stand, and heat the whole residue cautiously with a small Bunsen flame. Watch it narrowly and do not allow any of it to melt. When the dishes are cold, weigh each again with care. The increase in weight over the previous value in each case gives the weight of chlorine which has combined with the known weight of lead.

	Dish No. 1.	Dish No. 2.
Wt. of dish with lead		
Wt. of dish, empty		
Wt. of lead		
Wt. of dish with lead chloride		
Wt. of dish with lead		
Wt. of chlorine		

	Dish No. 1.	Dish No. 2.
Wt. of lead		
Wt. of chlorine		
Wt. of lead chloride		

	No. 1.	No. 2.
Per cent lead (x)		
Per cent chlorine (x')		

Calculate from each of the two sets of data the percentage of lead (x) and of chlorine (x') in lead chloride:

Wt. of lead used: Wt. of lead chloride :: x : 100.
Wt. of chlorine found: Wt. of lead chloride :: x' : 100.

Compare the results of the two measurements and interpret (?). From the mean of your two results, calculate the equivalent weight **[C 122; I 155]** of lead.

b. To secure almost ideal results, two pieces of pure silver foil of about 0.5 g. and 0.6 g. should be substituted for the lead in **10 a.** Record the weights as shown above.

Dilute 5 c.c. of concentrated nitric acid with 5 c.c. of distilled water in the graduated cylinder and add to the silver in each dish 5 c.c. of the diluted acid. When the action is over, and the cover-glasses have been rinsed, as in **a**, add 2 c.c. of pure, dilute hydrochloric acid to the contents of each dish. This causes precipitation of a compound of silver and chlorine. Evaporate the liquids to dryness [HOOD] and heat the residues at once until signs of melting are seen. Weigh each dish. The increase in weight over the previous value in each case gives the amount of chlorine which has combined with the known weight of silver.

Calculate from each of the two sets of data the percentages of silver (x) and of chlorine (x') in silver chloride:

Wt. of silver used: Wt. of silver chloride :: x : 100.
Wt. of chlorine found: Wt. of silver chloride :: x' : 100.

Compare the results of the two measurements and interpret (?). From the mean of your two results, calculate the equivalent weight [C 122; I 155] of silver.

Before cleaning the dishes, transfer the silver chloride to the bottle for silver waste.

c. Dulong and Petit's Law. According to Dulong and Petit [C 40; I 58], if the atomic weight of an element is multiplied by its specific heat in the solid form, the product is a number which lies between 6 and 6.8.

Take the values of such equivalent weights as you have found experimentally, and multiply each by the corresponding specific heat (Pb 0.031; Ag 0.054). If the result is about 6.4, the atomic weight is the same as the equivalent weight. If not, multiply the equivalent weight by the smallest integer which will bring the final product within the limits 6 to 6.8. The integer used is the valence of the element, and the product of the equivalent weight and the valence is the atomic weight. Show the working in your notes and give a list of the atomic weights and valences found.

28. Multiple Proportions

a. [Two students working together.] Fit a hard glass tube with corks through which pass short pieces of narrow glass tubing (Fig. 15, p. 34). Fix the tube in a clamp upon the ring-stand, attaching the clamp close to one end so that the rubber covering of the clamp may be away from the central part which is to be heated. Make sure that the apparatus is air-tight. Dry some pulverized cupric oxide by heating it in a hard glass test-tube. Weigh two clean, dry, porcelain boats, and place in one about 1.5 g. of the cupric oxide and in the other 2.5 g. or more of cuprous oxide * [Instructor] and weigh each again. In recording the weights and in handling the boats be careful to distinguish the one from the other. Place the boats in the hard glass tube, so that the points of the boats touch in the center of the tube. Connect the end nearest to the cuprous oxide with a source of dry hydrogen (Kipp's apparatus and drying-bottle, or laboratory supply; see Exercise 18).

b. Pass a gentle stream of hydrogen through the apparatus until a test (?) shows that the air has all been displaced. Reduce (why?) the speed of the gas until the bubbles in the washing-bottle can easily be counted. Now heat the boats moderately, beginning with that containing the cuprous oxide. What collects in the cooler end of the tube? Where does it come from? When the action, which requires 10–15 minutes, is finished, allow the boats to cool in a stream of hydrogen. Weigh the boats and contents (?), taking care not to interchange them. To ascertain whether the action is complete, heat the boats once more in hydrogen, cool, and weigh again.

c. Determine by difference the weights of oxygen and copper in each case, and calculate from the data how much copper is combined with 8 parts of oxygen in each of the two oxides. What is the ratio of the two values of copper? Show that the result illustrates the law of multiple proportions.

Assuming 16 and 63.6 to be the atomic weights of oxygen and of copper, respectively, calculate from the data the formula of each oxide. Construct the equations representing the action of hydrogen upon each oxide.

* Pure cuprous oxide can be kept successfully if sealed up in small bottles, which are not opened until needed.

CHAPTER VII

SOLUTION

29. Solvents and Solubility

a. Take two large crystals of cupric sulphate of equal size and yet of such size that each can be slipped into a test-tube. Provide two dry test-tubes with corks to fit. Pulverize one of the crystals very finely in the mortar so that no large particles are visible. Place the powder in one test-tube and the crystal in the other. Add from the graduated cylinder 20 c.c. of water to each. Cork the tubes quickly, note the time on a watch (?), and shake the tubes gently. When the powder has all dissolved, note the time again (?). Estimate the fraction of the original crystal which remains in the other tube, then continue shaking it until it also has dissolved, and note the time again (?). Compare the total times required to dissolve each (?). Why does pulverization make this difference in the rate of solution? To save time, in what form should you use a substance to be dissolved?

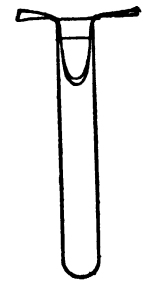


FIG. 17.

b. Take again two nearly equal-sized, but much smaller crystals of cupric sulphate. Fill two test-tubes with water. Put one of the crystals into one of the tubes. Why does it fall to the bottom? Place the other crystal in the second tube (Fig. 17), so that it rests on a narrow strip of ordinary paper and is only just covered by the water. Set both tubes upright in the rack. How long does each crystal take to dissolve? Explain the difference in time.

If you had to dissolve a large amount of material quickly, with the least expenditure of effort, how should you proceed (in answering, take the results of both **a** and **b** into account)? While the tubes are standing, go on with **c**, **d** and **e**.

c. Place 1 c.c. of powdered rosin in each of two dry test-tubes. Add to one 5 c.c. of alcohol and to the other 5 c.c. of water and shake both (?). Pour the alcoholic liquid into a large beaker full

of water and stir (?). In what ways is a suspension like a solution (?) and how does it differ?

Could you remove rosin (or varnish or a similar gum) from clothing with water? With alcohol?

d. Place a small piece of lard, half the size of a pea, in each of two test-tubes. Add 2 c.c. of water to one and 2 c.c. of carbon tetrachloride to the other and shake (?). How could you remove grease from clothing? (In removing a grease-spot, place the part flat on a piece of blotting paper, to absorb the solution, and rub the spot with a rag dipped in the solvent.)

e. Use small pieces of solid paraffin as in **d**, employing water and gasoline or benzene as solvents.

f. Take 10 c.c. of water in each of three test-tubes. To one add a single drop of alcohol and shake. Does the alcohol dissolve? Add more alcohol a few drops at a time until about 5 c.c. have been added. Has the amount added yet become greater than the water can dissolve?

To the second tube add carbon tetrachloride in the same way, and answer the same questions (?). To the third add gasoline (or benzene) in the same way, and answer the same questions.

If you had a mixture of sugar and fat on a piece of cloth, how could you remove first one and then the other component of the mixture?

g. 10 c.c. of water and 10 c.c. of ether are shaken together in a separatory funnel (?). After a few minutes, the lower layer is carefully run off. A small portion of it is warmed in a test-tube and a lighted match applied to the mouth of the tube (?). A few drops of the upper layer are added to some anhydrous copper sulphate (prepared as in Exercise 23 **d**) on a watch-glass (?). What do you observe in each case? Explain briefly.

30. Solubility and Temperature. Saturation

a. Test of Degree of Solubility. Place 1 c.c. of powdered calcium sulphate in a test-tube and shake with 10 c.c. of water for two or three minutes. Filter the mixture, catching the clear filtrate in a clean test-tube. Treat as in Exercise 21 **a** to see whether any dissolved (?). Examine 1 c.c. of powdered calcium carbonate (chalk) in the same way (?). Compare the deposits on the watch-glasses (?). Which substance is more soluble? What conclusion

should you have drawn from mere shaking with water without completing the test?

Was the solution you evaporated saturated? Was it concentrated? What is a saturated solution?

On what factors does the amount of a substance that will go into solution depend? How is the solubility usually expressed?

What are the amounts of the above salts dissolved by 100 c.c. of water at 18° [C and I, inside front cover]? In what ratio is calcium sulphate more soluble than calcium carbonate? In what ratio is calcium chloride more soluble than calcium sulphate? Which of all these substances are spoken of as "insoluble"?

b. Take about 10 c.c. of water in a test-tube, add to it not more than 1 c.c. of lead nitrate solution, and mix. Now add about 2 c.c. of dilute hydrochloric acid (?). Repeat, heating the mixture to the boiling-point before adding the hydrochloric acid (?). Examine this tube again, after the contents have cooled (?). Interpret the result. Is lead chloride an "insoluble" substance [C and I, inside front cover]? What sort of curve of solubility would this substance exhibit [C 163; I 225]? Draw a curve of this type in your notes (?).

c. Pulverize 6 g. of potassium dichromate. Describe the change in color and explain it (?). Shake the powder with 10 c.c. of water in a test-tube until the liquid is saturated. What evidence is there that a good deal dissolves?

Now warm the contents of the test-tube gently, with occasional shaking (?). Is the substance more or less soluble as the temperature rises? When all has dissolved set the tube in the rack and examine it when it has cooled (?). Describe the contents.

Warm the contents of the tube carefully (to avoid cracking the tube) once more until all has dissolved. Then hold the tube in running water to cool it rapidly (?). Describe the contents (?). Note two differences (in size of particles and in color) between the results of slow and of rapid cooling and explain each (?).

d. Take about 6 g. of sodium chloride and boil with 10 c.c. of water in a test-tube. Pour the clear liquid immediately into another test-tube. Examine this when cool (?). Is salt much less soluble in cold than in boiling water? How would its curve of solubility differ from that of potassium dichromate? Draw a curve of this type in your notes (?).

e. [Quant.] Reduce to a fine powder 10–15 g. of potassium dichromate, using the larger amount in warm weather, the smaller in cool. Prepare a saturated solution of the substance by placing it in a flask with 50 c.c. of water and shaking at intervals for ten minutes. So much of the solid must be taken that an undissolved residue remains.

Take the final temperature of the solution. Now pour the clear solution into a burette attached to the ring-stand, filling the apparatus completely to the point of the nozzle with the liquid (6 b). Read the level of the lower side of the meniscus. Weigh [Quant.] a clean, dry evaporating-dish, run into it about 20 c.c. of the solution, and weigh [Quant.] the dish and contents. Read also the level of the meniscus and note the volume of solution used. Now evaporate the weighed portion of the solution completely to dryness upon a water bath, or on a beaker of boiling water, and weigh again. Determine by difference the weights of the dry dichromate here found, and of the water in which it was dissolved. Calculate from the data the weight of dichromate which would be dissolved by 100 c.c. of water at the observed temperature (?).

From the volume of the part of the solution evaporated, and the weight of dichromate found in it, calculate also the molar solubility [C 160; I 222] of potassium dichromate at the observed temperature. Compare the results with those for potassium chromate K_2CrO_4 [C and I, inside front cover] at 18° (?).

Reference for additional work. Preparation of Crystals of Sparingly Soluble Salts; Fernelius and Detling, Journal of Chemical Education 11, 177, 1934.

31. Solution of Gases in Liquids

Half fill a 1-liter bottle with distilled water, cork, and shake vigorously till the water is saturated with air. Take the temperature of the water and also the barometric reading. Fit a small flask (100 c.c.) with a one-hole cork and delivery tube (Fig. 18) and measure its content up to the lower surface of the cork. Completely fill the whole apparatus, including the delivery tube, with the prepared water, and boil, collecting the gas in a small test-tube inverted over water. When no more gas comes over, equalize the levels of the water in the tube and trough



FIG. 18.

(or beaker) and mark the level in the tube with a thin rubber ring (cut this from a piece of rubber tubing). Measure the volume which the air occupied. Correct the volume for the aqueous vapor present only, obtaining thus the volume of the air when dry and at the observed temperature and pressure. Calculate the volume of air dissolved by 100 c.c. of water at the observed temperature and pressure (?). What proportion of its own volume of air has the water dissolved? Why is this result not quantitative?

32. Two Immiscible Solvents; Extraction

Place one small particle of iodine in each of three test-tubes and add to one water, to the second potassium iodide solution, to the third carbon disulphide, and shake each (?). If any iodine remains undissolved, pour off that solution into a clean test-tube. Now add a drop or two of carbon disulphide to the first two solutions, shake again (?), and describe carefully what seems to have happened. Deduce from this the relative solubility of iodine in the three solvents [C 175; I 243].

33. Supersaturated Solution.

Heat some anhydrous sodium sulphate strongly in a porcelain dish and allow it to cool. Take about 10 c.c. of water in each of two test-tubes. To one portion add Glauber's salt (hydrated sodium sulphate, $Na_2SO_4,10H_2O$), previously pulverized in a mortar, until, after shaking, a considerable excess remains undissolved. Saturate the other portion with the cold anhydrous sodium sulphate in the same manner. Perform the last operation rapidly, taking care not to introduce any particles of the hydrate, and do not let the solution stand before use. Now decant the two liquids into clean test-tubes, disregarding the cloudiness of one of them. Then add a little of the anhydrous substance to the solution first made and a small crystal of Glauber's salt to the contents of the second test-tube and shake both (?). After a short time, examine the contents of each again (?). Interpret the results [C 165; I 228].

34. Freezing-Points, Deliquescence, Boiling-Points

a. If pulverized ice were to be added to water until the solid no longer melted, what would be the temperature of the mixture? If ice were to be added to the aqueous solution of some substance,

until the ice no longer melted, how would the temperature differ from that of water and ice? Why does this difference exist [C 172; I 237]? Why does salt thrown upon ice cause the latter to melt?

b. Place some dry potassium carbonate (or pulverized calcium chloride) in a small beaker or crucible. Set the vessel in an evaporating dish containing water, and invert over it a larger beaker so that the edge of the latter is under the liquid. Examine the material from day to day (?). Remembering that there is moisture upon the surface of even "dry" bodies, and that therefore a solution of potassium carbonate was present with the solid, explain the change [C 168; I 233]. To what class of substances do those which deliquesce all belong? Is deliquescence a physical or a chemical change?

c. Fix a test-tube containing about 10 c.c. of water in a clamp upon the ring-stand. Suspend the thermometer from a ring by means of a thread, in such a way that the bulb is immersed in the water. Boil the water, using a small Bunsen flame, and read the temperature (?). Now add to the boiling water about 2–3 g. of dry calcium chloride and, after solution is complete, read the temperature of boiling again (?). Add another, equal portion of calcium chloride, boil, and repeat the temperature reading after the whole has dissolved (?). Explain [C 171; I 236].

Reference for additional work. Approximate Molecular Weights from the Boiling-point Rise; Rose and Billinger, Journal of Chemical Education, 7, 2715, 1930.

35. Volume Changes and Thermal Effects

a. [Quant.] Take about 25 g. of potassium carbonate and determine its weight to the nearest tenth of a gram. Assuming the specific gravity of this substance to be 2, calculate the volume of the amount you have taken (?). Place in the graduated cylinder exactly 85 c.c. of water and take its temperature. What is the sum of the volumes of the water and the carbonate, separately? Add the weighed specimen of potassium carbonate to the water, dissolve by repeated inversion of the cylinder, closing the mouth of the latter with the hand, and read the volume of the solution (?). Read also the temperature of the solution immediately (?). Is there always a change in volume, or in temperature, on dissolving two substances in one another?

What relation exists between the sign of the thermal effect when a substance is dissolved in a nearly saturated solution of the same

substance, and the change of solubility with temperature [C 222; I 322]? What do you infer in this case?

b. Examine the solubility curve of anhydrous sodium sulphate [I 229] (?). Will this compound give out or absorb heat in dissolving in water [I 323]? Verify your conclusion by trying the experiment (?).

c. Repeat a, using about 25 g. of ammonium chloride (sp. gr. 1.5). Make the same observations and answer the same questions.

CHAPTER VIII

HYDROGEN CHLORIDE AND CHLORINE. CHEMICAL EQUILIBRIUM

36. Hydrogen Chloride — Preparation

a. Place a few small crystals of each of the following chlorides (ammonium chloride NH_4Cl, calcium chloride $CaCl_2$, and potassium chloride KCl) in separate test-tubes and add a few drops of concentrated sulphuric acid to each (?). Is the material boiling (feel the bottom of the tube; sulphuric acid boils above 300°)? What word should be used to indicate the evolution of a gas from a liquid that is not boiling? Waft a little of the gas towards the nose, but do not bring the latter too near to the tube (odor)?

To learn the behavior of the gas with water vapor, blow the breath across the mouth of one of the tubes (?).

Moisten pieces of blue and of red litmus paper with water (to dissolve the gas) and place them in the mouth of one of the test-tubes (?). What chemical property does the result show the aqueous solution of the gas to possess?

Dip a glass rod in ammonium hydroxide solution. Smell the rod (?). The gas which is dissolved in and given off by this solution is ammonia (NH_3). Now insert the glass rod into the mouth of one of the test-tubes (?). The product is formed from the ammonia gas and the hydrogen chloride gas.

Light a wooden splint and plunge the flame into the test-tube (?). Does the gas burn or support combustion?

b. Of what elements is hydrogen chloride composed? What is its formula? What proportions by weight of the constituents are indicated by this formula?

Write the equations for the original actions by which, in **a**, you obtained the gas. Note that the three chlorides suggested will give, respectively, $(NH_4)HSO_4$, $CaSO_4$, and $KHSO_4$, as one of the products. Where is this one of the products? To which of the

varieties of chemical change do these actions belong [C 184; I 257]?

Write the equation for the interaction of ammonia and hydrogen chloride. To which of the four varieties of chemical change does this action belong?

c. [HOOD.] In a 250 c.c. flask (Fig. 19), fitted with dropping-funnel and L-shaped delivery tube, place about 30 g. of common salt. Use the shortest possible rubber connections here, and in **41 b** (chlorine), as rubber tubing is destroyed by these gases. Admit concentrated sulphuric acid through the funnel. Collect the gas in three dry bottles by upward displacement, allowing the tube to pass through a perforated square of paper or card so that the gas may not escape into the room. Cover, when filled, with glass plates and reserve for **37**. Place about 10 c.c. of distilled water in a test-tube, attach a nozzle to the delivery tube, and allow the gas to bubble into this for a few minutes (?). Reserve the aqueous solution also for **37**. Write equations for the two possible interactions of salt and sulphuric acid. Which of the two takes place under the above conditions?

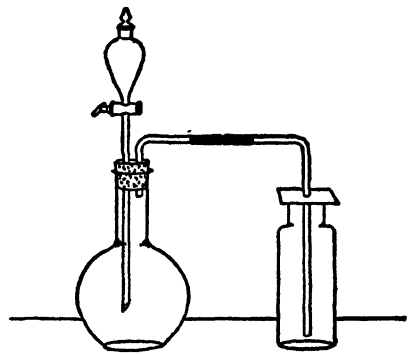


FIG. 19.

37. Properties of Hydrogen Chloride and of Hydrochloric Acid

a. Invert one of the bottles of the gas in a dish of water (?). Relate this property to that observed on blowing moist air into the gas (**36 a**). If any gas remains, what should you expect it to be? Test your conclusion experimentally (?).

b. Pour a little ammonium hydroxide solution on a strip of filter paper and plunge this into the second bottle (?). Describe the difference between these fumes and those formed by the action of moist air upon the gas (**36 a**).

c. Devise a way of proving, in a rough way, that the gas is heavier than air, and use the third bottle of gas for carrying it out.

d. Six properties of hydrogen chloride (or its solution) have now been considered. Make a list of these, and note opposite each whether it is a physical or a chemical property (?).

e. Perform the following experiments with the aqueous solution prepared in **36 c.**

(1) Test the solution with litmus paper (?).

(2) To a part add some zinc dust (?). What is the gas liberated (see Exercise **16 d**)? Make the equation for this action (?). Name three other metals which would react in a similar way with hydrogen chloride solution (?). Write equations for these three actions (?).

(3) To a part add a crystal of sodium carbonate [**C 441; I 622**] (?). What is the gas liberated (see Exercise **16 d**)? Make the equation for this action (?). Name three other substances which would react in a similar way with hydrogen chloride solution (?). Write equations for these three actions (?).

(4) Dilute the remaining portion of the acid solution with an equal volume of water and distribute it between three test-tubes. To one test-tube add a drop or two of mercurous nitrate solution (?), to the second a drop of lead nitrate solution (?), and to the third a drop of silver nitrate solution (?). After allowing the contents of each tube to settle, pour away the liquid, add water, and boil (?). Allow to cool, and note, by the appearance of crystals, which of the precipitates is soluble in hot water.

These precipitates are given, not only by hydrochloric acid, but by any chloride, and are, therefore, means of recognizing the presence of the chloride radical which is common to all chlorides.

38. Theory of the Method Used in Preparing Hydrogen Chloride

a. Make the equation for the action in **36 c**, and write the name of the substance under each formula (?).

b. Take 5 c.c. of *saturated* sodium-hydrogen sulphate solution. Add to it concentrated hydrochloric acid, a very little at a time, shaking the mixture after each addition (?). Examine the precipitate with a lens and describe the form of the particles (?). Make the equation for this action (?).

c. Compare the two equations last written. What substance, by its escape as a gas from the mixture, permitted the first action to go to completion? If this substance had remained dissolved, what

difference would this have made in the result? What substance, by its separation as a precipitate, permitted the second action to go to completion? Explain why the separation of a product permits the completion of a reaction [C 180; I 251].

39. Sodium Hydroxide

a. Recall the action of sodium on water [C 97; I 132] as seen in the class-room. Write the equation for this action, and place the name of the substance under each formula (?). To which of the four varieties of chemical change [C 184; I 258] does this action belong?

b. Take 1 c.c. of sodium hydroxide solution (2*N*) and dilute it with 10 c.c. of water. Dip a clean glass rod in the diluted liquid and taste it [Immediately rinse the mouth out with water. Taste substances only when told to do so] (?). Dip red and blue litmus paper in the solution (?). Rub the liquid between the fingers (?). Use the same solution in **c**.

c. To 1 c.c. of cupric sulphate solution add one-third of the diluted sodium hydroxide solution (?). Make the equation and attach to each formula the name of the substance (?). To which variety of chemical change does this reaction belong? Where is the other product of the reaction and how should you proceed so as to separate the precipitate and finally obtain the other product in solid form?

d. To 1 c.c. of aluminium sulphate solution add a few drops (shake between drops) of the sodium hydroxide solution (?). Make the equation and answer the same questions (?).

e. To the rest of the sodium hydroxide solution add one drop of phenolphthalein solution (?). Litmus and phenolphthalein are called indicators. How does each behave with a base [C 263; I 389]?

f. What substance have we previously found to have the same effect on phenolphthalein as has sodium hydroxide (Exercise 21 **c**)? What is its formula [C 406; I 569]?

Dilute 1 c.c. of ammonium hydroxide solution with 10 c.c. of water and try with it the tests in **b** and **d** (?).

40. Chlorine — Preparation and Properties

Caution: Chlorine gas, when breathed, has a very irritating action in the throat. For this reason the majority of the practical demonstrations

upon the properties of chlorine are better carried out in the form of lecture experiments (see Experiment 41), and only small-scale methods of preparation are here presented. If any of the gas is carelessly inhaled, breathing the vapor of alcohol (sprinkled on a handkerchief) or ammonia will be found to give relief. Perform the following experiments in a HOOD, or place where there is a good draft.

a. Fill a small trough with water. Place in a test-tube a very few crystals of potassium permanganate and add cautiously a drop or two of concentrated hydrochloric acid (make sure that you do NOT add some other acid by mistake). Leave the tube open (uncorked). What is the color of the gas?

As soon as the tube appears to be filled with the gas close the tube quickly with the cork, invert the tube instantly in the water contained in the trough and pull out the cork. Keeping the mouth under the water, shake the tube and note whether or not the gas dissolves (?).

b. Scatter about 1 c.c. of potassium permanganate crystals into the 300 c.c. beaker. Add 2–3 c.c. of concentrated hydrochloric acid and cover with a glass plate.

When the beaker has become filled with chlorine, light a taper and plunge the flame into the gas (?). The wax of the taper is composed chiefly of compounds of carbon and hydrogen. The black product is carbon (soot). What compound must have been formed? Verify your conclusion by testing the gas with ammonium hydroxide on a rod (?).

c. What did you observe that showed chlorine not to be lighter than air? What other physical properties and what chemical properties were observed?

Write the equations for the reactions that occur in **a** and **b**.

d. Prepare some strips of filter paper by dipping them in starch emulsion to which you have added one drop of potassium iodide solution [**C 284; I 272**].

Place small quantities of finely powdered manganese dioxide, potassium chlorate, lead dioxide, and pure litharge [**C 656; I 902**] in as many test-tubes, and add a little concentrated hydrochloric acid to each. Notice the color (?) and odor (?) of the gas in each case. If no action takes place in the cold, apply heat. Dip into the gas in one of the test-tubes a strip of the prepared paper (?). How do you account for the difference in the behavior of the two oxides

of lead? Do all compounds containing oxygen give free chlorine in this way? If not, state what is common to those which do and to those which do not (?).

41. Lecture Preparation of Chlorine*

a. [HOOD.] Fit up a 250 c.c. generating flask, as in Fig. 19, with a dropping-funnel and an L-shaped glass tube attached to the exit tube. Use the shortest possible rubber connections here (?). Test the apparatus to see that it is air-tight. Place in the flask about 20 g. of dry potassium permanganate, and fill the globe of the dropping-funnel with diluted, concentrated hydrochloric acid (1 water : 3 acid). [CAUTION! Do not use any other acid, by mistake.] Allow the delivery tube to dip to the bottom of a small beaker containing a little sodium hydroxide solution. Now admit the acid drop by drop, regulating the flow so that too rapid a stream of gas is not produced. The complete displacement of the air in the flask will be recognized by the color of the contents and the fact that the bubbles of pure chlorine are completely absorbed by the sodium hydroxide.

b. When the air has all been displaced, fill three dry bottles and one dry test-tube with the gas by upward displacement, observing the following precautions: Provide a piece of stiff paper or card, perforated with a hole for the reception of the delivery tube, to cover the bottles during the filling, and cover the vessels with glass plates as soon as they are full. See that the delivery tube reaches to the bottom (why?) of each vessel during the filling. Replace the end of the delivery tube in the sodium hydroxide when all the vessels have been filled. When the experiment is over, pour the contents of the generating flask into the sink in the hood, and not into one of the sinks in the open laboratory, and wash down with much water.

c. In one bottle of the gas scatter a pinch of finely powdered antimony [C 195; I 271] (?).

d. Take a clean piece of sodium and cut from it a very thin slice not more than one-half inch square (fingers and knife used in handling sodium must be dry!). Introduce this piece into a bottle

*Experiment 41 may be accomplished by careful students, but is best performed by the Instructor.

of chlorine (?) and cover at once with a glass plate. Examine after half an hour. If any of the metal remains unattacked, scrape off the white deposit and place it upon a watch-glass, and throw the sodium into the sink in the hood. Add the material on the watch-glass to that in the bottle and dissolve in 2 c.c. of water. Allow the solution to stand in a watch-glass until it dries, and examine the crystals with a lens (?).

e. Connect a glass nozzle with the illuminating-gas supply, and lower a small, burning gas-jet into the third bottle (?). Blow the breath into the bottle after withdrawing the jet (?).

f. Fill a test-tube with hydrogen from a hydrogen generator, a Kipp's apparatus, or from the laboratory supply. Bring this tube mouth to mouth with a tube of chlorine and mix the gases by repeated inversion. (Take care not to expose the mixture to direct sunlight (?).) Hold the mouth of each tube to the Bunsen flame (?). Close the mouth of one tube quickly with the thumb, add a few drops of water, shake, and test the solution with litmus paper (?).

g. Seven properties of chlorine have been considered. Make a list of these, and note which of them are physical and which chemical (?).

42. Chemical Equilibrium

a. Place 10 c.c. of water in each of two test-tubes, add to one a single drop of ammonium thiocyanate solution, and to the other a single drop of ferric chloride solution. Now mix the solutions (?). The radicals are $(NH_4)(CNS)$ and $(Fe)^{III}(Cl)^{I}_3$. Write the equation for the action which may be assumed to have occurred. Is there any evidence that interaction has taken place? Which of the four is the colored substance? Use the mixture for **b**.

b. When no precipitate is formed, is an action like the above complete? To answer this question, divide the mixture from **a** equally between four test-tubes. Keep one for reference. To the second add one drop of ferric chloride solution (?), and to the third a drop of ammonium thiocyanate solution (?). Interpret the result. Now add to the fourth tube a few drops of ammonium chloride solution (?) and explain.

What other action have we shown to be reversible (Exercise **38**)? Are all double decompositions of acids, bases and salts in

solution reversible, like these two? Why does precipitation tend to make the action more nearly complete?

c. To a few drops of a dilute solution of lead nitrate, in a test-tube, dilute hydrochloric acid is added in excess. What do you observe? Write the equation for the reaction. Heat the test-tube carefully with a small Bunsen flame (?) until the solution is almost at the boiling-point (?). What makes the reaction more complete at low temperatures than at high? Cool the contents of the test-tube rapidly by holding the tube under the cold water tap (?). Continue until all solid precipitating out has settled to the bottom of the tube and the supernatant liquid is quite clear. Decant some of this liquid carefully into a second test-tube (if impossible to separate from traces of precipitate, filter!) and bubble hydrogen sulphide gas H_2S (for preparation, see Exercise **64 a**) through it for a few seconds. What do you observe now? Write the equation for this second reaction. Which of the two reactions is more nearly complete? Devise a simple experimental method of confirming quantitatively the fact that your answer is correct (Hint: Read Exercise **21 a**).

d. To a few drops of dilute sulphuric acid, in a test-tube, calcium chloride solution is added in excess. What do you observe? Write the equation for the reaction. Filter the solution and add a few drops of barium chloride solution to the filtrate. Continue the question as in the last four lines of **c** above.

43. Another Incomplete Reaction

a. Weigh out 1 g. of calcium chloride (fused or granulated) and 1.2 g. of oxalic acid. Dissolve each, separately, in 10 c.c. of water, and heat the solutions to the boiling point. Add the oxalic acid solution to the calcium chloride solution, a little at a time, boiling for two minutes and allowing the precipitate to settle between the additions. When one drop ceases to produce any fresh precipitation in the clear part of the liquid, note what proportion of the original oxalic acid solution remains unused (?). Add this remainder, thus making sure that there is an excess of oxalic acid present, beyond that apparently necessary to precipitate all the calcium.

The radicals are $(Ca^{II})(Cl^{I})_2$ and $(H^{I})_2(C_2O_4{}^{II})$. Write the equation for the action (?). Write the name under the formula

of each substance (?), and a downward arrow beside that of the precipitate (?). To what variety of chemical change does this one belong?

b. Proceed now to find out whether this reaction is incomplete or practically complete. To do this, shake the mixture and pour it all on to a filter. Catch the filtrate in a clean test-tube, label it *F* (use in *c*). Set a vessel under the funnel, and wash the precipitate (calcium oxalate) with water. To do this pour water, a little at a time, from a test-tube on to the filter, so as to wash every part of it. When the filter has drained, set a test-tube under the funnel, puncture the filter-paper with a glass rod, and wash the calcium oxalate through into the test-tube.

If the reaction was reversible, the equation, when read backwards, represents a possible chemical action. Name the interacting substances in the reversed action (?). To the calcium oxalate, suspended in water, add the required reagent (?). Was the action a reversible one? The conclusion may be confirmed as follows:

c. If this reverse action occurs, it was in operation in the original mixture made in **a**. In that case, all the calcium could not have been precipitated, some must be present in the filtrate *F*, and the reaction was incomplete. The reaction may be completed by removing (or chemically altering) one product. Destroy the hydrochloric acid by adding to the filtrate *F* ammonium hydroxide a drop at a time and shaking (?). What does the result prove? Was this action more or less nearly complete than that in **42 a**? Why?

CHAPTER IX

ACIDS, BASES AND SALTS. IONIZATION

44. Displacement

a. Place several pieces of granulated zinc in a dilute solution of cupric sulphate and set aside until the change is complete (test?). Occasional agitation will hasten the change (why?). Filter. What is the precipitate [**C 228; I 330**]? Preserve the filtrate.

Before examining the filtrate take a few drops of cupric sulphate solution and a like amount of zinc sulphate solution in two test-tubes. Dilute each solution with water and add to each ammonium sulphide solution (?). What is the precipitate in each case [**C 322; I 472**], and what ions are required to form it?

b. To the filtrate from **a** add ammonium sulphide solution (?). What ions were present in the filtrate? What changes did the metallic zinc and the cupric ions, respectively, undergo in **a**? Formulate these changes in an equation.

What substances could have been substituted for the cupric sulphate without affecting the result so far as the consumption of zinc and the precipitation of copper were concerned? What substances, besides zinc, would have precipitated copper [**C 245; I 354**]? What other elements, besides copper, are displaced by zinc?

c. Which one of the elements displaced by zinc did we prepare in quantity by an action like the present (Exercise **17**)? Formulate this action in terms of ions. What is the significance of the fact that the acid employed in this action was considerably diluted with water? What are the products of the action of zinc upon concentrated sulphuric acid (Exercise **16 e**)? Explain [**C 233; I 337**].

d. Formulate the action in **16 a** in terms of ions. Explain the differences in activity of the various metals [**C 209; I 295**].

45. Double Decomposition

a. To a few drops of potassium chloride solution add silver nitrate solution (?). What kind of chemical interaction do salts

frequently show in solution [C 228; I 331]? Write the equation for this action. How can we tell whether the precipitate is silver chloride, or potassium nitrate, or both? Which is it [C and I, inside front cover]? What was the interaction of silver nitrate with hydrochloric acid (37 e)? To a few drops each of solutions of two other chlorides, such as ferric chloride and calcium chloride, add a little silver nitrate solution (?). Are these actions reversible [C 229; I 332]? Are they complete? Why?

To find out whether all substances containing chlorine give silver chloride in this way, try a few drops of potassium chlorate solution with the same silver compound (?). State now what radical a substance must contain in order that, with silver nitrate, it may yield silver chloride (?).

b. Why was no precipitate observed when solutions of silver nitrate and potassium chlorate were mixed? To answer this question, write the equation for the double decomposition which might occur, and consider the solubilities of the products [C and I, inside front cover] (?).

c. Place 3–4 c.c. of barium chloride solution in a test-tube and dilute with water. Add sodium sulphate solution cautiously and agitate continuously, until no further precipitation occurs (?). Filter, concentrate the filtrate by evaporation, and pour it into a watch-glass to crystallize (?). Two salts are obtained, one by precipitation and one by evaporating the filtrate.

Formulate the action in detail [C 246; I 355].

Name the components of the filtrate and explain how they are affected by the evaporation and crystallization.

Upon what factor does the completeness of the double decomposition depend? Is, or is not, barium sulphate a highly ionized substance [C 249; I 364]?

Aside from double decompositions, what means have we for learning of what radicals a salt (like barium chloride) is composed?

d. To a little calcium chloride solution in a test-tube add sodium hydroxide solution (?). Exactly as in c above, formulate, study and explain the whole action.

e. To a little cupric sulphate solution add a little dilute hydrochloric acid (?). In what respects does the result differ from those in c and d, and why? Can any acids be prepared by precipitation and if so, which [C 526; I 393]?

46. Ionization of Acids, Bases, and Salts *

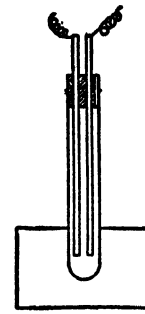


FIG. 20.

a. Name several distinct methods by which we may ascertain experimentally whether a substance is ionized in solution or not, and may learn the apparent extent of the ionization [C 250–1; I 365] (?). Define ionization, first in theoretical terms (?), and second in terms of the experimental evidence (?).

Obtain [Storeroom] an electrolytic cell† (Fig. 20). Half fill the cell with the substances named below in turn. See very particularly that the electrodes in the cell are not touching one another. Connect with the terminals on the lamp board‡ (Fig. 22), and note whether the lamp glows or not (?). The cell is in series with the lamp and, if the lamp glows, the solution is a conductor, otherwise it is a non-conductor. Wash the cell and electrodes and wipe the latter very carefully after each trial.

The following substances, or solutions, show the behavior typical of various classes of materials. After giving the result in your notes, name the class which is illustrated in each case.

If a solution is a conductor, what conclusion is to be drawn in regard to the condition of the dissolved body? In each such case, write an equation showing the materials present in the solution, and write the name under the formula of each substance (?).

1. Pure (glacial) acetic acid (?).
2. Distilled water (?).
3. 0.1 *N* aqueous solution of sodium chloride (?).
4. 0.1 *N* aqueous solution of sodium hydroxide (?).
5. 0.1 *N* aqueous solution of hydrogen chloride (?).
6. 0.1 *N* aqueous solution of ammonium hydroxide (?).

* The experiments of this exercise may be postponed until after the work in exercise 47 or 48 has been done. The apparatus should be set up by the instructor and explained to the class before use. For an alternative and simpler set-up, see Currier and Buser, Journal of Chemical Education, 11, 629, 1934.

† The cell consists of a glass, flat-bottomed, specimen tube (about 75 × 22 mm.) fitted with a two-hole rubber stopper in which a vertical groove has been cut to permit the escape of gases. The electrodes are pieces of tin about 10 cm. long.

‡ A storage battery of three lead cells or five Edison cells in series may be used, but is always in danger of being ruined by short-circuiting through

7. 0.1 *N* aqueous solution of acetic acid (?).

8. 0.1 *N* aqueous solution of ammonium chloride (?).

9. 0.1 *N* aqueous solution of ammonium acetate (?).

10. 0.1 *N* aqueous solution of sugar (?). Now, dry the cell by washing first with alcohol and then with ether.

11. Toluene in the dried cell (?).

12. Hydrogen chloride dissolved in dry toluene (?). What difference between water and toluene do tests 5 and 12 bring to light?

b. Each of four wide glass tubes is fitted up as follows: The lower end is closed tightly with a two-holed rubber stopper, through which pass an electrode and a small tube with stop-cock and nozzle. The upper end is also plugged with a two-holed stopper through which pass loosely a long narrow tube enclosing a second electrode and a funnel for use in filling the tube. The four tubes are fixed upright on a board side by side, and each is connected up with a direct-current circuit and a signal lamp (Fig. 21). The tubes are now filled with tenth-normal solutions of (1) hydrochloric acid, (2) acetic acid, (3) sodium hydroxide, and (4) ammonium hy-

carelessness. Protection by means of a fuse leads to continual interruptions of the work. Where *direct* current is employed in the lighting system, the best plan is to use the circuit through two resistances of such ratio to each other as to give the desired potential by the drop over one of them. Thus, if we place a

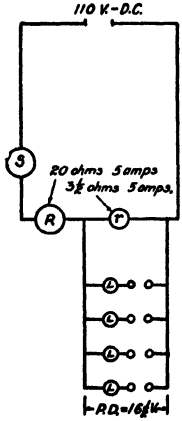


Fig. 21.

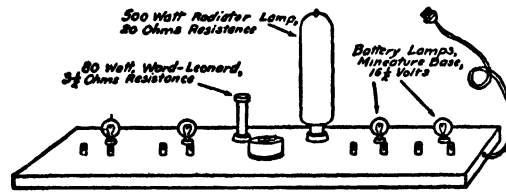


Fig. 22.

20-ohm resistance and a 3.5-ohm resistance on a 110-volt circuit (Fig. 21, diagrammatic), the potential drop over the lower resistance will be about 16.5 volts. If these resistances be of sufficient carrying capacity (say, 5 amperes), then four different current outlets may be provided — each one with plenty of current for one of the electrolytic cells previously described. Each of these outlets is in series with a small battery lamp, used as an indicator of the flow of current through the cell (Fig. 21).

Where *alternating* current only is available, a small rotary transformer, now commonly employed for charging automobile batteries, may be used.

droxide, respectively. What do you observe when the circuit is completed, the upper electrode remaining near the top of the tube in each case? Explain. What do you observe as the upper electrodes in (2) and (4) are pushed down towards the lower electrodes? Explain.

c. One-half of the solution filling each of the tubes in **b** is withdrawn. The part withdrawn from (3) is added to (1), and the part withdrawn from (4) is added to (2). How is the conductivity of the solution affected in each case? Explain by formulating the reactions in detail.

d. Non-ionic Actions. In previous class-room and laboratory experiments we have observed the formation of electrolytes in other ways than those illustrated in this chapter. Certain of these other ways are non-ionic, or not distinctly ionic. Give illustrations of such of these ways as you recall: acids, two ways; bases, one way; salts, four ways; together with the reference numbers of the laboratory exercises in which they occur (?).

47. Acids and Bases. Neutralization

a. Examine distilled water in respect to (*a*) taste, (*b*) behavior with litmus, (*c*) conductivity (class-room experiment).

b. Dissolve a small piece of potassium hydroxide in water and examine the solution in respect to (*a*) taste, by diluting a little and tasting one drop, (*b*) behavior with litmus, (*c*) behavior with phenolphthalein, (*d*) conductivity (class-room). These properties belong to aqueous solutions of all bases (compare Exercise 39). Aside from the water, what component alone is common to all solutions of bases, and has the above properties? Name this component and give its formula (?).

c. Examine a dilute aqueous solution of sulphuric acid in respect to (*a*) taste, (*b*) behavior toward litmus, (*c*) behavior with phenolphthalein, (*d*) conductivity (class-room), (*e*) action on a piece of marble, (*f*) action on an iron nail (clean this with the file before use). These properties are shown to a pronounced degree by all aqueous solutions of strong acids (compare Exercise 16 **d**). Aside from the water, what component alone is common to all solutions of acids, and has these properties? Name and give the formula of this component (?).

d. Place 3 c.c. of sodium hydroxide solution in a test-tube. Add

about 1 c.c. of concentrated hydrochloric acid. Is there evidence of chemical action (touch the back of the hand with the bottom of the test-tube)? Keep the mixture for **e**.

Make the ordinary [**C 226; I 328**] and ionic [**C 259; I 385**] equations for this action, which is a "neutralization."

e. Since acids and bases act oppositely on indicators, like litmus and phenolphthalein, it is possible to find out when the proportions of the two materials required for complete interaction have been taken, for the mixture will then be without action on an indicator.

Dilute the mixture prepared in **d**. Moisten a glass rod in it, and touch the edge of a piece of blue and of a piece of red litmus paper with it (?). If the blue turns red, there is excess of acid. Add sodium hydroxide solution a drop at a time, shaking between drops, and moistening the rod and testing as before. Continue until no effect is produced on litmus of either color. If, by accident, too much alkali is added, or if the mixture was alkaline in the beginning, use drops of dilute hydrochloric acid in the same way.

When the liquid is neutral to indicators, taste it by touching the tongue with the glass rod (?).

Set the solution aside to evaporate by itself. When it has dried up, examine the solid. What is the form of the crystals? What is the substance?

48. Titration *

a. A normal solution of any acid is one containing 1 g. of the hydrogen radical (H) per liter, accompanied, of course, by an equivalent amount of the negative radical of that acid. Thus, one liter of normal hydrochloric acid (HCl) will contain $1 + 35.5$ g. of the acid. Similarly, a normal solution of a base contains 17 g. of hydroxyl radical (OH) per liter. Thus one liter of normal sodium hydroxide (NaOH) will contain $23 + 17$ g. of the base. What weight of acetic acid (H) (CO_2CH_3) is contained in one liter

* In the event of a class threatening to get too far ahead in its laboratory work, as compared with lecture work, this exercise may be utilized to fill the gap at any stage between Chapters XII and XIX of the *College* or *Inorganic Chemistry*, or at any point after Exercise 30 of this *Outline*. Before any of the experiments in this exercise are performed, however, the conception of **normal solutions [C 160; I 221]** should be thoroughly explained and grasped.

of the normal acid? What weight of potassium hydroxide KOH is contained in one liter of the normal solution of this base? What weight of sulphuric acid H_2SO_4? What weight of calcium hydroxide $Ca(OH)_2$?

b. Titration of a Base with a Standard Acid. Fill a burette with the normal acid. Allow some of the acid to flow out, until all air has been expelled from the tip, and until the meniscus has reached the graduated portion of the burette. Hold the burette so that the surface of the acid is on the same level with the eye, and read the level of the bottom of the meniscus. Observe that the graduation is downwards, so that a reading two-tenths of a c.c. above the 2 c.c. mark is 1.8 c.c. (not 2.2 c.c.). Record the reading (?).

Take exactly 10 c.c. of sodium hydroxide solution in the graduated cylinder (dry this first). Pour it into a beaker. Rinse out the cylinder three times with a little water (about 5 c.c. each time), and pour each rinsing into the beaker too (?). Set the beaker on a sheet of white paper under the burette, and add a drop or two of phenolphthalein solution (?). Stir vigorously with a thin glass rod.

Now allow the acid to run in a rapid succession of drops into the beaker. Stir vigorously after each addition of a few drops. As soon as the acid begins to decolorize the indicator round the point where it enters, proceed more cautiously. Add only one drop at a time, and stir. The aim is to have the solution distinctly pink before the final drop of acid is added, and perfectly colorless when that drop has been allowed to flow in. If, at the first attempt, you overshoot the mark, wash out the beaker, take a fresh portion of sodium hydroxide solution, read the level of the acid in the burette, and try again.

When the titration has been successfully performed, read the level of the acid in the burette (?). Subtract from this reading that recorded at the beginning (?). The difference (?) is the volume of normal acid required for complete interaction with (neutralization of) 10 c.c. of the solution of the base.

c. Since one liter of the normal acid contains 1 g. of available hydrogen, 1 c.c. of the acid contains 0.001 g. of hydrogen radical. Calculate the weight of hydrogen radical used in your experiment (?). How many figures in your result are significant? Neglect all

figures, in subsequent calculations, beyond your limit of experimental error.

Now, 1 g. of hydrogen radical interacts with 17 g. of hydroxyl (OH). Using the weight of hydrogen just found, calculate the weight of hydroxyl contained in the portion of base you took (?).

Finally, using the proportion indicated in the formula NaOH, calculate the total weight of sodium hydroxide which contains the weight of hydroxyl you found (?).

d. Knowing from the result of **c** the weight of sodium hydroxide in 10 c.c. of the solution, calculate the weight per liter (?).

Calculate the concentration of the solution in terms of a normal solution of sodium hydroxide as unity (?).

e. Titration of an Acid. Wash out the burette, fill it with the sodium hydroxide solution as in **b**, and read the level of the meniscus (?).

In **c**, par. 2, we found the weight of hydroxyl in 10 c.c. of this solution. Calculate the weight in 1 c.c. (?). We may now use this solution containing a known concentration of a base for measuring quantities of acids.

f. Take exactly 10 c.c. of white vinegar in the graduated cylinder (dry this first). Pour it into a beaker, rinse the cylinder three times with water (as in **b** above), and set the beaker on a piece of white paper under the burette. Add 4 drops of litmus solution, or enough to give the liquid a distinct, but not strong pink color. Stir with a thin glass rod.

Now titrate this solution with that in the burette, exactly as described in **b** (third par.). Aim to stop when the tint is pinkish-violet, halfway between pink and blue. Repeat, if necessary to secure a sharp result. Then read the level of the meniscus (?) and subtract from the former reading to learn the volume of base used (?).

g. Using the weight of hydroxyl per c.c. found in **e** (second par.), calculate the weight of hydroxyl used in **f** (?).

Calculate the weight of acid hydrogen in the 10 c.c. of vinegar (?).

Finally, using the formula of acetic acid $(H)(CO_2CH_3)$, calculate the total weight of acetic acid in the 10 c.c. of vinegar (?). How much is this per liter? What per cent?

These methods, and others like them, are known as **volumetric**

methods, and are largely used in analyses made for commercial (as well as scientific) purposes.

49. Neutralization of Slightly Ionized and of Insoluble Substances

a. Consider the degree of ionization of acetic acid [**C 254; I 363**]. To neutralize 1 liter of normal acetic acid, would more or less alkali be required than to neutralize 1 liter of normal hydrochloric acid? In what way, precisely, would the details of the change be different in the case of acetic acid [**C 259; I 386**]? Name some of the consequences of this difference [**C 260; I 387**].

b. Dilute a few drops of cupric sulphate solution with much water and add excess of sodium hydroxide solution (?). Fit a filter paper properly into a funnel. Filter the mixture, and wash the precipitate (?) and filter paper repeatedly with distilled water to remove soluble substances. Now place a clean test-tube below the funnel, perforate the bottom of the filter paper, and wash the precipitate through into the test-tube by means of a stream of water from the wash-bottle. To the suspended cupric hydroxide cautiously add dilute hydrochloric acid in amount just sufficient to give a clear liquid. Concentrate the liquid on the sand bath until a drop, removed to a watch-glass, shows signs of crystallizing when cold. Then remove the dish promptly from the sand bath and allow it to cool. Examine the crystals (?).

Formulate this action in detail [**C 246; I 355**], taking account, however, of the fact that one of the interacting substances is an "insoluble" solid [**C 158; I 219**]. Describe in detail the stages through which the final production of solid cupric chloride is accomplished.

To what class of chemical changes [**C 184; I 258**] does the foregoing action belong?

CHAPTER X

THE HALOGENS

Chlorine (Exercise 40 and 41) and the elements to be studied in this chapter form a group having very similar properties, and are called the halogens. Recall the facts about chlorine and hydrogen chloride, and use them as a guide in trying to understand the chemistry of the rest of the group. Remember particularly that chlorine is colored, has a powerful odor, and does not cause fumes in moist air; and that hydrogen chloride is colorless, and causes dense fumes in moist air. The corresponding substances throughout the group may be expected to present properties like these. Thus, the elements are all colored substances, the hydrogen compounds are all colorless and fume in moist air. The hydrogen compounds, hydrogen chloride, hydrogen bromide, etc., are known as the hydrogen halides.

50. Bromine

Caution: Be very careful in all experiments which involve the use or the formation of free bromine. If you are reckless enough to breathe too much of it, inhale some concentrated ammonia vapor at once (compare Exercise 25). If you spill any upon your hands, wash it off immediately, and cover with a paste of sodium hydrogen carbonate and water (see Note 16, p. 3). Bromine burns are very painful and exceedingly slow in healing, so do not take any more chances than you can help.

a. Take 1 c.c. of water in a test-tube and add slowly 2 c.c. of concentrated sulphuric acid. Pulverize about 0.5 c.c. of potassium bromide, add 1 c.c. of manganese dioxide, mix, and add the mixture to the diluted acid.* Warm *very gently* with a small flame (?). Note the color (?) and odor [CAUTION] (?) of the vapor. What was the color of the potassium bromide? Does a compound show the colors of elements contained in it? Should you expect it to do so?

If any of the bromine vapor is condensing on the sides of the

* In this experiment, as well as in **52 a**, you will not obtain good results unless you powder your materials finely and mix them intimately. Do *not* use large lumps. If the experiments are properly done, no HBr or HI should appear.

tube, describe its properties (?). Write the equation for the reaction [**C 268; I 404**] (?).

b. To 10 c.c. of water in a test-tube add about 2 c.c. of carbon disulphide, close with the thumb, and shake (?). Are the liquids miscible (mutually soluble)?

To this mixture add a few drops of bromine-water [**C 269; I 404**]. (CAUTION: Do *not* add more than a few drops and, above all things, be careful not to add any free bromine that may be undissolved at the bottom of the bottle!) Close the test-tube with the thumb or with a cork if you prefer, and shake again. Is the bromine, judging by color, equally soluble in both water and carbon disulphide? If more so in one, how much more (?) and in which?

Repeat, using either chloroform or ether instead of carbon disulphide, and answer the same questions.

c. Test for a Bromide. Take a crystal of potassium bromide (color?) and dissolve it in 5 c.c. of water (color of solution?). Add 2 c.c. of carbon disulphide and shake (?). Why is the carbon disulphide not colored by the bromine?

Holding the tube steady, add now a drop or two of chlorine-water [**C 194; I 270**], and observe carefully whether any color appears, and, if so, in which layer of liquid (water layer or carbon disulphide) it makes its appearance (?). Why? Shake vigorously and allow the mixture to settle (?). What substance has been liberated? Write the equation [**C 272; I 403**] (?).

Infer from this result the relative activities of chlorine and bromine (?). Chlorine acts in the same way upon the bromides of all metals. The result measures the relative affinity of chlorine and bromine for what?

d. Summarize the properties of bromine: color (?), odor (?), density of vapor compared with air (?), relative solubility in water and carbon disulphide (?), relative activity as compared with chlorine (?) and iodine (?).

51. Preparation of Hydrogen Bromide

a. Fit up a 250 c.c. flask with a dropping-funnel and exit tube, and connect with a **U**-tube (Fig. 23). Render the apparatus air-tight and test it (?). Fill the **U**-tube with dry, broken glass or porcelain (why?), mixed with a little red phosphorus (why?).

Connect the other limb of the U-tube with a second, larger U-tube [Storeroom] containing about 10 c.c. of water. Place about 5 g. of red phosphorus mixed with twice its weight of sand in the flask, add 5 c.c. of water, and mix by shaking. Pour into the globe of the funnel about 8 c.c. of bromine [EXTREME CARE. Do not spill upon the hands (Note 16, p. 3)]. Allow the bromine to flow drop by drop on to the phosphorus, and let the gas dissolve in the water in the second U-tube. A large volume of air is expelled before the hydrogen bromide reaches the second U-tube. Disconnect the second U-tube and reserve the solution for use in b: How could hydrogen chloride be prepared in the same way?

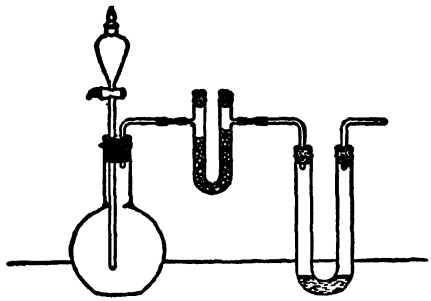


FIG. 23.

Try the effect of moist air upon the gas issuing from the main apparatus (?). Hold in the gas a rod dipped in ammonium hydroxide (?).

b. Divide the solution into seven portions and examine its behavior toward (1) litmus (?), (2) zinc in contact with a platinum wire (?), (3) silver nitrate solution (?), (4) mercurous nitrate solution (?), (5) lead nitrate solution (?), (6) powdered manganese dioxide (warm) (?). Boil (3), (4), and (5), after pouring away the supernatant liquid and adding more water to each (?). Compare these results with those found in the case of hydrochloric acid (37 e).

c. To the seventh portion add a few drops of chlorine-water, a few drops of carbon disulphide, and shake (?). This result, and that in 50 c, indicate the relative affinities of chlorine and bromine for what (?), and how?

52. Iodine

a. Pour into the evaporating dish 1 c.c. of water and add 2 c.c. of concentrated sulphuric acid. Pulverize finely about 1 c.c. of potassium iodide, add 2 c.c. of manganese dioxide, mix, and add the mixture to the acid. Place the evaporating dish upon the ring

on the stand and set the beaker with about 50 c.c. of water upon it so that the vapor of the iodine may condense on the bottom of the beaker.

Heat the mixture gently with a very small flame, which does not touch the dish. Observe the color of the vapor (?), and the crystals (form?) on the bottom of the beaker. What was the color of the potassium iodide (?), and the form of its crystals? Are its crystals like those of iodine either in form or color? While the crystals are accumulating, proceed with **d**.

b. Place in as many test-tubes 1 c.c. each of water, alcohol, carbon disulphide, chloroform, ether, and potassium iodide solution. Scrape some of the crystals of iodine off the bottom of the beaker with a wooden splint, add one crystal to the contents of each of the four test-tubes and shake (?). Is the iodine heavier or lighter than water?

Tabulate the results as follows, giving the solvent (?), degree of solubility (slight, considerable, very great), and the color of the solution (look through it at a piece of white paper):

Solvent	Solubility	Color of Solution
Water:		
Etc.:		

The solution in alcohol is the lotion called "tincture of iodine." That in potassium iodide solution is used in testing for starch (Exercise **101 b**).

c. Divide the contents of the first test-tube (containing water and iodine) into two parts. To one, add an equal volume of carbon disulphide and shake (?).

Take 15 c.c. of starch suspension (for preparation, see Exercise **101 a**) and add the second portion to it (?). Pour the mixture into the graduated cylinder and add water so long as a sample poured out into a test-tube continues to show an easily perceptible color. Why is the use of starch considered to be a delicate test for iodine? Does it show the presence of iodine in combination [**C** 273; **I** 272]?

d. Test for an Iodide. Take a crystal of potassium iodide (color?) and dissolve it in 5 c.c. of water (color of solution?). Add 2 c.c. of carbon disulphide and shake (?). Why is not the color of iodine visible?

Holding the tube steady, add now a drop or two of chlorine-

water, and observe carefully whether the color appears in the carbon disulphide or in the aqueous layer (?) and what color it is (?). Then shake vigorously and allow the mixture to settle. What substance has been liberated? Write the equation [**C** 275; **I** 408]. To what variety of chemical changes does this one belong?

e. Repeat **d**, using bromine-water instead of chlorine-water (?).

f. Summarize the properties of iodine: color of solid (?), of vapor (?), density of vapor compared with air and with bromine vapor (?), density of solid compared with water (?), solubilities in four solvents (?), relative activity as compared with chlorine and bromine (?).

Write the equation of the reaction in **a**, and discuss [**C** 193; **I** 268].

53. Preparation of Hydrogen Iodide

a. Use the apparatus in Fig. 23. Place in the flask a mixture of finely powdered iodine (20 g.) and red phosphorus (1 g.) intimately mixed in the mortar. Charge the **U**-tubes as in **51 a**. Place a little water in the dropping-funnel, and allow the water to drop very slowly upon them (?). After the air has all been expelled, and the solution in the second **U**-tube has become sufficiently concentrated, remove the second **U**-tube. Test the issuing gas with moist air (?) and with ammonia (?) as in **51 a**. Hold in the gas a piece of filter paper dipped in starch emulsion alone (?). Explain (?). Reserve the contents of the second **U**-tube for use in **c**.

b. Alternative Method [Hood]. Place 5 g. of powdered iodine with 50 c.c. of water in a small flask provided with a perforated cork and a glass tube extending to the bottom. Pass hydrogen sulphide (for preparation, see Exercise **64 a**) from a Kipp's generator, or from the laboratory supply, through the mixture, loosening the cork once or twice at first to permit the air to be displaced by the gas, until the iodine is all gone and the solution no longer becomes brown on being shaken. Agitate constantly to hasten the process. Describe what happens. Towards the end of the operation, why does the iodine dissolve [**C** 554; **I** 409] (?) and why does the whole action then proceed much more rapidly? Warm and filter the solution.

c. Using the material obtained in either **a** or **b**, carry out the same experiments with the solution as were made with the solution

of hydrobromic acid in 51 b and c (?). Compare the results with those of 51 b and c (?).

54. Comparison of Hydrogen Halides

In connection with this experiment, it must be kept in mind that an odor similar to that of rotten eggs shows the presence of hydrogen sulphide (16 e), and an odor of burning sulphur the presence of sulphur dioxide (14 c).

Remember, also, that the hydrogen compounds of the halogens are all colorless.

a. Hydrogen Chloride. Pulverize about 1 g. of potassium chloride (color?), place it in a test-tube, and add one or two drops (not more) of concentrated sulphuric acid (?).

Blow the breath across the mouth of the tube (?).

Test the gas with moistened blue litmus paper (?).

Lower into it a glass rod dipped in ammonium hydroxide solution, which will give off ammonia gas (?). Write the equation (?).

b. Is any colored gas visible in a? Why is the color of chlorine not observable?

c. Hydrogen Bromide. Repeat a in every detail,* using potassium bromide; make the same notes (?) and answer the same questions (?).

d. Is there a colored gas or vapor visible in c? Name it (?). Can you observe any other property which identifies the substance? By what kind of chemical action could this colored substance be formed from the product identified in (c)? By what name is such a reaction known? Was there any corresponding product formed when sulphuric acid acted upon a chloride? How could you distinguish a bromide from a chloride?

e. Can you recognize still another gaseous product by its odor (refer to beginning of experiment)?

The work in c, d, and e leads to the recognition of three gaseous or vaporous products. Do not attempt to put all of these in one equation. Construct one equation for the formation, from the original materials, of the gas recognized in c (primary action), and make a second, separate equation for the formation of the other two products from the interaction of sulphuric acid with the gas recognized in d (secondary action). What two properties of sulphuric acid (?) and what property of hydrogen bromide are illustrated by this set of observations?

*You will not get the desired results in this experiment unless you stick to the directions. You are told to take *one or two drops* of concentrated sulphuric acid. This does *not* mean half a test-tube full.

f. Hydrogen Iodide. Repeat **a** in every detail (see footnote on preceding page), using potassium iodide; make the same notes (?) and answer the same questions (?)

g. Warm the tube from **f** (?). What is the colored vapor? Does it form crystals on the tube? Continue as in **d** above.

h. Stop heating, and let the vapor condense. What other gaseous product can you now recognize by its odor [CAUTION]?

Was this odorous gas formed from the potassium iodide or the sulphuric acid (in answering, consider the formulæ of these substances and of the gas)? By what sort of chemical action must this gas have been formed? Could hydrogen iodide have produced such an action? Write an equation to illustrate your answer (?). Why, then, was iodine liberated?

In case the above directions are not followed implicitly, and large pieces of potassium iodide are taken, or too much sulphuric acid is used, still another gas (sulphur dioxide) may be formed along with or instead of one of the above, and, in addition, a sublimate of free sulphur may be seen on the tube [C 315; I 465].

i. Using the results of this exercise, how could you recognize a bromide and an iodide, and distinguish them from a chloride?

What other method of recognizing bromides and iodides did we learn before?

55. Hydrogen Fluoride *

a. Cover a square of glass with a thin layer of paraffin by warming it very cautiously far above a Bunsen flame and rubbing it on one side with solid paraffin. Moisten about 3 g. of fluorspar in a leaden dish [Storeroom] with concentrated sulphuric acid (do not cover with the acid). With the end of a file draw some design upon the paraffin-coated side, thus exposing parts of the glass to the action of the vapor. Now cover the leaden dish with the glass, paraffin side down, and set it in a moderately warm place, but not so warm that the paraffin is likely to melt. After half an hour or more, remove the glass cover, warm, and wipe off the melted paraffin with filter-paper (?).

b. Write equations representing the action, and state what becomes of each of the components of the glass [C 278; I 416]. Try the test of a rod dipped in ammonium hydroxide and held over the

* If desired, this experiment may be performed by the instructor.

contents of the lead dish (?). Does the gas fume with moist air? What substances, beside fluorspar, would serve the purpose of this experiment? Why could not hydrochloric acid or nitric acid be substituted here for sulphuric acid?

c. How may fluorine be liberated from a fluoride? Why can it not be isolated from fluorides by the action of oxidizing agents, as was the case with the other halogens?

56. Identification of Halogen Compounds

a. Imagine that there are given to you four white substances, and that you know them to be the fluoride, chloride, bromide, and iodide of some metal. State what experiments you would make, and what reasoning you would use, in order positively to identify the halogen constituents of each. In two of these cases, two different actions have been encountered in this chapter and might be used, and in the other two cases only one. Still another kind of action might readily be thought of [**C** 190, 268; **I** 265, 403]. Negative results, say by showing that one is not a chloride, bromide, or iodide, and is therefore a fluoride, must be confirmed by a positive experimental test.

b. If the four hydrogen halides were given you in gaseous condition in four jars, how should you proceed by chemical means to identify each?

c. Examine your notes on Exercise 44. Formulate the following actions in terms of the hypothesis of ions:

(1) Free chlorine and bromide-ion.

(2) Free chlorine and iodide-ion.

(3) Free bromine and iodide-ion.

(4) Free iodine and sulphide-ion.

Arrange these four elements in a series similar to the electromotive series of the metals [**C** 245; **I** 354]. Where should you place fluorine in this series [**C** 279; **I** 418]? Indicate the approximate position of oxygen [**C** 275; **I** 412]?

CHAPTER XI

OXIDIZING SUBSTANCES. OXYGEN COMPOUNDS OF THE HALOGENS

57. Hydrogen Peroxide

a. To prepare a solution of sodium peroxide, take 100 c.c. of cold (preferably iced) water in a flask, and about 1 c.c. of pulverized sodium peroxide on a watch glass. Add the peroxide to the water, a very little at a time, shaking and cooling the mixture in running water, or adding ice, during the process.

Test a drop of the solution on litmus paper (?). Now, while still shaking and cooling in the same way, add dilute sulphuric acid a few drops at a time, until the mixture is acid. Write the equation (?). What does the solution now contain?

b. Take 15–20 c.c. of the solution in a test-tube, and place about 1 c.c. of pulverized manganese dioxide on a piece of paper. Light a wooden splint, throw the manganese dioxide into the solution (?), and test the gas in the tube for oxygen (?). Write the equation (?). The manganese dioxide (catalyst) is unchanged. Is hydrogen peroxide stable or not?

c. Take 2 drops of lead nitrate solution $Pb(NO_3)_2$, dilute with 5 c.c. of water and add 2 drops of ammonium sulphide solution $(NH_4)_2S$ (?). Pour the mixture on to a filter. The precipitate is lead sulphide, formed by double decomposition. Write the equation (?). Wash the precipitate and whole filter-paper with water and, when the water has run through, wash once more. Then pour upon the precipitate some of the hydrogen peroxide solution [**C 288; I 428**] (?). Write the equation (?). To what class of substances does hydrogen peroxide here show itself to belong? What practical use is made of this reaction?

d. To a part of the remainder of the hydrogen peroxide solution add some starch suspension (prepared as in Exercise **101 a**) containing a drop of potassium iodide solution (?). In writing the equation for this action, remember that the solution of hydrogen peroxide

from a contained a slight excess of *dilute* sulphuric acid, which will interact with the potassium iodide (?). The product of this action then interacts with the hydrogen peroxide [C 288; I 428].

e. Test for Hydrogen Peroxide. Take about 1 c.c. of potassium dichromate solution and, to liberate dichromic acid, add an equal volume of dilute sulphuric acid. Take now another portion of your hydrogen peroxide solution, add 2–3 c.c. of ether, close with the thumb and shake. Then add to it one drop of the solution containing dichromic acid and shake again (?).

f. Prepare a solution containing free permanganic acid and sulphuric acid by adding a large excess of dilute sulphuric acid to 5 c.c. of potassium permanganate solution (equation?). Add some of this mixture to the final portion of hydrogen peroxide solution [C 288; I 428]. Test for oxygen the gas which comes off (?). What happens to the MnO_4 radical? What variety of chemical activity does the hydrogen peroxide show here?

g. Suspend lead dioxide, barium dioxide, and pulverized manganese dioxide, separately, in water, add dilute sulphuric acid and shake for some time, cooling as in a. Filter, and apply to each filtrate the test described in e (?).

What are the differences in behavior and constitution between a true peroxide and those oxides which are sometimes incorrectly called peroxides [C 698; I 427]?

h. What are the radicals of: potassium chlorate, hypochlorous acid, sodium peroxide, lead dioxide, potassium permanganate?

References for additional work. The Making of Ozone as a Laboratory Exercise; Lisk, Journal of Chemical Education, 9, 2099, 1932. Catalytic Decomposition of Hydrogen Peroxide; Billinger, Journal of Chemical Education, 9, 144, 1932.

58. Hypochlorous Acid from Bleaching Powder

a. Take about 2 c.c. of bleaching powder* with 20 c.c. of water in a test-tube, shake from time to time and finally filter to obtain a clear solution. Meanwhile arrange an apparatus to generate carbon dioxide as in Exercise 96 b. (The time of the class may be conveniently saved by the instructor at this point by having a Kipp generator for carbon dioxide set up for general use.) Pour most

*From a freshly opened "tin can" of the substance. When kept in a bottle it is likely to be decomposed by the carbon dioxide in the air.

of the clear bleaching powder solution into another test-tube, reserving a small portion for use in **b**, and pass carbon dioxide through it for 5 minutes. The precipitate is calcium carbonate $CaCO_3$. Filter again, to obtain a clear solution of hypochlorous acid [**C 291; I 433**] for use in **c**.

b. In the rest of the bleaching powder solution dip strips of litmus paper. Leave one in the solution (?). Does bleaching powder solution bleach? Hang the other in the air (?). What acid here liberates the hypochlorous acid? To what class of chemical actions does that on the litmus belong?

c. In the hypochlorous acid solution from **a** place small pieces of (1) litmus paper, (2) paper with printing on it [**C 462; I 651**], (3) paper with writing in red ink [**C 284; I 422**] and black ink [**C 716; I 986**], (4) paper with writing in pencil [**C 436; I 444**], and (5) colored calico. Observe and record the effect on each (?). Which of these owe their color or blackness to free carbon, and which to colored organic compounds? Does hypochlorous acid oxidize free carbon? What does it oxidize?

d. How could you prepare an aqueous solution of pure calcium hypochlorite [**C 289; I 429**]?

e. Take 10 c.c. of an aqueous solution of chlorine in a test-tube. To the solution add a drop of indigo solution [**C 290; I 430**] (?).

f. What evidence does experiment **e** furnish that hypochlorous acid is a more active oxidizing agent than is atmospheric oxygen? Why is it thus more active?

59. Chlorates

a. Dissolve 3 g. (weighed on rough scales) of solid potassium hydroxide in 7 c.c. of water in a test-tube and saturate (Test?) the solution with chlorine.* Crystals will appear during the process of saturation and will increase in quantity as the liquid afterwards cools. Filter off the crystals on a small filter-paper, and examine the filtrate (in **b**) and the crystals (in **c**) separately.

b. Add to the filtrate dilute nitric acid (this is to destroy potassium hydroxide, in case any remains; no equation needed) and

*Small cylinders of chlorine gas may be used, or the method described in Exercise 41 **a** may be employed. In either case the experiment should be carried out under a hood, and every precaution taken against breathing the gas.

then test with a few drops of silver nitrate solution (?). What radical is shown by this test to be present (Exercise 45 a)? What product is thus shown to have been formed by the interaction of chlorine and potassium hydroxide?

c. Examine the crystals from a with a lens and describe them. Dry the crystals, heat them in a narrow tube, and test for oxygen (?). Dissolve the residue from this operation in distilled water and add silver nitrate solution (?). What substances constituted the crystals and the residue, respectively? From the behavior of the former substance during making, what do you infer as to its solubility? Is the inference correct [C 164; I 226]?

d. What effect is observed on adding silver nitrate solution to a solution of *pure* potassium chlorate? How may the chlorate radical be distinguished from that of the chlorides? The crystals of potassium chlorate made in a are not free from traces of potassium chloride (why?), and could not therefore be utilized for this test. What method should you suggest for purifying the chlorate?

e. To a minute amount of finely powdered potassium chlorate add two drops of pure, concentrated hydrochloric acid (?). The yellow substance is formed by decomposition of one of the products [C 301; I 446] (?). How would a chloride behave with hydrochloric acid?

Give three ways of distinguishing chlorides from chlorates.

60. Perchlorates

a. Measure 600 c.c. of water into your 1-liter bottle, and mark the level reached. Observe the temperature and pressure of the air and calculate the weight of potassium chlorate which will be necessary to give 600 c.c. of oxygen under these conditions (the tension of aqueous vapor may be neglected, as the vapor will occupy only about 10 c.c. of the 600 c.c. at 18°) and at the same time leave a maximum amount of perchlorate and chloride as a residue [C 302; I 447]. This stage is reached, with careful heating, when about one-fifth of the total oxygen has been evolved: in other words, take so much of the chlorate as, if completely decomposed, would furnish five times 600 c.c.

Fill the 1-liter bottle with water and invert it in the pneumatic trough. Weigh the calculated amount of chlorate into a hard glass test-tube, which has previously been closely fitted with a one-hole

cork and delivery tube, and see that the apparatus has been made air-tight. Gently heat the chlorate and collect in the 1-liter bottle enough oxygen to fill the bottle to the mark, measured, of course, when the mark is at the same level as the water in the trough. Proceed slowly towards the end so as to allow the gas to cool, stop heating when the mark is reached, and remove the delivery tube at once from the water. Pour the melted substance into a mortar before it has time to solidify. Pulverize the mixture.

The mixture consists mainly of the chloride and perchlorate of potassium. The solubilities (grams of the salt dissolved by 100 c.c. of water) of these salts are as follows:

	15°	20°	100°
Potassium chloride	33	35	56
Potassium perchlorate	1.5	1.8	20

To separate the substances, shake the powder persistently with a small amount of cold water. Cut, fold, and place in a funnel a filter paper just large enough to hold the undissolved material. Collect the latter upon the filter and wash it repeatedly with a few drops of cold water until the liquid coming through the filter gives no precipitate with silver nitrate solution (?). Calculate the amount of water which at 100° will dissolve the residue, assuming it to be potassium perchlorate. Dissolve it in this amount of water by boiling, and allow the solution to stand for an hour or two. Collect the crystals upon a filter, wash them as before, and dry them.

b. Dissolve a little of the substance in distilled water and test with silver nitrate solution (?). Explain (**45 b**).

To a minute amount of the crystals add two drops of pure concentrated hydrochloric acid [**C 302; I 447**] (?). Why does the result differ from that when potassium chlorate was treated with the same acid (**59 e**)?

Place about 1 g. of the crystals in a narrow test-tube, heat and test for oxygen (?).

How could you distinguish a perchlorate from a chloride, and from a chlorate?

61. Bromic and Iodic Acids

a. Take two test-tubes and place in one a minute fragment of iodine and in the other 2–3 drops of bromine-water. Add about

5–10 c.c. of water and a little carbon disulphide to each, and shake (**50 b** and **52 c**). The carbon disulphide is added simply for the purpose of collecting the halogen and making its presence obvious. Now pass chlorine (generated as in **59 a**), a few bubbles at a time, through (or add chlorine-water, a few drops at a time, to) the water in the test-tubes, alternately, and shake vigorously after each addition of chlorine until a change is seen [**C 305; I 450**] (?). Which of the halogens is first affected, and why?

b. To about 10 c.c. of water in a test-tube add a single drop of potassium iodide solution and then a single drop of potassium bromide solution. Shake. Pour away three-fourths of the solution and add water. Introduce also a few drops of carbon disulphide. Now pass chlorine (generated as in **59 a**), a few bubbles at a time, into the liquid, or add chlorine-water a little at a time, shaking vigorously after each addition of chlorine (?). Continue until no further changes occur, and explain all the changes which are observed. This procedure is used in analysis for recognizing a bromide in presence of an iodide.

c. Prepare some dilute bromic acid by taking 2–3 c.c. of potassium bromate solution and adding an equal volume of dilute sulphuric acid (?). Make the equation for this double decomposition. Is the action complete (**42 b**)? In what follows, disregard the substances present with the bromic acid, and place the latter only in the equation. Drop into this solution a single small crystal of iodine and shake repeatedly, allowing the mixture to stand for some minutes after each shaking (?). Pour off the solution from any undissolved iodine, to the clear liquid add a few drops of carbon disulphide, and shake (?). What free halogen is here detected? What does this show in regard to the relative tendencies of bromine and iodine to unite with oxygen?

What inference can you draw from a on the relative activity of chlorine, as compared with bromine and iodine, towards oxygen? What would be the action of iodine upon a solution of chloric acid?

Which variety of chemical change was here observed? How could you show, by a single experiment, that, although no change is visible, the bromic acid actually is formed when the sulphuric acid is added, above, and that it is the bromic acid, and not the potassium bromate, which interacts with the iodine?

Reference for additional work. Time Experiment [**C 304; I 486**].

CHAPTER XII

SULPHUR

62. Sulphur

a. Rhombic Sulphur. Place about 0.5 c.c. of powdered roll sulphur in a dry test-tube, add 2 c.c. of carbon disulphide and shake (?). Pour the solution into a watch-glass and set it aside to evaporate away from all flames.

Examine the crystals with the eye and with a lens and make a drawing of two of them (?). Are they brittle or soft? Color? Are they transparent? After 24 hours (or more), are they still transparent?

b. Monoclinic Sulphur. Fold a filter-paper as if for filtration, and put water in the trough. Half fill a dry test-tube with roll sulphur. Hold the test-tube with the clamp from the iron stand and heat *very gently*, turning the tube in the Bunsen flame, until its contents have completely melted. Dark brown patches show overheating at these points — just-melted sulphur is pale straw-color.

Hold the filter-paper by the edge at the three-fold side and pour the melted sulphur into it. Watch the crystals grow. When crystals have formed at the surface and reached the center, pour the remaining liquid sulphur promptly into the trough of water, and open up the paper immediately.

Examine the crystals with the eye and with the lens and make a drawing of two of them (?). Are they brittle or soft? Color? Are they transparent? After 24 hours (or more), are they still transparent? If not, into what form of sulphur have they turned?

Examine the part that was poured into water. Is it brittle or soft? Dry a small piece of it and shake it with 1 c.c. of carbon disulphide (?).

c. Amorphous Sulphur. Half fill the same test-tube with roll sulphur and melt. Continue heating this time until the sulphur boils and note the changes in color and fluidity which occur (?).

Pour the boiling sulphur into the trough of water, moving the tube about during the process.

Examine the product. Is it crystalline? Is it brittle or soft? Is it transparent? After 24 hours (or more) is it still transparent? After 24 hours (or more), dry a part of it and shake with a little carbon disulphide (?). To find out whether any has dissolved, pour part of the liquid on to a filter, catch a few drops of the filtrate on a watch-glass, and allow them to evaporate (?).

What is the insoluble material? Color? Examine with a lens (?). Is it crystalline?

What would have been the result if the boiling sulphur had been allowed to cool slowly, instead of being chilled in water?

Reference for additional work. Sulphur Extraction Working Model; Weaver, Journal of Chemical Education, 10, 309, 1933.

63. Sulphides of Metals

a. Place about 2 c.c. of roll sulphur in a dry test-tube and fasten the tube upright in the clamp on the stand. Boil the sulphur and then drop into the tube a strip of copper foil (?). Does the temperature of the copper change noticeably? Was it heated thus by the flame, the sulphur vapor, or what?

Examine the residue when cold and describe the properties of the product (?). Name it (?) and write the equation (?).

b. Mix thoroughly in the mortar 1 c.c. of zinc powder with 1.5 c.c. of powdered roll sulphur. Place the mixture in a test-tube and clamp the latter on the stand. Heat the lower part of the material and, when the reaction begins, withdraw the flame.

Was the temperature at any time higher than that which the flame could have produced? What was the source of the heat? Describe the product when cold (?). Name it (?), and write the equation (?).

c. Repeat **b** with mercury in place of zinc (use two or three small globules from a dropper) and answer the same questions.

d. Recall and record here a case of the union of sulphur with a metal which was observed previously (**8 d**). Under the same conditions (pressure, temperature, contact), do iron and mercury combine more or less readily with sulphur than with oxygen? Give reasons for your answer (?).

Does sulphur appear to have about the same activity as has oxygen, or much more or much less?

64. Hydrogen Sulphide

Be very careful in all experiments that involve the liberation of hydrogen sulphide or sulphur dioxide, and do not let more of either gas get into the room than you can possibly help. Even if you do not object to the odor, your neighbors probably will. Do not forget, besides, that hydrogen sulphide is actually *poisonous* if its concentration gets above a certain limit [C 314; I 464]. Work under a well-ventilated hood, if available, and don't invite trouble.

a. Take a test-tube fitted with a 1-hole stopper and a bent glass tube (Exercise 3 **d**), and fit on to the bent glass tube a rubber connection ending in a straight glass tube. Remove the stopper, hold the test-tube almost horizontal, and slip into it carefully about 3 c.c. of ferrous sulphide. Add dilute hydrochloric acid and replace the stopper. Note the color (?) and odor (?) of the gas. Avoid breathing it, however, as far as possible.

b. Place the straight delivery tube in a test-tube half filled with water, so that it reaches the bottom, and let the gas bubble through the water for several minutes. Keep the solution for use in the later sections.

Now set fire to the gas at the end of the delivery tube (?). What products are formed when the gas burns? Hold a porcelain dish in the middle of the flame for a few moments (?). What substance is deposited, and must, therefore, exist uncombined in the interior of the flame? What other substance does this justify us in assuming to be liberated in the same region? What do these facts indicate regarding the stability of the gas when heated, and the difficulty, therefore, of making the compound by the direct union of its elements? What are the products of the complete combustion of the gas, and in what two stages does this combustion take place? Make equations showing both stages (?).

c. Smell the solution made in **b** (?) and test it with litmus paper (?). To what class of substances does hydrogen sulphide belong? What other name is given to its aqueous solution [C 315; I 465]?

Take 4 test-tubes and in each place about 2 c.c. of a solution of a different one of the following salts: (1) Cupric sulphate, (2) Arsenious chloride $AsCl_3$,* (3) Mercuric sulphate $HgSO_4$, (4) Anti-

*Dissolve arsenic trioxide in dilute hydrochloric acid.

mony trichloride $SbCl_3$. Add a part of the solution of the gas to each (?). If you do not get good results, pass the gas itself through each solution.

What variety of chemical change will an acid and a salt undergo in solution [C 228; I 331]? Make equations for the four actions accordingly (?). Explain the precipitation in terms of ions.

Pour away a part of the contents of each test-tube, including a part of the precipitate, add a large excess of dilute hydrochloric acid, and shake (?). Explain the results. Divide the metallic sulphides obtained in this experiment into two classes, and characterize those classes.

d. About 10 c.c. of the solution of hydrogen sulphide in water is divided into two parts. To one a few drops of lead nitrate solution are added (?). The other is boiled for five minutes, and a few drops of lead nitrate solution are then added (?). What do you conclude?

e. Take another 5 c.c. of the solution in a test-tube and add 2–3 g. of iron dust (pulverized iron). Shake vigorously and then allow the mixture to stand (?). After an hour collect the insoluble matter upon a filter and wash until it no longer smells of hydrogen sulphide. Transfer the precipitate to a test-tube by puncturing the paper and washing through. Add dilute hydrochloric acid to the solid product and note the odor (?). What substance must have been present in the precipitate, and how was it formed? Account for the extreme slowness of the action of iron upon the solution of hydrogen sulphide [C 249; I 390].

f. Allow some of the solution made in **b** to stand for some days exposed to the air (?). Explain the turbidity (?).

g. If **53 b** was performed, record here the action which took place (?). If **53 b** was not performed, place a single crystal of iodine in 5 c.c. of water and saturate, as in **b**, the liquid with hydrogen sulphide [C 274; I 411] (?).

What ionic substance is shown by **64 c** and by **64 e** to be present in the solution of hydrogen sulphide [C 315; I 470]? Explain the actions in **f** and **g** in terms of ions.

h. To 2–3 c.c. of potassium dichromate solution add dilute sulphuric acid in large excess (?). What change may be assumed to have taken place? Now saturate the mixture with hydrogen sulphide (?). What are the colors of the solution and of the precipi-

tate, respectively? Show that two kinds of ionic chemical change are here illustrated (?).

i. Take 2–3 c.c. of potassium permanganate solution and treat exactly as in **h** (?). Answer the same questions (?). What chemical property of hydrogen sulphide is illustrated in **h** and **i**?

j. Take about 10 c.c. of sodium hydroxide solution and saturate it with hydrogen sulphide as in **b**. What is the product [**C 316; I 466**]? How should you proceed to prepare neutral (or normal) sodium sulphide (solid)?

Divide the solution into four parts, and to the first part add dilute hydrochloric acid (?). Formulate, study and explain this action [**C 258; I 393**], modifying the scheme of formulation to suit the case.

To the second part add some bromine-water [**C 279; I 418**] (?).

To the third portion add a little powdered roll sulphur and shake from time to time. Is sulphur soluble in water? What is here to be inferred? When the solution has become very yellow (?) in color, filter. Acidify the filtrate with dilute hydrochloric acid (*i.e.*, add more than an equivalent amount of the acid) (?). Recall an experiment with iodine which resembles this experiment with sulphur (?).

Allow the fourth part of the solution to remain exposed to the air for several days (?). When a change in color has occurred, add dilute hydrochloric acid in excess (?). Explain.

k. Summarize the observed properties of hydrogen sulphide (?). How could you identify hydrogen sulphide? How could you use it in identifying the metallic radicals in different salts?

65. Ionic Chemical Changes: Formation of an Inactive Acid

a. To 2–3 c.c. of sodium acetate solution add an equivalent amount of dilute sulphuric acid, and warm gently. One product may be recognized by its odor (?).

Formulate, study and explain this action [**C 258; I 393**]. Write a simple equation expressing the chief change which occurs.

b. Consider the action between ferrous sulphide and dilute hydrochloric acid in **64 a**. Formulate, study and explain this action also [**C 320; I 470**], modifying the scheme of formulation to suit the case. Does the escape of the hydrogen sulphide assist materially in making the action more nearly complete [**C 220; I 317**]? Does

it assist at all? What physical property does the escape of the hydrogen sulphide as a gas show this substance to possess?

c. Make a single general statement describing all the cases in which, when electrolytes are mixed, and no precipitation or volatilization occurs, a fairly complete chemical change will nevertheless take place [C 258; I 379].

Give a list of acids [C 249; I 363] which might be formed in accordance with the principle embodied in your statement.

Could any bases be formed in accordance with the same principle? Illustrate. Could any salts be so formed?

66. Hydrolysis

a. Test some sodium carbonate solution with litmus papers (?). Explain the reaction of the solution [C 319; I 469].

b. Repeat a with cupric sulphate solution (?) and explain (?).

c. Repeat a with solutions of potassium iodide, aluminium sulphate, lead nitrate, and sodium nitrate (?). Write the equation for hydrolysis in each case (?). Where there is a reaction towards litmus, explain it (?). If there is none, explain why (?).

d. Dissolve a single crystal of sodium sulphide in water, and test the solution with litmus paper (?). What ionic substance causes this reaction? Which of the two substances taken is capable of furnishing this ion? Formulate *in detail* the interaction of the two original substances and explain it [C 322; I 467].

67. Sulphur Dioxide

a. Place on a watch-glass a particle of sulphur and touch it with a warm platinum wire. (If platinum is not available, a piece of iron wire may be used.) Bring the wire with the adhering sulphur again into the flame. Withdraw and note the color (?) of the flame of burning sulphur and the odor (?) of the gas produced. Name the gas that has this odor (?), and write the equation (?).

b. Heat in a hard glass test-tube a few particles of iron pyrites. What is the sublimate? What gas is evolved?

c. [Hood.] Place a few copper shavings in a test-tube, cover them (and no more) with concentrated sulphuric acid, and fix the tube in a clamp on the stand. Place the bulb of the thermometer in the acid, heat slowly and continuously, and note the temperature at which chemical action becomes apparent (?).

Remove the thermometer and smell the gas (?). Heat the materials with a small flame while proceeding with **d**. Then set the tube aside and, the next day, examine and describe all the contents (?).

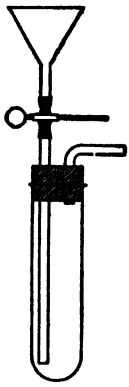


FIG. 24.

d. [HOOD.] If sulphur dioxide gas is not furnished in the laboratory from cylinders of the liquid, it may be prepared for use in later experiments as follows:

Fit a wide test-tube with a 2-hole stopper, straight tube reaching almost to the bottom, funnel, pinch-clamp, short rubber connection, and short L-tube. Set this up as in Fig. 24, using the triangle on a ring to support the funnel, and a clamp to hold the test-tube. Test for air-tightness (Exercise 3 **d**). Place in the test-tube about 10 c.c. of sodium bisulphite, and attach to the L-tube, by means of a rubber connection, a straight glass tube reaching down to the bottom of an upright, dry test-tube. Put dilute hydrochloric acid in the funnel, and admit it drop by drop to the apparatus. If there is little evidence of action (bubbling), the apparatus may be warmed very slightly to start the reaction.

Formulate in detail the equations which express this reaction [C 326; I 476].

68. Molecular Weight of Sulphur Dioxide

a. If this experiment is to be performed quantitatively, a gas washing-bottle (Fig. 25) will be required to dry the gas obtained as in 67 **d**, and should contain enough concentrated sulphuric acid to immerse the longer tube to a depth of half an inch. Attach the longer tube of the bottle by rubber tubing to the generating flask.

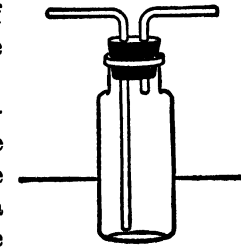


FIG. 25.

b. Clean and dry a 250 c.c. flask and provide it with a tightly fitting cork. Weigh the flask and cork. This gives the weight of the flask filled with air. Now, by means of a glass tube attached to the short exit of the washing-bottle and passing to the bottom of the flask, fill it completely with sulphur dioxide, by upward displacement of air, cork, and weigh again. To insure its being full, repeat this operation till no increase in weight occurs. Finally,

allow the gas to escape and determine its volume. To do this, use the graduated cylinder and fill the flask with water up to the cork (?). Observe the temperature and pressure of the atmosphere (?). Correct the volume to 0° and 760 mm. pressure.

To obtain the weight of the empty flask and its cork, subtract from the weight of the vessel filled with air the weight of a volume of air equal to the corrected volume (1 liter of pure, dry air weighs 1.293 g. under normal conditions, or the G.M.V. holds 28.995 g. of air).

The difference between this weight of the empty flask and that of the flask filled with sulphur dioxide is the weight of the gas. Using the volume of the flask at normal conditions, calculate the weight of the G.M.V. (22.4 l.) and of 1 l. of sulphur dioxide (?).

Enumerate carefully all the sources of error to which you should expect this way of determining the density of a gas to be liable (?). In doing this, consider each detail of the operation very critically.

Temp. ° Barometer (corr.)	mm.
Vol. of flask	c.c.
Vol. of flask, 0° and 760 mm.	**c.c.**
Wt. of flask + air	g.
Wt. of air (calc.)	g.
Wt. of flask, empty	**g.**
Wt. of flask + SO_2	g.
Wt. of flask, empty	g.
Wt. of SO_2	**g.**
Wt. of 22.4 l. SO_2	**g.**

69. Properties of Sulphurous Acid

Use a stream of sulphur dioxide from a cylinder of the liquefied gas, or from the apparatus described in **67 d.** Boil about 50 c.c. of water for two minutes, pour into a clean flask, cork immediately, and set it aside to cool for use in **b, c, d,** and **e.** Meanwhile perform **a, f, g,** and **h.**

a. Pass a stream of sulphur dioxide for a few minutes into a test-tube full of water. Test the solution with litmus paper (?). What compound is present in the aqueous solution of the gas? Note also the odor of the liquid (?). Formulate the interaction, showing all the substances present.

b. Pass sulphur dioxide through the water that was boiled, let-

ting the gas run for about 5 minutes [Hood]. Divide the solution into four portions. Boil one portion persistently in an evaporating dish [Hood] noting from time to time the odor and reaction towards litmus (?). Why should you not use the solution from **a** in this experiment?

c. To the second portion immediately add barium chloride solution (?). To ascertain whether this action is easily reversible, add excess of pure hydrochloric acid (?). Why should you not use the solution from **a** in this experiment?

d. To the third portion add bromine-water (?) until the color is permanent (?). Now add barium chloride to the mixture (?) and then pure hydrochloric acid (?).

What chemical properties of sulphurous acid are illustrated in **a, b, c,** and **d,** respectively?

e. Leave the fourth portion of the sulphurous acid for several days exposed to the air in an open test-tube or bottle. Then add barium chloride and pure hydrochloric acid, and compare the result with that in **b.**

f. To 2–3 c.c. of potassium dichromate solution, add three or four equivalents (a large excess) of dilute sulphuric acid. What substances does the mixture contain? Lead a stream of sulphur dioxide through the solution until no further change is observed (?).

g. Take 2–3 c.c. of potassium permanganate solution, treat as in **f** (?), and answer the same questions (?).

h. Fill a bottle with the gas by upward displacement, introduce some moistened litmus paper and a carnation or some leaves or grass, and a small piece of an apple, and close with a glass plate (?). Place another piece of an apple in an evaporating dish. Later, remove the first piece of apple from the bottle and place it on a watch-glass. After exposure to the air for a day or more, compare the pieces of apple (?).

What properties of sulphurous acid are illustrated in **e, f, g,** and **h,** respectively?

70. Sulphites

a. How should you prepare a solution of (1) sodium sulphite, (2) sodium bisulphite, from sulphurous acid? Write the equation in each case.

b. To 1 g. of sodium sulphite add any dilute mineral acid (that is to say, one of the common acids, but not an organic acid such as acetic) (?). Formulate this action completely.

c. Dissolve a minute amount of sodium sulphite in water and add bromine-water in excess (test? The color must remain). Remove the excess of bromine by boiling. Add barium chloride solution (?) and then pure hydrochloric acid (?). Compare this experiment with that in **69 d**, consider whether it is probably the molecular sodium sulphite, or the sulphite-ion, which is oxidized and make the equation accordingly (?).

d. Heat persistently about 1 g. of sodium sulphite in a porcelain crucible, supported on the clay triangle over a blast-lamp. When cool, acidify with hydrochloric acid (?) and note the odor. If any sulphur is precipitated, account for its formation.

e. Place about 1 g. of sodium bisulphite in a hard glass test-tube and heat cautiously with the tube in a horizontal position (why?). Note the odor (?) and whether any vapor condenses (?). This behavior is typical of that of many acid salts. What would be the final effect of heating sodium bisulphite more strongly and for a longer time?

71. Preparation of Sulphuric Acid

a. (Two students working together.) Obtain a distilling-flask (25 c.c.), rubber connections for a safety bottle, a screw-clamp, and a Chapman pump from the storeroom. Fit up with your one-liter bottle the apparatus as in Fig. 26. Charge the hard glass tube with about 10 g. of granular pyrite,* and place a small, loose plug of asbestos just beyond the pyrite to retain any unburnt sulphur. Put into the distilling-flask about 10 c.c. of pure concentrated nitric acid. The safety bottle, half filled with water to show the rate at which air is being drawn through the apparatus, is attached to the water pump. The total air admitted is regulated by the screw-clamp between the pump and the safety bottle, while the proportions which pass over the pyrite and which carry over the nitric acid vapor, respectively, are regulated by pinching one of the tubes with the finger and thumb.

* In case very pure pyrite is not available, it is better to depart from the common manufacturing process by substituting a boat containing a little sulphur.

b. First heat the pyrite in a very slow stream of air until the sulphur burns. Then warm the nitric acid and, by pinching the tube admitting air to the pyrite-burner, divert part of the air current so that it may carry over a little of the vapor of the acid. Heat the pyrite strongly and continuously. Repeat the introduction of air laden with nitric acid at intervals, whenever the disappearance of the red fumes in the bottle shows that a further supply is needed.

c. After a crust of white crystals (?) has formed in the bottle (there may be considerable delay before crystallization starts), remove the attachments and blow the gases from the interior by

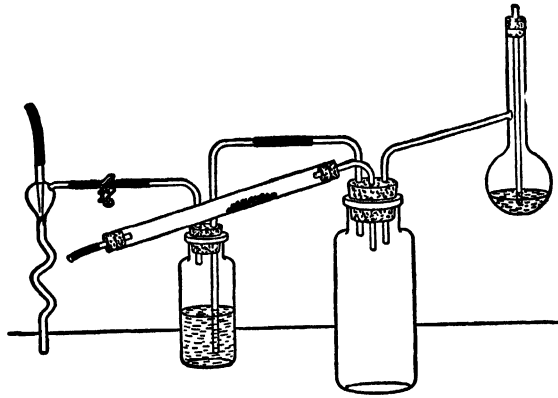


FIG. 26.

means of the air blast. If crystallization fails to begin after a reasonable time (note that an interaction even between the molecules of gases may be slow, in spite of the completeness of the mixing), the cause is either the introduction of too much water along with the nitric acid, or the high temperature produced by the chemical actions taking place in the bottle. Removing the attachments and cooling the bottle in a stream of water frequently brings crystallization about.

d. Add 4–5 c.c. of water and wash down the crystals with it. Describe all that happens (?). If more of the product is required, the apparatus may be connected up again and a further supply of sulphur dioxide drawn into the bottle, and subsequently more nitric acid vapor can be added. Finally any remaining crystals may be decomposed by water.

e. Filter the liquid in the bottle through a very small filter paper into a dish, rinsing the bottle with 2–3 c.c. of water, and evaporate on the sand bath [HOOD] until the liquid begins to fume strongly (?). This will remove any nitric or nitrous acid that it may contain. Use the result for 72 a and b.

Be very cautious in all of your dealings with concentrated sulphuric acid. It is good neither for the clothes nor for the skin. On no account empty residual acid into the sink until it is quite cold, or you may need a new pair of eyes. It is not worth while taking any chances.

72. Properties of Sulphuric Acid

a. Dip a match-stick into the liquid from 71 e (or into a few drops of concentrated sulphuric acid), and make marks on a sheet of paper. Place both paper and stick in a warm place (?). What property of the acid is here observed? Have you encountered this property before (refer to 23 e)?

b. After the acid prepared in 71 e is cold, take 5 c.c. of water and pour into it about 1 c.c. of the acid [CAUTION! Never pour the water into the acid. Why?]. Touch the back of the hand with the bottom of the test-tube (?). Test the solution with litmus paper (?). To 2–3 drops of the acid add barium chloride solution (?). To learn whether the action is easily reversible, add pure hydrochloric acid to the mixture (?). The formation of this precipitate, and its insolubility, furnish a distinctive test for what radical? Which substances contain this radical? To the rest of the acid add a minute amount of cupric oxide (pulverized) and warm gently for one minute or more (?). Can an oxide of a metallic element be formed in presence of sulphuric acid? What property of sulphuric acid is shown in b?

c. Pass a current of hydrogen sulphide through 2–3 c.c. of concentrated sulphuric acid. Note the odor (?) and precipitate (?). What property of sulphuric acid is shown in c? What other evidence of this property have we previously observed (see 16 e and 54)?

d. Place a small piece of sulphur in 2–3 c.c. of concentrated sulphuric acid, and heat (?). Note the odor (?).

e. Heat a little charcoal with sulphuric acid and note the odor (?). What property of sulphuric acid is shown in d and e? Why would not dilute sulphuric acid show this property?

f. [HOOD.] Take 2–3 c.c. of concentrated sulphuric acid in a test-tube. Suspend a thermometer so that the bulb is completely immersed in the acid. Heat the contents of the tube by means of a small flame and note the temperature at which any effect (?) is observed, and that at which it is conspicuous. Relate this temperature to that observed in 67 c. [CAUTION! During the heating remember that, if the tube should crack, the hot acid may splash on the clothes and hands and produce severe burns. Hold the burner in the hand, and place a large beaker below the test-tube. Exercise proper caution. Be very careful not to wash out this tube until the acid has cooled.]

73. Sulphuric Acid as a Dibasic Acid

a. (Two students working together.) Fill a burette with a solution of potassium hydroxide [Instructor]. Add 15 c.c. of concentrated sulphuric acid slowly to 35 c.c. of water in a beaker, and fill another burette with the diluted acid, when cold. Ascertain as in 48 what volume of the alkali will neutralize 5 c.c. of the acid. Concentrate the mixture in an evaporating dish to about 10 c.c., remove the dish from the water bath, and allow the resulting solution to crystallize. Dry the crystals on filter paper. To a second portion of the acid (use no phenolphthalein. Why?), twice as great as before, add exactly the same amount of the alkali. Evaporate to about 5 c.c. and treat as before.

Compare the two lots of crystals as regards (a) form, (b) taste, (c) reaction of their solution towards litmus. Confirm by studying the same properties of the pure substances. Explain the differences in these three respects between your own preparations and the pure ones, if any are observed. Explain, in terms of the hypothesis of ions, the difference in the reactions of the two products towards litmus.

Formulate, study, and explain the actions [C 337; I 492]. Take the components of the original solutions one by one, and describe what happens to each, (a) during complete neutralization, (b) during semi-neutralization in the second part of the experiment.

How many grams of potassium-hydrogen sulphate are required to give 1 liter of a solution of normal concentration in respect to (a) potassium-ion, (b) hydrogen-ion, (c) sulphate-ion?

b. Make a solution of sodium bicarbonate and test it with lit-

mus paper (?) and with Congo red paper (?). Why do some acid salts show little or no acid reaction towards indicators?

Define carefully, and illustrate, the terms: normal (neutral) salt, acid salt, and basic salt [C 227; I 368].

74. Sulphates

a. What would be the effect of heating perfectly dry specimens of each of the salts prepared in **73 a** [C 337; I 492]? In what way is the behavior of potassium bisulphite different (**70 e**), and why?

b. Place some ferric sulphate in a porcelain crucible supported on the clay triangle, and heat strongly [HOOD] with the blast-lamp, continuing the heating after all the water has been driven off (?). What are the properties of the vapor given off (?), and what is it? What is the residue? Relate this result to that in **72 f**. Recall action of heat on dehydrated gypsum (**24**). Classify the sulphates in accordance with this distinction.

75. Thiosulphates

a. Dissolve about 5 g. of sodium sulphite in about 20 c.c. of water in a small flask. Add 4–5 g. of flowers of sulphur to the solution and boil gently over a small flame for 10–15 minutes. Filter off the clear solution.

b. To a portion of the filtrate add excess of any dilute mineral acid (?). Note the odor (?).

c. Heat persistently about 1 g. of sodium thiosulphate in a porcelain crucible over a blast-lamp (?). Note the appearance of the residue (?). When cold, add dilute hydrochloric acid (?) and identify the products. If any odor was observed during the heating, can you now account for it?

76. Reduction of Sulphur Compounds

Mix a pinch of any salt of a sulphur acid with an equal amount of anhydrous sodium carbonate. Slightly char the end of a match from which the head has been removed, and rub the charred part, which should be about an inch in length, with a heated crystal of hydrated sodium carbonate. Moisten the above mixture with water, place some of it on the end of the match, and heat in the

reducing region of a small Bunsen flame. Put the result on a clean silver coin lying in a watch-glass and moisten with one drop of water (?). Examine the coin (?). Then add some dilute mineral acid and note the odor (?). This, known as the "hepar" test, is a test for sulphur in any form of combination.

CHAPTER XIII

THE ATMOSPHERE, NITROGEN, AMMONIA

77. Nitrogen from the Air

a. (Two students working together.) Set up the apparatus as shown in Fig. 27, and connect the rubber tube on the left with the water supply. Roll up the copper gauze and insert it in the middle of the hard glass tube.

b. Heat the copper gently at first, using a Bunsen burner with a wing-top (?). Increase the flame gradually until the whole length

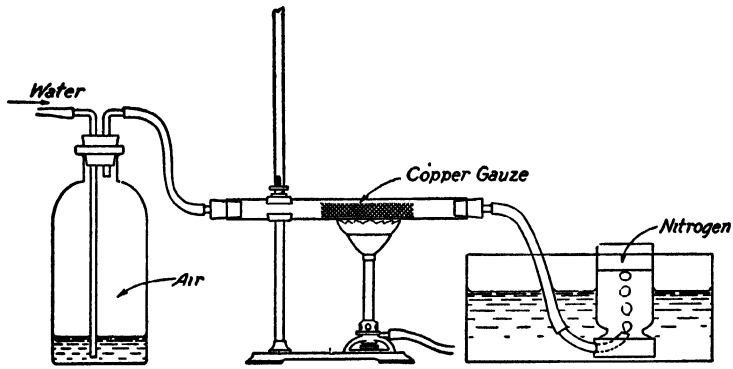


FIG. 27.

of the gauze is strongly heated. Now turn on the water carefully so that the air in the large bottle is slowly displaced and driven over the hot metal.

c. Collect two bottles of the gas that passes over into the trough and cover the mouth of each with a glass plate. Test the first with a lighted taper (?). Leave the second uncovered for a few minutes and test with a taper again (?).

d. Examine the gauze after it has cooled. How has its appearance been changed? What is the material formed? Write the equation (?). How could you prove this and, at the same time, recover the gauze in its original form [C 121; I 163]?

78. Proportion (by Volume) of Oxygen in the Air

a. Provide a large test-tube with a two-hole cork (a rubber stopper is apt to slip out in use). Into one hole fit a short piece of glass tubing terminating in a rounded nozzle, the tip of which projects but little beyond the bottom of the stopper. Into the other hole fit a short glass rod. Test the apparatus for air-tightness. Connect the upper end of the glass tube with a short-stemmed funnel by means of a piece of rubber tubing (15 cm. long) as in Fig. 28, and support the funnel in a clamp.

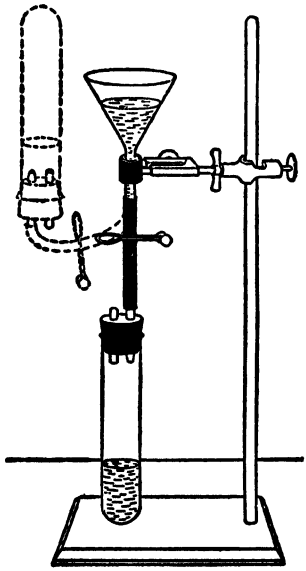


FIG. 28.

b. Disconnect the test-tube, temporarily, and remove the glass rod from the cork. Prepare an alkaline solution of potassium pyrogallate by mixing 3 c.c. of pyrogallic acid solution with 20 c.c. of a solution of potassium hydroxide specially prepared for this experiment, and pour this into the funnel. The following operations should consume as little time as possible, as the alkaline solution gradually absorbs oxygen from the air of the room, and thereby becomes useless for further absorption. Now open the clamp and permit this solution to fill the rubber and glass tubes completely down to the opening of the nozzle. Replace the test-tube, fitting the cork tightly into its mouth. Finally, reinsert the glass rod, and so inclose a volume of air equal to the content of the test-tube and at the temperature and pressure of the atmosphere.

c. Now open the clamp, taking care not to warm the test-tube by handling (use a piece of filter-paper when touching the test-tube). A few drops of the alkaline solution will enter the test-tube and, as the oxygen is absorbed, more of the solution will flow in. Close the clamp and invert the test-tube once or twice in order to bring the liquid thoroughly in contact with the inclosed air. Finally, while the test-tube is in the inverted position, reopen the clamp and equalize the levels of the liquid in test-tube and funnel

by raising or lowering the former. Then close the clamp, restore the test-tube to its original position, and mark the levels of the surface of the liquid and of the bottom of the cork by means of paper labels or rings cut from rubber tubing.

d. Disconnect the test-tube and wash out the liquid, taking care not to get the alkaline solution upon the hands. Then, by means of a burette, or graduated cylinder, filled with water, measure the volumes required to fill the test-tube up to the lower and upper marks respectively (?). The former is the volume of the oxygen, the latter that of the air. Calculate the percentage of oxygen in the air by volume (?).

Reference for additional work. A Method for the Quantitative Determination of Oxygen in the Atmosphere; Cooke, Journal of Chemical Education, 6, 105, 1929.

79. Other Components and Density of Air

a. Place 2–3 c.c. of clear barium hydroxide solution in a small beaker and leave it exposed to the air for some hours (?). Explain the result, and write the equation for the action (?).

b. Blow air from the lungs through a glass tube into 2–4 c.c. of clear barium hydroxide solution (?). Explain (?).

c. Fill two bottles with water and invert them in the trough. By means of a tube, fill one with air from the lungs immediately after drawing a breath. Fill the other with air after the lungs have been almost emptied. Slip a glass plate under each bottle and set both upright on the table. Light a taper and plunge it into one bottle (?) and then into the other (?). Explain the result (?).

d. How may the presence of aqueous vapor in air be demonstrated (34 **b**)? How may its quantity be measured?

e. The weight of a measured volume of air, or of nitrogen, may be determined by the method described in 97 **f**. From the data so obtained the density may be calculated.

80. Nitrogen from Its Compounds

a. Place about 10 g. of pure sodium nitrite and about 8 g. of ammonium chloride in a 250 c.c. flask fitted with safety and delivery tubes (Fig. 14, Exercise 17). If **b** is to be performed, insert between the flask and the delivery tube a U-tube containing calcium chloride for drying the gas.

Clamp the flask by the neck to a ring-stand, add about 15 c.c.

of water, and warm gently [CAUTION!]. As soon as the action begins, remove the flame, bring a dish of cold water under the flask, and cool it for a few seconds at a time so that the action may not become too violent, but may run uniformly. After sufficient time has been allowed for the displacement of air from the apparatus, fill a bottle with the gas over water in a pneumatic trough. Has the gas odor or color? Does it support combustion?

Write the equation for the reaction in detail. How does the product in this experiment differ from that obtained in 77 c?

b. (Two students working together.) In a piece of hard glass tubing, fitted with corks and short pieces of glass tubing, place a porcelain boat half filled with powdered magnesium. Connect one end of this tube to the outlet tube of the flask in **a**, generating nitrogen. Heat the magnesium strongly (two Bunsen burners may be necessary). What action is noticed? What is the color of the product? Transfer the contents, when cold, to a dry test-tube, close with a cork, and use in **81 g**. May the same product be formed when magnesium is heated in the air? What other compound would be formed under the latter conditions? Examine the glass tube and name the shining black substance on the inside surface [**C 523; I 658**] (?).

81. Ammonia

a. From Organic Matter. Mix on a sheet of paper 0.5 c.c. of gelatine with an equal quantity of soda-lime (a mixture of caustic soda and quicklime) and place in a dry test-tube. Place moistened litmus papers (blue and red) in the mouth of the tube and heat gently. Note the odor (?) and effect on litmus (?). Insert a glass rod wet with concentrated hydrochloric acid (?).

Almost all organic compounds containing nitrogen give ammonia when heated with soda-lime, and this is therefore a test for such compounds.

b. From an Ammonium Salt. Place a little ammonium chloride in the palm of one hand, a little slaked lime in the other, and rub the two together. Note the odor (?) and effect on moistened litmus paper held over the mixture (?).

Repeat, using a mixture of ammonium sulphate and slaked lime (?). Write the equation for both reactions.

c. Take one-fourth of a test-tube full of ammonium chloride

and mix it thoroughly on paper with an equal volume of slaked lime. Place it in a test-tube provided with a one-hole stopper and L-tube long enough to reach the bottom of the inverted bottle (Fig. 29). Clamp the tube so that the mouth is inclined very slightly downwards (to prevent condensed moisture running back). Arrange the perforated card on a ring, and first slip an inverted test-tube over the L-tube. Provide a test-tube containing a few drops of concentrated hydrochloric acid. Also, place water in the trough.

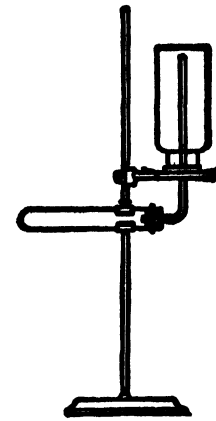


FIG. 29.

Warm the mixture very gently with a small flame. Dip the end of a thin glass rod in the hydrochloric acid, and bring it close to the perforation in the card to ascertain when the test-tube is filled with the gas. Dense smoke will notify you of this condition. Remove the test-tube, closing it firmly with the thumb, and with the other hand set a bottle (to be used in e) over the L-tube.

d. Place the mouth of the test-tube under water and remove the thumb (?). Is the gas soluble in water? How does its behavior compare with that of chlorine (Exercise 40 a) in this respect?

e. Warm a second bottle by moving it rapidly through the flame. Do not let it rest in the flame or it will crack. Place in the bottle a few drops of concentrated hydrochloric acid, cover it with a glass plate, and rotate it horizontally so as to spread the acid as completely over the inner surface as possible.

Now, ascertain by use of the rod dipped in hydrochloric acid (refer to c above) whether the first bottle is full of ammonia. When it is, raise it off the tube, and slip a glass plate under the mouth. Bring the two bottles mouth to mouth and remove both plates. Invert the pair of bottles once or twice to mix the gases (?). What is the deposit? Describe its physical properties (?). Write the equation for the action (?).

f. Swing the L-tube downwards so that its free end is just above (but not touching!) the surface of about 5 c.c. of water in the bottom of a beaker. At the end of 5 minutes pour the solution into

a test-tube, cork it up, and reserve for use in Exercise 82. During the five minutes, swing the water round in the beaker occasionally to submerge the surface layer. Concentrated ammonia has a density of 0.88, *i.e.*, 1 c.c. weighs 0.88 g. Will the solution float or sink? What difference would it make if the beaker were left at rest? Contrast with Exercise 29 b.

If you were required to determine the density of gaseous ammonia, which of the various methods should you select (15, 68, or 97 f)?

g. To the product from 80 b add a little water, boil, and note the odor (?). What other substances would behave in the same way as magnesium nitride?

82. Hydroxide and Salts of Ammonium

a. Ammonium Hydroxide. Dip a rod in the solution made in Exercise 81 f and touch litmus papers with it (?). To what class of substances does the material in solution belong? Write the equation for the formation and reaction of this material (?).

b. Pour a part of the solution into an evaporating dish and boil it. From time to time observe its odor and reaction towards litmus papers (?), proceeding meanwhile with c. What must have happened to the compound in the solution? Is it a stable or an unstable compound [C 406; I 569]? Write the complete equation (?).

c. Place the rest of the solution in a beaker, add dilute hydrochloric acid a little at a time, stirring with a rod and testing the liquid on litmus papers until the liquid is neutral. Evaporate the liquid in a dish almost (but not quite) to dryness (lower the flame towards the end), allow it to cool and describe the residue (?). Write the equation (?).

d. Ammonium Salts. Place not over 0.2 c.c. of ammonium chloride in the bottom of a dry hard glass test-tube. Clamp the latter in a horizontal position, and place in the mouth of the tube moistened litmus papers (red and blue). Heat the salt and watch the test papers for any changes and describe them (?).

Is there evidence that the salt decomposed? What were presumably the products? Make the equation (?). Would these products recombine (partially at least) in the cool part of the tube? Is there any sublimate visible (?) and if so, what is it?

e. Test for Salts of Ammonium. Take 2 c.c. of sodium hydrox-

ide solution and add a few particles of any salt of ammonium (for example, the sulphate). Warm, and observe the odor (?).

Write the equation as a double decomposition (?). Which of the products decomposes further to give the ammonia?

The evolution of ammonia when a strong base is added to a solution of any ammonium salt is used as a test for the latter. Why would not simply heating the salt by itself (as in **d**) serve as a test? What salt of ammonium that we have used gives, when heated, no ammonia? Name other salts of ammonium which likewise give no ammonia [**C 420, 693; I 595, 958**] (?). Conversely, what substance when heated gave ammonia, yet contained no ammonium salt (**a**)? What other substances behave thus [**C 401; I 562**]?

CHAPTER XIV

OXIDES AND OXYGEN ACIDS OF NITROGEN

83. Preparation of Nitric Acid

a. Put about 20 g. of powdered sodium nitrate in a tubulated retort. Insert the neck of the retort into the mouth of a flask (Fig. 30). Clamp the retort so that the body rests on the wire gauze over a tripod and the flask is partly immersed in a vessel of cold water. Through a funnel or thistle-tube pour about 15 c.c. of concentrated sulphuric acid upon the sodium nitrate, place the stopper in the retort, and wait until the acid has moistened the entire mass.

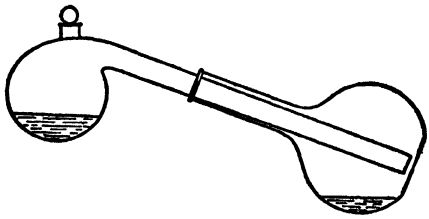


FIG. 30.

Caution: Sulphuric acid and nitric acid both produce severe wounds on the flesh and destroy clothing. The nitric acid to be prepared is "fuming," and the greatest care must be used in handling it. With large classes, sections a and b of this experiment are preferably performed in the lecture-room.

Heat the retort very gently [HOOD], and distil at as low a temperature as possible until no more liquid condenses in the neck of the retort (meantime, proceed with **d**). Allow the retort to cool before touching it. What is the brown gas seen in the retort (?), and whence does it come [C 412; I 578]? What is the residue in the retort? Write the equation.

b. Note the color of the acid prepared in **a** (?). Blow some air from the blast through the acid (?). What is the color of pure nitric acid? To what substance was the color of this sample due, and by what action was it formed? What property of nitric acid does its formation indicate? Blow the moist air of the breath over this specimen (?). What property does this indicate?

c. Divide the distillate between three dry test-tubes. In one place a piece of white woolen yarn (?), in the second a small piece of copper (?), and in the third a piece of a splint (?).

The action on copper is a test for nitric acid, by itself, or mixed with other substances. Write the equation.

d. Test for the Nitrate Ion NO_3^-. (Follow the directions with care.) Pour into a test-tube 3 c.c. of ferrous sulphate solution. Add to it two drops of dilute nitric acid and shake. Incline the tube very slightly, and pour concentrated sulphuric acid (not over 2 c.c.) in a steady stream down the wall of the test-tube so that (being a heavy liquid) it flows to the bottom and collects below the ferrous sulphate solution (?). Describe the coloration in the layer where the liquids meet (?).

Repeat the test, adding a small crystal of sodium nitrate, instead of the nitric acid, and shaking.

How should you recognize an unknown substance to be a nitrate? Devise a second test with the help of section c above.

e. Is the action of sulphuric acid upon sodium nitrate reversible? Take 2–3 c.c. of saturated sodium-hydrogen sulphate solution and add to it an equal or even greater volume of pure concentrated nitric acid. Cool the mixture in a stream of cold water and stir with a glass rod (?). The salt solution must be saturated, otherwise the experiment will fail. Examine with a lens the crystalline product that separates out (?). If the action is reversible, what enabled us to obtain a large yield of nitric acid in a [C 220; I 317]?

f. Will other acids behave like sulphuric acid? Mix some pulverized sodium nitrate with phosphoric acid, agitate for a minute or two, and apply the copper test as in a (?). Could phosphoric acid be used in the preparation of nitric acid as in a? Why? Could hydrochloric acid be used? Could hydrofluoric acid be used? Give reasons for your answers.

84. Nitric Oxide.

a. Fit up a generating bottle as in Fig. 14 (Exercise 17 a). Place in it copper shavings or clippings. Invert one bottle, one test-tube, and the graduated cylinder, all full of water, in the trough. Pour some water through the thistle-tube, and an equal volume of concentrated nitric acid, and wait for the action to start. Then

fill the bottle and test-tube with the gas, collect about 30–40 c.c. (only) of the gas in the graduated cylinder, and leave them standing in the trough.



Fig. 31.

Note the color of the gas in the generator just after the beginning of the action (?) and again later (?).

Note also the color of the liquid in the generator. This is characteristic of cupric salts, and is the color of the cupric-ion Cu^{++}.

b. What is the color of the gas? Use the test-tube full of the gas to test its solubility in water as in Exercise 40 **a** (?). What happens when the test-tube is opened to the air (this action is examined further in **d**)?

c. Place in the deflagrating spoon a little red phosphorus. Cover the bottle full of the gas with a glass plate, and set it upright on the table. Plunge a burning taper into the gas (?), withdraw it instantly, and cover the bottle. Set fire to the phosphorus, and when it is burning vigorously, plunge it into the same bottle (?). Write the equation.

Heat the spoon, to burn off the adhering phosphorus, before putting it away.

d. Fit a wide test-tube with a 2-hole stopper, L-tube and rubber delivery tube, and a dropper (Fig. 31). Place in the test-tube about 1 c.c. of sodium peroxide. Fill the dropper with water, and immerse the delivery tube in the trough. Pinch the dropper cautiously so as to allow one drop of water at a time to fall on the peroxide. When the air has been displaced from the test-tube and delivery tube (test?), read the volume of the gas collected in **a** in the graduated cylinder (?), and allow the oxygen to ascend, a few bubbles at a time, into the latter (?). Note the change in color (?). Slightly shake the water in the cylinder to bring it in contact with the gas. Does the volume change (?) and, if so, in which direction? Remember that oxygen gas is being *added*.

Finally, close the cylinder with a glass plate, set it upright, and test the water in it with blue litmus paper (?).

Write the equations for all the reactions that occur in this section.

e. Which component of the air caused the nitric oxide to become brown in **b**? What is the brown gas? What property of

the brown gas have you learned in **d**? What reaction to litmus had the water in the cylinder (?) and what was the substance formed [**C 415; I 586**]? What great industrial process is based on this reaction [**C 416; I 588**]?

f. Prepare 10 c.c. of a concentrated solution of ferrous-ion (use either ferrous-ammonium sulphate or washed crystals of ferrous sulphate) and divide it into two portions. Into one pass a gentle stream of nitric oxide (?). Boil the liquid (?).

g. Add to the second portion an equivalent amount of dilute sulphuric acid, heat to boiling, and add nitric acid drop by drop (mix after each drop) until there is no further action (?). What gas is liberated?

h. Take 2–3 c.c. of concentrated nitric acid in a test-tube, warm it slightly, and lead through it a stream of nitric oxide (?). By waiting until the air has been wholly displaced, make certain whether the colored gas is formed by an interaction of the nitric oxide with the nitric acid, or simply by contact with the air in the test-tube (?). To observe the color of a gas, do not look across the test-tube, but down the tube at a sheet of white paper.

85. Nitrogen Tetroxide

a. Fit a hard glass test-tube with a cork and L-shaped exit tube, and see that it is air-tight. Place 8-10 g. of lead nitrate in the tube and clamp it in a horizontal position. Tap the tube until the salt settles in a layer, leaving a wide channel above it. Prepare a concentrated solution of sodium hydroxide by dissolving 2 g. of the solid in 7 c.c. of water and allow the delivery tube to reach the bottom of this solution. Now heat the lead nitrate (?) persistently until gas is no longer given off, or until the liquid is no longer soapy to the touch. If all the gas is not absorbed in the alkali, test the escaping bubbles for oxygen (?). Label the solution and set it aside for use in **88 e.**

b. What is the residue? This behavior when heated is typical of the nitrates of the heavy metals, and may be used for identifying them. Which nitrates, when heated, would leave the metal, instead of the oxide [**C 107; I 584**]? Why do commercial specimens of mercuric oxide [**C 632; I 870**], when heated in the preparation of oxygen, frequently give off a brown gas?

Reference for additional work. Oxidation of Ammonia to Nitric Acid—A Demonstration; Haut, Journal of Chemical Education, 11, 575, 1934.

86. Properties of Nitric Acid

a. Tabulate the properties already observed (**83**). Test dilute nitric acid with litmus paper (?).

b. Add 1 g. of sulphur to 2–3 c.c. of concentrated nitric acid and boil [HOOD] for two or three minutes (?). Is there any evidence of action? Pour the clear liquid into another test-tube, dilute with water, and test for the sulphate radical (?). What property of nitric acid is here shown?

c. The interaction of dilute (**16 d**) and of concentrated (**16 e**) sulphuric acid with metals has already been studied. Try the action of (a) magnesium and (b) zinc, separately, either upon dilute or upon concentrated nitric acid, and of (c) copper upon both, and explore the whole action thoroughly in each of the four cases as follows:

Fit up a side-necked test-tube with a dropping-funnel passing through a perforated cork, and attach a delivery tube (or use an ordinary test-tube with cork and delivery tube). Place a small amount of the metal in the tube and admit the acid from the dropping-funnel. After the air has been displaced, collect the gas over water in a test-tube inverted in the pneumatic trough (or in an evaporating-dish).

If the gases in the generating tube remain colored, nitrogen tetroxide is present. If the gas is at first colored, but becomes colorless, nitric oxide is present: confirm by admitting air to the tube in which it has been collected (to see color, look down the tube) (?). Hydrogen, if liberated alone, would show neither of these properties, but might be identified by its inflammability (?). If both hydrogen and nitric oxide are liberated, why may we not feel confident of being able to cause the former to burn when thus diluted? How can the nitric oxide be separated (**84 d** or **f**) so as to leave the hydrogen in an inflammable condition? Examine the gas in each case for these three substances.

If ammonia is formed in any of these four cases by complete reduction of the nitric acid, where will it be found, and in what condition? (Consider all the circumstances carefully, or you will answer wrongly.) Test for its presence (**82 e**) (?).

Evaporate on a water bath [HOOD] the solution remaining in

the side-neck test-tube after any one of these experiments (?). Collect the residue and heat it in a dry test-tube (?). In what form of combination was the metal (**85 b**)?

d. Place in a test-tube a small piece of granulated tin, and add cautiously some concentrated nitric acid (?). When the action has exhausted itself, add much water and boil. Fit a small filter paper carefully into a funnel, collect the solid product upon the filter and wash thoroughly both precipitate and paper with water. Test the filtrate as it runs through to see whether it becomes neutral (?). Inference? Spread the filter paper with the precipitate upon a water bath or radiator to dry and ascertain as in **85 a** whether the product is a nitrate (?). Why would the test in **83 d** be unsuitable here?

e. Comparing dilute and concentrated nitric acid with the same forms of sulphuric acid, what points of resemblance and of difference have you observed?

Account for the differences in the actions of dilute and of concentrated nitric acid in **c**, **d**, and **e**, in respect to the gaseous product of reduction which is typical of each.

f. To 1–2 c.c. of nitric acid add 3–4 c.c. of pure, concentrated hydrochloric acid, warm gently, and note the appearance and odor (?). Will these acids, singly, attack all metals? Explain (?). What metals are attacked only by the mixture (*aqua regia*), and why [**C 418; I 592**]?

87. Nitrous Oxide

a. In a large test-tube provided with a 1-hole stopper and rubber and glass delivery tube, place 10 g. of ammonium nitrate. Clamp the test-tube at an angle of 45°. Fill one bottle and two test-tubes with water and invert them in the trough (use warm water [?], if available).

Heat the nitrate cautiously but continuously with a small flame, and allow the gas to come very slowly. If, before the vessels are filled with gas, the nitrate threatens to give out [explosion possible], first remove the delivery tube from the trough, then stop heating, and add more ammonium nitrate.

Watch the water in the delivery tube. Does anything else appear to be produced along with the nitrous oxide gas? What is it?

Be careful, in this experiment, not to let the reaction run away from you. The decomposition of ammonium nitrate *evolves heat,* and you do not want to induce such a rapid rush of gas that your apparatus will blow up. There is absolutely no danger in this experiment if you follow instructions, but the picture opposite p. 403 of the *College Chemistry* will demonstrate to you what can happen when a large amount of ammonium nitrate suddenly decomposes.

b. Use one test-tube of the gas, as in Exercise 40 a, to find out whether the gas is soluble in cold water (?). Does the gas differ from oxygen in this respect?

c. Into the second test-tube thrust a glowing splinter (?). Does the gas differ from oxygen in this respect?

d. Line the deflagrating spoon with asbestos paper and place on it a little sulphur. Set fire to the sulphur, without heating the spoon. Immediately, while it is still burning feebly, thrust it into the bottle of the gas (?), and then remove it and cover the bottle. Heat the spoon until the sulphur burns briskly and thrust it into the bottle once more (?). How does the gas differ in behavior from oxygen? Note the odor in the bottle (?). What is formed when sulphur is burned in nitrous oxide?

e. Name two respects in which nitrous oxide differs from oxygen (?). When nitrous oxide is added to nitric oxide, no brown gas (Exercise 84 d) is formed: this is another difference. Devise a means of testing this statement experimentally. Submit your arrangement to the instructor for approval before trying it.

88. Nitrites and Nitrous Acid

a. Take 2–3 g. of sodium nitrate in a hard glass test-tube, and heat strongly and persistently with the blast lamp until the evolution of gas ceases. Test the escaping gas for oxygen. Use the residue in b. Write the equation for the reaction. What nitrates behave in this way when heated?

How does lead nitrate behave when heated? What other nitrates behave in the same way? How does ammonium nitrate behave when heated?

b. When the residue from a has cooled, add not more than 3 c.c. of water, shake vigorously until the whole has dissolved, and divide into three parts. To one portion add dilute sulphuric acid (?). How could a nitrite be distinguished from a nitrate?

c. To 5 c.c. of starch emulsion add a drop of potassium iodide

solution and some dilute sulphuric acid, and then introduce a little of the solution from **b** (?).

d. Dilute 1–2 c.c. potassium permanganate solution with a large excess of dilute sulphuric acid, and add a drop of this mixture to the solution from **b** (?). The actions in **b**, **c**, and **d** serve for the detection of nitrites and nitrous acid. What other characteristic property of nitrites has been encountered (**80 a**)?

e. Examine now the solution obtained by leading nitrogen tetroxide into sodium hydroxide (**85 a**). Take a portion of the solution and acidify (test?) with dilute sulphuric acid (?). To the mixture add a drop of diluted potassium permanganate solution (?) or some starch emulsion containing a drop of potassium iodide (?). What substance was present?

To ascertain whether this alkaline solution contains a nitrate as well as a nitrite, the latter must first be eliminated. To the remainder of the alkaline solution, transferred to a small flask, add at least 5 g. of ammonium chloride [Hood] and heat to boiling (?). Explain the evolution of ammonia (?). What other gas is given off (**80 a**)? When the action is entirely over, add about 10 c.c. of water, and shake. Prepare 2–3 c.c. of a concentrated solution of ferrous-ammonium sulphate (or of ferrous sulphate), add to it 1–2 c.c. of the solution to be examined, and complete the test for a nitrate described in **83 d** (?). Write now the equation for the action of nitrogen tetroxide on sodium hydroxide.

89. Identifying an Unknown Substance*

a. Obtain [Instructor] a single, unknown solid substance. It will contain one of the following negative radicals:

chloride	sulphite	chlorate
bromide	bisulphite	perchlorate
iodide	sulphate	nitrate
peroxide	bisulphate	nitrite
sulphide	thiosulphate	hydroxyl (base)

*Before you go on to Exercise **89**, read carefully through pages **533-9** of the *College Chemistry* or pages **671-7** of the *Inorganic Chemistry*, and answer the questions at the end as far as possible without reference to preceding chapters. When you have finished, turn back to these chapters to ascertain how well (or how badly) you made out on the questions. It is no use trying to identify a substance unless you know its distinctive properties. On the other hand, a perfect book knowledge of properties will not be of

In the case of a salt (except one of ammonium) we shall limit ourselves to identifying the negative radical only. The other positive radicals will, in any case, be limited to (Na), (K), and (Ca).

Record at the time the result of each observation. Record negative results also.

b. External Examination. Begin by recording the state (?), crystalline form (?), color (?), and odor (?).

c. Solubility and Reaction of Solution. Use a few particles to find out whether it is soluble in water (?). If in doubt, proceed as in Exercise **21 a.** Apply a drop of the solution to litmus papers (?).

d. Effect of Heating. Heat 0.5 c.c. in a dry test-tube. Watch the substance. Does it melt (?), or otherwise change (?)? Note also gases or vapors.

If WATER VAPOR is given off and condenses (?), the substance may be a hydrate, an acid salt, or calcium hydroxide. Incline the tube downwards, drive all the water off, dry out the tube with filter-paper, and continue heating. Does it now change (?), or give gases or vapors?

If a SUBLIMATE (solid deposit in the tube) appears (?), what is it? Note the odor (?) and apply the test for the positive radical (?).

A COLORLESS GAS with an ODOR (?) may be ammonia or sulphur dioxide (?).

A COLORLESS, ODORLESS GAS may be oxygen (test?). Which three of the above radicals will give oxygen? What substance will remain, in each case, when all the oxygen has been driven off? Keep the tube and residue for use in **f.**

much benefit to you, unless you can make a successful analysis. Here is your opportunity to correlate your lecture and your laboratory work to a more intimate extent than has been possible in any way hitherto. See that you make the best use of it.

The identification of unknowns is exceedingly instructive, since it forces you to recall the more significant physical and chemical properties of practically all the important substances you have studied in the preceding weeks of the course. Keep your eyes open all the time, and remember that a negative result is often just as significant as a positive one. When you think you have discovered what your unknown is, always try to invent for yourself a confirmatory test, utilizing the work done in previous experiments whenever possible. Do not guess, for you are almost certain to be wrong. Work systematically and observe intelligently, and you will soon find that you can spot the unknown every time.

A COLORED GAS may be nitrogen tetroxide (?). Inference?

e. Action of Concentrated Sulphuric Acid. To 0.5 g. of the substance add two or three drops (not more) of concentrated sulphuric acid (?). If a pale yellow gas appears [CAUTION!] do not heat, as the gas (?) is explosive. If no gas appears, warm gently (?).

A COLORLESS GAS (bubbling) which FUMES in the breath (?). Two possible sources (?).

A COLORLESS GAS, NON-FUMING, with an ODOR may be hydrogen sulphide or sulphur dioxide. One possible source of former (?) and three of latter (?).

A COLORLESS GAS, NON-FUMING, ODORLESS may be oxygen (?).

A COLORED GAS may be vapor of iodine or of bromine (?). It may be nitrogen trioxide (?). If yellow, it is chlorine dioxide (?). Inference as to radical (?).

No GAS (no bubbling) indicates a sulphate or a base (?).

f. To the residue from **d**, par. 5, add two or three drops of concentrated sulphuric acid (?). What is the inference if the gas is brown (?) and if it is colorless, but fumes in the breath?

g. Conclusion. In some cases the foregoing experiments fail to distinguish between two possible radicals. Apply special tests in these cases. In each case, if a special test exists, confirm your conclusion by applying it.

h. Report. State your conclusion, with reasons therefor (?).

i. Obtain a second unknown, and proceed as before (?).

CHAPTER XV

PHOSPHORUS

90. Phosphine

a. Place a very small piece of calcium phosphide in a little water in a test-tube (?). Note the odor * of the gas evolved (?). Is this gas combustible? Is its kindling temperature low or high? Try the reaction of the gas (not the liquid) with moist litmus papers (?). What mode of forming ammonia is similar to this, and how is it similar?

b. Repeat, using dilute hydrochloric acid instead of water (?). What mode of forming hydrogen sulphide is similar to this, and how is it similar? In what ways does phosphine differ from ammonia [C 426; I 605]? Which of the differences are shown in these experiments? Why should we expect ammonia and phosphine to be alike? Test with litmus the water in which the calcium phosphide was placed in **a** (?), and explain.

91. Metaphosphoric Acid

a. Throw 2 g. of phosphorus pentoxide, in minute portions at a time, into a beaker containing 10 c.c. of cold distilled water (?). Allow the liquid to stand for a few minutes, or until clear. Test the liquid with litmus paper (?). What acid is present [C 431; I 608]? Use the solution for **b** and **c** and **92 a**. Why could not the product made by burning phosphorus in a closed volume of air be used in this case?

b. To a part of the solution from **a** add silver nitrate solution, a little at a time, shaking between additions, until a permanent precipitate (color?) is formed (?). Is an action like this reversible? Is this action incomplete? To answer, add diluted (1 : 4 water) ammonium hydroxide solution, one drop at a time, observe whether

* Do not get too friendly with phosphine. Its smell is intensely disagreeable, and the gas is actually poisonous. Waft the gas gently towards you with your hand; do not put your nose directly over the mouth of the tube.

the precipitate increases, and explain. The first action of **b** is a reaction of what ion? What other substance would give it?

c. To 1 c.c. of albumen solution, add one or two drops of the solution from **a** [C 432; I 612] (?). This is a reaction of the free acid only, and not of metaphosphate-ion.

92. Orthophosphoric Acid

a. Dilute the remainder of the solution of metaphosphoric acid from **91 a** with 10 c.c. of water. Fit a small flask with a one-hole rubber stopper (or perforated cork), and insert a long piece of glass tubing, to act as a condenser. Boil the solution in this flask gently for an hour or more. If necessary, add more water to make up for the loss by evaporation. Cool the solution, treat portions of it with silver nitrate and with albumen, as in **91 b** and **c**, and answer the same questions. How may the formation of this acid, during the boiling, be hastened [C 429; I 608]?

Like all double decompositions, the one with silver nitrate is reversible, and is therefore incomplete. Name the interacting substances in the reverse action (?). To stop this reverse action, destroy the acid by adding ammonium hydroxide solution one drop at a time, noting the effect, shaking, and examining again. What evidence is there that the action now goes further forward?

Finally, add concentrated nitric acid (?). Which way does the action now go?

b. Heat 1 g. of red phosphorus with 5 c.c. of dilute nitric acid in a test-tube (?). When the action has ceased, filter, if necessary, and drive off the water and excess of nitric acid completely by evaporation [HOOD] on a water bath. Mix with a few drops of concentrated nitric acid the syrup which remains, and evaporate once more. It is essential that all the nitric acid be finally removed (why?). Redissolve the syrup in water and test with litmus paper (?).

Treat part of the solution with silver nitrate as in **91 b**, and answer the same questions (a black precipitate with silver nitrate is metallic silver, due to reduction by phosphorous acid [C 432; I 612] formed by incomplete oxidation).

c. Place in a test-tube 5 c.c. of the solution of ammonium molybdate in nitric acid, add to it two drops (only) of the solution of orthophosphoric acid prepared in **b**, and warm gently (?).

This is a very delicate test for phosphoric acid, or orthophosphate-ion.

93. Phosphates

a. Take some sodium phosphate (secondary sodium orthophosphate) solution and test it with litmus paper (?). What ions are present? Are acid salts always acid towards litmus? If not, explain why they are not. Explain also the actual reaction of this solution.

b. To a very small part of the sodium phosphate solution add silver nitrate solution until the precipitation is complete (?). What is the precipitate (see **92 a** and **b**)? To confirm this conclusion, test the reactions towards litmus of the sodium phosphate (**a**), and silver nitrate solutions singly (?). Test the mixture with litmus paper (?). What ion is evidently formed, and what product is therefore present?

c. Prepare a little "magnesia mixture" by adding to 1 c.c. of magnesium sulphate solution a few drops of ammonium hydroxide and then excess of ammonium chloride solution. Add to the rest of the sodium phosphate solution a little of this mixture (?). Scrape the walls of the test-tube, beneath the liquid, with a glass rod (?). In making the equation, disregard the ammonium chloride, which is added only to prevent precipitation of magnesium hydroxide. This is another test for the presence of what ions?

d. Heat strongly [Blast-lamp] 2 g. of dry sodium phosphate in an open crucible for twenty minutes, or until no further change is observed (?). Dissolve the cold mass in water (it dissolves very slowly), and test a portion of the solution with silver nitrate solution (?). This is a reaction of what ion? Take the remainder of the solution, liberate the acid (?) by adding acetic acid, and introduce a few drops of the liquid into a solution of albumen (?).

Make a table showing the effects of the three phosphoric acids upon albumen and the colors of their silver salts. How could you identify salts of the three acids?

e. Heat strongly [Blast-lamp] 2 g. of microcosmic salt as in **d**. Note the odor (?) and reaction towards moistened litmus paper (?) of the vapors given off. Dissolve the residue in cold water and use the tests tabulated in **d** to learn what salt has been formed.

f. Make a bead on a straight platinum wire as in Exercise **2 f**,

using microcosmic salt instead of borax. Of what must the bead consist? Now fuse with it (2 g) a minute particle of cupric oxide (?).

What difference do your experiments show as to the relative stabilities of $NaPO_3$, $NaNO_3$ (88 a), and $KClO_3$?

94. Halides of Phosphorus

a. What were the actions of water on the tribromide (51 a) and tri-iodide (53 a) of phosphorus?

b. Place 2–3 c.c. of phosphorus trichloride in a dry test-tube and blow the breath over the tube (?). Add water drop by drop (?) until about 5 c.c. has been used, then boil the solution. Test the vapor with litmus paper (?) and with a rod dipped in ammonium hydroxide (?). Evaporate [HOOD] the solution to a syrup on the water bath (?).

c. Transfer part of the syrup from **b** to a small test-tube and heat until the gas evolved may be ignited at the mouth of the tube (?). Note the odor of this gas before igniting it (?). Continue heating until the action is over. Ascertain according to 93 **d** which of the phosphoric acids constitutes the residue (?).

d. Dilute 1 c.c. of potassium iodide solution with water and dissolve in the liquid a crystal of iodine. Add to this solution a little of the syrup from **b**, and shake (?).

e. Place upon a watch-glass 5 or 6 small granules of phosphorus pentachloride and blow the breath over them (?). Throw them into 2–3 c.c. of water in a test-tube (?) and boil. Test the solution with litmus (?). To a very small part of the cold solution add excess (test?) of silver nitrate solution (?). Filter. What remains upon the paper (?)? To the filtrate add diluted (1 : 4 water) ammonium hydroxide one drop at a time (shake between drops) (?).

CHAPTER XVI

CARBON. OXIDES OF CARBON. HYDROCARBONS

95. Carbon

a. Place 10 c.c. of limewater in a 250 c.c. bottle. Burn a splinter of wood in the bottle, taking care not to drop any ashes into the liquid. Close the bottle with the hand and shake (?). If the change is not distinct, repeat the burning, using the same limewater, and shake again. What elements does wood contain? Make the equations for the formation of the carbon dioxide and for its reaction with the limewater.

b. Mix intimately in the mortar 5 g. of cupric oxide and 0.5 g. of powdered charcoal. Place this on a strip of paper, folded V-shaped, slip it into the hard-glass test-tube held horizontally, tilt so as to slide the mixture to the bottom of the tube, and withdraw the paper. Insert the stopper and L-tube. Place 10 c.c. of limewater in a test-tube. Clamp the tube containing the mixture in a horizontal position, at such a height that it can be heated, and let the L-tube project to the bottom of the limewater. If the tube is too short to reach the bottom, add a straight glass tube and rubber connection. The purpose is to compel any gas which may be given off to bubble through the entire depth of the limewater.

Heat the mixture, beginning at the end farthest from the stopper, at first gently and then strongly and persistently until bubbles almost cease to pass. What changes take place in the limewater [C 444; I 732]? Finally, take the tube out of the limewater and then remove the flame. When the tube is cold, grind the contents in the mortar with water, and wash away the lighter particles. Examine the residue (?). Make the equation for the action (?). What important industrial processes depend on this reaction? What was oxidized and what reduced in this reaction?

96. Carbon Dioxide

a. Place a few small pieces of magnesite (magnesium carbonate) in a hard glass test-tube fitted with a cork and L-tube and heat strongly. Pass the gas through 5 c.c. of limewater in a test-tube (?). What is the residue [C 588; I 796]?

b. Fit up a generating-bottle (Fig. 14, Exercise 17) and connect with two wash-bottles (Fig. 25, Exercise 68) containing water and concentrated sulphuric acid, respectively (what is the use of each of these? The latter is unnecessary if h is omitted). Place in the flask some pieces of marble and pour upon them diluted hydrochloric acid. Collect the gas in three bottles by upward displacement of air, and cover them with glass plates.

What substances could be substituted for marble in this experiment? What other sources of carbon dioxide have been encountered in previous experiments?

c. To one bottle add a little water, close tightly with the hand, and shake (?). Is the gas soluble in water, or not?

d. Light a taper and pour the gas from the second bottle over the flame, as you would water (?). Does the gas support combustion? Is the gas heavier or lighter than air?

e. Set an empty bottle (filled with air) over the remaining full one, and mouth to mouth with it, and withdraw the plate. After ten minutes, replace the glass plate between the bottles, remove the upper bottle, along with the plate, and set it upright upon the table. Slip the plate aside for a moment, add some limewater, replace the plate, and shake (?). Did the greater density of the carbon dioxide prevent its diffusing into, and displacing a part of the air? What are the relative rates of diffusion of air and carbon dioxide?

f. Take two test-tubes containing distilled water, pass a current of the gas into one, to saturation, and test each with litmus paper (?). Boil the solution, and test again with litmus (?). Explain.

g. Lead the gas into a little sodium hydroxide solution in a test-tube until the solution is saturated. Let the solution stand until it dries spontaneously (first residue). Heat the dry residue (?) in a test-tube, and determine what two things are given off.

To this residue after heating (second residue) add dilute hydrochloric acid until all action (?) ceases. Evaporate the solution on

the water bath, and examine and taste this final residue (?). Having recognized the products of the last action, and taking into account the preceding observations, state what the nature of the second and first residues must have been (?). Write equations for all actions (?).

h. Molecular Weight of Carbon Dioxide [Quant.]. Determine the weight of a measured volume of the gas by the method used for sulphur dioxide (68), and calculate the weight of the gram-molecular volume (?). What further information must we have to enable us to determine the formula?

97. Carbon Monoxide

Caution: The gas is poisonous (HOOD). Do not allow it unnecessarily to escape into the room. With large classes it is safer to perform this experiment as a lecture demonstration.

a. Fit a 200 c.c. flask with a 2-hole stopper, L-tube and rubber delivery tube, and the funnel and straight tube with pinchclamp as shown in Fig. 24 (Exercise 67). Place the flask on the ring of the iron stand (with wire gauze), at a suitable height for heating by a small flame. Hold the funnel erect in the clamp. Extend the delivery tube, if necessary, by adding a bent glass tube so that the gas may be collected over water. Remove the stopper, pour into the flask about 1 cm. depth of concentrated sulphuric acid, and replace the stopper. Pour some formic acid (care!) into the funnel, and never allow this entirely to run out during the experiment. Be careful to wash off any acid that you get on your hands *immediately* (?).

Warm the sulphuric acid gently (small flame), and then admit the formic acid a drop or two at a time. Collect three bottles full of the gas. What will the **first** bottle largely contain? Do not, *under any circumstances,* bring it near an open flame. What would happen if you were foolish enough to attempt to introduce a lighted taper into it? Let the bottle stand on the desk, open and mouth upwards, for a full minute. Now (not before!) try the lighted taper experiment (?). Explain.

b. Light a taper, raise the **second** bottle out of the water and plunge the taper up into it. Does the gas burn? Does the taper burn in the gas?

c. Slide the glass plate under the **third** bottle of the gas and remove from the trough. For a moment, move the plate to one side sufficiently to pour in a little limewater, taking care to let as little gas escape from the bottle as possible. Shake (?). Now light a taper, set fire to the gas in this bottle, replace the cover instantly, and shake again (?). What product is formed when carbon monoxide burns? Make the equation (?).

d. Pass a slow stream of the carbon monoxide over a little pulverized cupric oxide, heated in a boat in a hard glass tube (?). What gas is formed? What remains in the boat? What is here the reducing agent?

e. Heat about 10 g. of oxalic acid crystals with concentrated sulphuric acid in a generating-flask (Fig. 14, p. 32), and fill a bottle over water with the gas (?) which is given off.

Devise a way of ascertaining roughly the relative volumes of the components of this gas, and measure the proportion in a test-tube full of the mixed gases.

f. Molecular Weight of Carbon Monoxide [Quant.]. Obtain [Storeroom] a round-bottomed, 250 c.c. flask. Fit it with a rubber stopper through which passes a short, straight tube. Attach to the latter a short piece of rubber tubing closed with a strong pinch-clamp. Make a mark on the neck at the bottom of the stopper, so as to be able to measure the exact content of the flask up to the stopper. Place 30 c.c. of water in the flask, insert the stopper, remove the clamp, and boil the water with a small flame for about five minutes, so as to drive out all the air. Close the rubber tube with the clamp and remove the flame quickly, wipe the flask and allow it to cool. When it has assumed the temperature of the air, weigh the whole carefully, suspending the flask on the balance by a thread tied round the neck (?). Connect with the apparatus delivering pure carbon monoxide, and open the clamp a very little so as to admit a slow stream of the gas. When the flask is full, close the clamp, disconnect from the generating apparatus, open the clamp for an instant to restore the pressure to that of the atmosphere, and weigh again (?). The gain in weight represents the weight of the carbon monoxide. Read the barometer and thermometer (?). Subtract from the barometric reading the aqueous tension at the observed temperature. Ascertain the volume of the flask by filling with water to the mark from the graduated cylinder.

Calculate the weight of the G.M.V. of the gas (?).

To what class of gases would this method of determining the density and molecular weight be applicable? Why could not this method be used for carbon dioxide?

98. Methane

a. Mix about 2 c.c. each of powdered soda-lime and sodium acetate and place the mixture in a test-tube. Clamp this in a horizontal position * and insert in it a 1-hole stopper with L-tube pointed upwards. Tap the test-tube to cause the mixture to settle and heat it gently (small flame). Slip a test-tube over the vertical part of the L-tube. When the gas in this test-tube, on being lighted (after removal to a distance), burns quietly, set fire to the jet issuing from the apparatus.

b. Describe the structure of the flame (?). How luminous is the flame? Hold a dry bottle so that the flame burns inside it. If a dew appears in the bottle, what is it? Inference (?). Withdraw and close the bottle, and shake the contents with some limewater (?). Inference (?).

What volume of oxygen is required for the complete combustion of one volume of methane, and what ratio will the resulting volume of gases bear to the original volume of methane, at 0° and at 100°, respectively?

99. Ethylene [Hood]

a. Fit a 250 c.c. flask with a doubly-bored cork, through which pass a dropping-funnel and L-tube (Fig. 19, Exercise 36). Attach a gas-washing bottle containing a little water, and connect an L-shaped delivery tube. Test the apparatus to see that it is air-tight. Place in the flask about 20 g. of phosphorus pentoxide, and clamp it to a ring-stand over a sand bath. Introduce into the bulb of the dropping-funnel some alcohol. Finally, heat the phosphoric anhydride, and admit the alcohol drop by drop.

b. Fill a bottle with the gas (*not* a mixture of the gas and air [?]) over water and apply a light (?). Quickly pour some limewater into the bottle, and shake (?). Attach a nozzle to the exit tube of the washing-bottle and raise the other tube clear of

* If you do not clamp your tube in the position indicated, you will certainly crack it during the experiment.

the water in the washing-bottle (why?), ignite the gas, and observe the luminosity of the flame. What commercial use has ethylene [C 462; I 651]? Hold a cold, dry beaker over the flame (?). What are the products of complete combustion of all hydrocarbons?

c. Detach the nozzle, reattach the delivery tube to the exit tube, and lower the other tube of the washing-bottle once more. Place 1 c.c. of bromine [CAUTION!] in a test-tube, cover it with 5 c.c. of water, put the test-tube into a beaker filled with cold water, and allow the gas to bubble into the bromine. When the color of the bromine has disappeared, examine the contents of the test-tube (?). Is the product colored? Is it soluble in water? What do you infer as to its specific gravity? Detach the dropping-funnel, wash it out, and place in it the contents of the test-tube. Draw off the lower, oily layer into a dry test-tube and note its odor (?). Try its solubility in alcohol (?).

d. Why is the accepted formula for ethylene preferred to the simplest? What volume of oxygen would be required to burn one volume of the gas completely? What would be the relative volumes of the products at 0° and 100°, respectively? What volumes of bromine vapor and ethylene would be required for complete combination, and what would be the relative volume of the product (in the state of vapor)?

100. Acetylene

a. Fill a test-tube with water and invert it in water in an evaporating-dish. Introduce a small piece of calcium carbide under the mouth of the tube (?). Test the water with litmus (?). When the tube is filled with gas, bring a light to the mouth of the tube (?). Note the luminosity of the flame, and compare with flames of methane and ethylene (?).

b. Can you state a general method for making hydrides of nonmetals (such as C_2H_2, PH_3, NH_3)? Can SH_2 and ClH be formed similarly?

CHAPTER XVII

COMMON ORGANIC COMPOUNDS, NATURAL AND SYNTHETIC

101. Starch and Sugars

a. Shake about 0.5 c.c. of starch with 20 c.c. of water and then boil (?). Add a few drops of the liquid to 5 c.c. of Fehling's solution* and warm the latter (?). Does starch change Fehling's solution?

Place three-fourths of the remaining starch suspension in a flask, set it on the wire gauze, add 5 or 6 drops of concentrated hydrochloric acid, and boil gently for ten minutes. Place the funnel in the mouth of the flask, to diminish the loss by evaporation, and add a little water when necessary so as to keep the volume constant.

b. While this is going on, cool the rest of the starch suspension in running water and pour it into a beaker nearly full of cold water. Add one drop from 5 c.c. of a solution of potassium iodide in which a single crystal of iodine has been dissolved (?).

c. Cool the contents of the flask (from **a**) and add sodium carbonate solution drop by drop, shaking between drops, and touching the edge of a piece of litmus paper with a glass rod dipped in the liquid, until the liquid gives a faint alkaline reaction.

Now add a few drops of this liquid to 5 c.c. (measured) of Fehling's solution and warm the latter [**C** 470; **I** 749] (?). Add more of the liquid, boil again, and continue until the blue color is gone. It takes 0.005 g. of glucose to reduce and decolorize 1 c.c. of Fehling's solution. What amount of glucose was contained in the part of the liquid you added?

d. Dissolve about 0.5 g. of sucrose (ordinary sugar) in 20 c.c. of water and repeat **a** and **c** with this liquid. Does sucrose reduce Fehling's solution? Do acids hydrolyze it to give glucose? Write

*Make two solutions: No. 1, 69.3 g. of $CuSO_4,5H_2O$ with water to make 1 liter; No. 2, 350 g. Rochelle salt and 100 g. sodium hydroxide with water to make 1 liter. Mix equal volumes (measured) just before use.

the equation. The hydrogen-ion of the acid acts as a catalyst. Why is it not included in the equation?

e. Dissolve about 0.5 c.c. of molasses in water and test for glucose as in **a**, par. 1 (?).

f. Tabulate the physical and chemical properties of starch, glucose, and sucrose separately as follows: color (?), solubility (?), action on Fehling's solution (?), action of dilute acids (?).

Reference for additional work. A Laboratory Reproduction of the Viscose Process; James, Journal of Chemical Education, 8, 1171, 1931.

102. Acid and Alkaline Soils

a. Litmus Test. Place a red and a blue piece of litmus paper on a large watch-glass. Make the soil to be tested into a paste with distilled water, and press it on to the litmus papers. Leave the soil in contact with the paper for 15 minutes. Note whether the soil gives an acid or an alkaline reaction.

b. Measurement of Acidity in Soil. Place 100 g. of an acid soil in a 400 c.c. (or 12 oz.) wide-mouthed bottle. Add 250 c.c. of normal potassium nitrate, stopper the bottle, and shake the bottle by hand at intervals of five minutes. Let the mixture stand overnight. Withdraw 125 c.c. of the clear liquid from the top, boil it for ten minutes to expel carbon dioxide, cool it, and titrate with normal solution hydroxide, using phenolphthalein as indicator. Tabulate the results:

(1) Titration	..... c.c. NaOH
(2) Titration	..... c.c. NaOH
Average	..... **c.c. NaOH**

Calculate how much calcium carbonate would be required to neutralize the soil.

103. Fertilizers

a. Essential Plant-Foods. *Nitrogen:* Dissolve 16 g. of ammonium nitrate in 500 c.c. of distilled water. *Phosphorus:* Dissolve 5 g. of mono-calcium phosphate, or di-sodium phosphate, in 500 c.c. of distilled water. *Potassium:* Dissolve 10 g. of potassium sulphate in 500 c.c. of distilled water. Prepare these solutions carefully, using chemically pure salts, and label each bottle.

b. Pot-Culture Test for Plant-Food Requirements. Procure sufficient of a poor quality of soil to fill eight ordinary four-gallon butter jars. In the center of each pot make a drainage hole about

½ inch in diameter, cover this with a copper-wire netting, and place upon this a piece of glass wool extending over the hole. Fill each pot with the soil, pressing it in firmly.

Plant the series with wheat, oats, or other suitable crop. Remove the surface layer, distribute the seed, and return the soil removed. Use sufficient seeds so that a uniform number of strong seedlings may be left in the pot (about 20 seeds). Place the pots either in a greenhouse, or in the open, but so that they will be protected from severe wind or heavy rain. Water regularly.

To the first pot add no fertilizer. To the remaining pots add, at the time of planting, and weekly thereafter, 10 c.c. of the prepared solutions, as follows: Pot 2, Ammonium nitrate; Pot 3, Phosphate solution; Pot 4, Potassium sulphate; Pot 5, Ammonium nitrate and phosphate solution; Pot 6, Ammonium nitrate and potassium sulphate; Pot 7, Phosphate solution and potassium sulphate; Pot 8, All three solutions.

c. When mature, the crop should be harvested uniformly, and weighed. Afterwards, separate the grain from the straw, and weigh the grain. Compare the yields secured from the different fertilizers. What conclusions do you draw from your results?

104. Fermentation*

a. Mix 250 c.c. of molasses with 1500 c.c. of water in a bottle or large flask. Break up a cake of yeast, shake it with water until it is completely suspended, and add it to the molasses. Plug the mouth of the bottle loosely with cotton, and set the whole in a warm place for several days. This quantity will serve for 10–15 students. For individual experiments, take one-tenth of the above amounts.

b. Fit to the bottle a 1-hole stopper, L-tube, and rubber tube, terminating in a straight glass tube. Take 15 c.c. of limewater in a test-tube, insert the glass tube to the bottom of this, and shake the fermented liquid round in the bottle (?). Note the gas evolved and its reaction with limewater (?). In what form of solution was the gas before shaking [C 165; I 228]?

* You will certainly be disappointed if you attempt to reproduce this experiment on a large scale at home. The product obtained will not be satisfactory, and your friends will lose all confidence in your ability as a chemist. You will be well advised, therefore, to confine your studies on C_2H_5OH to the laboratory.

c. Filter off 100 c.c. of the fermented liquid, place it in a flask and distil as in Fig. 16, Exercise 21 **b**. After 30 c.c. has come over, empty and wash the flask, and redistil the distillate until 6–8 c.c. has come over. Note the odor of the distillate (?). Test it with litmus papers (?). Saturate a tuft of asbestos wool with the liquid, set the tuft on the base of the stand, and apply a light (?). Hold a cold, wide-mouth bottle over the flame, to recognize one product (?). Close the bottle and test the gas in the bottle by shaking with limewater (?). Make the equation for the combustion (?). If you burned alcohol vapor and pure oxygen, what relative volumes should you use; and what relative volumes of the products (measured as gases) would be formed?

d. To a few drops of alcohol in a test-tube add 1 c.c. of sodium hydroxide solution. Pulverize one or two (not more) crystals of iodine, add a part of the powder to the mixture, shake vigorously, and warm (?). The amount added must not be sufficient to give a permanent brown tint to the liquid. The precipitate is iodoform CHI_3 [C 455; I 640].

e. Summarize the observed physical and chemical properties of alcohol (?).

105. Acetic Acid

a. Take 5 c.c. of acetic acid and note its odor (?). Test it with litmus papers (?). To the acid add 3–4 g. of litharge [C 656; I 902] and boil gently for a few minutes (?). Filter, if necessary, while hot, and set the clear solution aside to crystallize (?). What is the common name of the product [C 658; I 905]?

To show that acetic acid is a weak acid [C 254; I 364], take 15 c.c. of water in each of two test-tubes. To one add the 5 c.c. of acetic acid and to the other add an equal volume (5 c.c.) of dilute sulphuric acid. Add a little zinc dust to the contents of each tube, and compare (?). Which reaction goes faster? Why [C 249; I 145]?

If acetic acid had been added to the starch (Exercise 101 **a**) or sucrose (Exercise 101 **d**), instead of hydrochloric acid (a very active acid), what change in the procedure would have been necessary to get the same result?

b. To about 0.5 c.c. of sodium acetate add 2 c.c. of water and 1 c.c. of concentrated sulphuric acid. Warm and note the odor (?).

Test the vapor with litmus papers (?). Make the equation, assuming that the second product is $NaHSO_4$ (?).

c. Summarize the properties of acetic acid (?). How would you proceed to test for an acetate?

106. Destructive Distillation of Wood and Coal

a. Wood. Take half of a hard glass test-tube full of sawdust and wood chips. Arrange the apparatus as in Fig. 32. The test-tube is inclined slightly downwards towards the mouth. The wide test-tube, in which the distillate is to be caught, is surrounded by cold water, and a nozzle is inserted in one of the holes in the stopper.

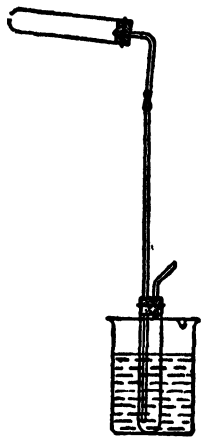


FIG. 32.

Heat the contents of the test-tube, at first gently, and later strongly, until no more vapors are evolved. During the heating, set fire to the issuing gas (?). Is the flame luminous, or not? Compounds of what element must be present?

b. Examine the condensed liquid. What liquid or liquids are seen? Test the liquid with litmus papers (?). What dissolved substance causes this reaction [**C 488; I 769**]? Examine, describe, and name the residue in the hard glass test-tube (?). Place it in a corked test-tube for use in Exercise **107**. Name five observed products from distilling wood (?).

c. Coal. Charge a hard glass test-tube with crushed soft coal, attach a clean test-tube to catch the distillate, and repeat **a** and **b**.

To test for hydrogen sulphide in the coal gas, dip a glass rod in lead nitrate solution, wipe it on a small piece of filter-paper, and hold the latter in the unlighted gas (?). What compound is formed on the paper (Exercise **64 d**)?

To test for ammonia in the condensed liquid, add a portion to a few grams of slaked lime in a test-tube and heat (?).

107. Wood Charcoal and Bone Black

a. Charcoal. Hold first a splinter of wood and then a splinter of charcoal in the flame (?). Describe how each burns (?). What is the cause of the flame in one case (?), and of the absence of flame in the other (?)?

b. Place a splinter of charcoal in a test-tube half-filled with water. Is charcoal heavier or lighter than water?

Hold the splinter of charcoal under the water by means of an iron wire, one end of which is twisted round it, and boil the water for five minutes. Remove the wire from the splinter. Does the latter now sink or float? Is carbon specifically lighter or heavier than water? Why is fresh charcoal lighter [C 488; I 770]?

c. To a test-tube half full of water add two or three drops of litmus solution. Add about 4 c.c. of powdered charcoal, boil for five minutes, and filter. Where is the litmus? What classes of substances, especially, are readily adsorbed by charcoal [C 489; I 771]?

d. Bone Black. Heat about 15 c.c. of bone black [C 504; I 785] in the crucible (covered). The purpose of the heating is to make the charcoal more active by driving out gases and moisture already adsorbed on the surfaces of its pores. Take two test-tubes half filled with water, and add to one enough molasses to confer a distinct tint, and to the other a few drops of cupric sulphate solution. Reserve a small portion of each for comparison with your final filtrates. When the bone black has cooled, put about 4 c.c. of it into each of your colored solutions, and shake vigorously.

Filter the dilute molasses. If the filtrate is still colored (?), pour it through the filter again. Taste the filtrate (?). Filter the dilute cupric sulphate, and examine the filtrate (?).

What difference do you observe? Was the sugar removed, or only the coloring matter? Explain (?). What commercial use is made of this property of bone black [C 471; I 750]?

108. Tests for Food Components

a. Starch. Place water in a test-tube, add a pinch of starch, shake, and boil (?). How does the starch change? Cool the suspension in running water, and when it is cold (not before), divide it into two parts and to one add a drop of the solution of iodine in potassium iodide (?). Keep the other half for use in **d.**

b. Glucose. Shake about 0.5 c.c. of glucose in 5 c.c. of water. Add 5 c.c. of Fehling's solution and boil (?).

c. Lactose (Milk-Sugar): Repeat **b** with about 0.5 c.c. of milk-sugar (?).

d. Maltose from Starch. To 5 c.c. of the starch suspension prepared in **a** (which itself gives no reaction with Fehling's solution,

Exercise **101 a**), add about 1 c.c. of saliva, mix, and set aside for fifteen minutes. Then add 5 c.c. of Fehling's solution and boil (?). How was the maltose produced [**C 497; I 783**]?

e. Protein. To a few particles of egg albumen, add a few drops of concentrated nitric acid (?). Add some water to wash off the acid, and pour away the liquid, leaving the solid residue. To the latter add a few drops of ammonium hydroxide (?).

Repeat with a scrap of woolen yarn (?).

Account for the effect of nitric acid on the skin and nails (?).

f. Fat. Place on small pieces of unglazed paper (1) a particle of fat, (2) a drop of cottonseed oil, and (3) part of a crushed almond; put them in the evaporating dish, and warm gently until the fat melts. Examine the papers (?).

Reference for additional work. Hydrogenation of Oils; Haub, Journal of Chemical Education, 8, 1856, 1931.

109. Food Components of Milk

a. Heat 50 c.c. of milk to boiling in the evaporating dish. With a glass rod, fish out the skin which forms on the surface and transfer it to a test-tube. Apply to it the test in Exercise **108 e** for protein (?). Name the substance [**C 496; I 779**].

To the milk add a few drops of acetic acid and stir (?). How is this result to be classified? What sort of substances cause milk to curdle? What is the connection with "sour milk"? Filter the acidified milk and test the residue on the filter for protein (?).

b. To 5 c.c. of the filtrate add 5 c.c. of Fehling's solution, and boil (?). What is shown to be present (Exercise **108 c**)?

c. To 5 c.c. of the filtrate from **a** add iodine solution (?). For what food component is this a test? Is it present?

d. Put a few drops of unboiled milk on a piece of unglazed paper and heat as in Exercise **108 f** (?). Result?

e. Which food components have you found in milk?

f. Test for Formaldehyde in Milk. To 5 c.c. of milk in a test-tube add an equal volume of water, and, by means of a glass rod, one drop (not more) of formaldehyde solution and shake. Take 5 c.c. of concentrated sulphuric acid and add to it by a glass rod one drop of ferric chloride solution. Now hold the test-tube of milk almost but not quite vertical, and pour the sulphuric acid in a continuous stream down the side of the tube so that it may go to the bottom and form a layer under the milk. What color appears

where the liquids meet? Repeat with diluted milk free from formaldehyde (?).

110. Food Components of Flour

a. Take about 10 c.c. of flour, make it into a dough with water, and then place it in a small piece of cheesecloth. Bring the corners together and with a thread tie the cloth so as to enclose the dough in a bag.

Knead the bag in water in the evaporating dish so long as the liquid squeezed out appears to be more milky than that in the dish. Then pour the milky liquid into a beaker to settle.

Open out the cloth and wash the contents in running water until the wash-water is no longer milky.

b. Test portions of the residue in the cloth for starch (?), glucose (?), and protein (?), and record the results (?).

c. Test a pinch of the dry flour for fat (?).

d. Pour the water away from the sediment in the beaker (from **a**) and test portions of the solid for starch (?), glucose (?), and protein (?), and record the results (?).

e. Summarize the food components found in flour (?).

f. Baking Powder. Weigh out 2 g. of potassium bitartrate (cream of tartar). Write the equation for its interaction with sodium bicarbonate (?). Calculate how much of the latter salt will be required (?). Weigh out this amount, and mix the two salts on paper. In practice, cornstarch is also added (why?), but is not here required.

Put half the mixture in cold water in a beaker (?). Put the other half in water previously heated (?). Why do soda biscuits rise so rapidly when placed in the oven?

111. Esters. Soap

a. Formation of an Ester. To 1 c.c. of sodium acetate in a test-tube add 2 c.c. of alcohol and 1 c.c. of concentrated sulphuric acid. Agitate for a minute or two, warm very slightly (do not boil!), and note the odor [**C** 457; **I** 642] (?). This is a test for acetic acid or an acetate. Write the equation (?), and name each substance (?).

b. Hydrolysis of an Ester. Place 10 c.c. of water in one test-tube and 0.5 c.c. of methyl acetate $CH_3(CO_2CH_3)$ in another. Test

each with blue litmus paper (?), then mix and test again [**C 499; I 781**] (?). If the result is not definite, wait a few minutes and test the mixture once more. Write the equation (?), and name each substance (?).

c. Saponification of an Ester: Soap Making. Mix in a test-tube 5 c.c. of cold, saturated sodium hydroxide solution and 5 c.c. of alcohol, shake, and allow to settle (?). Pour off the upper alcoholic layer into another test-tube, add to it an equal volume of fat or cottonseed oil, and shake (?). Put the liquid into an evaporating dish on the wire gauze and set fire to the contents. Warm the dish with a very small flame to assist in driving off the alcohol. Stir until the flame goes out, and then stop heating. The pasty mass is a soap, mainly sodium oleate and sodium palmitate [**C 505; I 786**], mixed with glycerine. Write an equation (?). Rub a little with water in the hands (?).

The alcohol is used simply as a common solvent for the fat and the alkali and is employed in the laboratory experiment to save time.

d. Dissolve the soap (**c**) in a little warm distilled water and cool. To one-quarter of the solution in a test-tube add hydrochloric acid and shake vigorously [**C 506; I 787**] (?).

To show that the precipitate is an acid, withdraw it by means of a glass rod, suspend it in 10 c.c. of water in another test-tube, add a few drops of sodium hydroxide solution and heat until solution takes place. Write the equation (?).

To what class of substances does **d** show soap to belong?

e. To another quarter of the soap solution add calcium chloride solution (?). Explain the action of hard water [**C 578; I 732**] on soap solution.

f. To the remainder of the cold soap solution, add sodium chloride solution (?). This is called "salting out" [**C 506; I 787**], and is a case of coagulating a colloid [**C 508; I 789**]. To what class of solutions does this show soap solution to belong?

112. Colloidal Suspensions

a. Preparation. Shake some arsenic trioxide with 25 c.c. of cold water vigorously for several minutes, filter, and to the filtrate add an equal volume of hydrogen sulphide solution. Arsenious sulphide As_2S_3 is formed, but remains in colloidal suspension.

b. Optical Examination. Pour the suspension into a square bottle, and examine it in sunlight, or, better still, by holding it close to an incandescent bulb. Look first through it towards the light (?). Does it appear to be transparent and clear, or not? Now look at it from a position at right angles to the direction of the light, and answer the same question (?). With an ultramicroscope, the particles in such solutions can be perceived, individually [C 507; I 788].

c. Coagulation. Divide the solution between 6 clean test-tubes. Keep one, corked, for reference and a second one for use in **g**. To the third add sodium chloride solution (?), to the fourth dilute hydrochloric acid (?), to the fifth calcium chloride solution (?), dissolve a little sugar in the sixth (?), and observe them from time to time. Note which coagulates last (?).

The positive ion is here the coagulating agent. How does valence affect coagulating power? Do non-ionized, non-colloidal substances like sugar produce coagulation?

After a day or two, does the arsenious sulphide in the reference test-tube coagulate or settle of its own accord?

d. Colloidal Rosin. Dissolve a single particle of rosin in 1 c.c. of alcohol. Add the solution to a test-tube full of water (?). Examine in the light as in **b** (?). Cork and keep, to see whether settling takes place (?).

e. Summarize the special properties of colloidal suspensions (?).

f. Colloidal Ferric Hydroxide. Boil 300 c.c. of distilled (or soft) water in a large beaker, and add to it, a few drops at a time, 3 c.c. of ferric chloride solution. The salt is thus hydrolyzed [C 543; I 681] to a significant degree, and contains suspended ferric hydroxide $Fe(OH)_3$ (color?).

Examine this suspension in the light as in **b** (?).

Take 5 test-tubes full of the prepared liquid, keep one for reference, and add to each of the others a very dilute solution of one of the following coagulants: sodium chloride, sodium sulphate, sodium carbonate, calcium chloride. This colloid is coagulated by the negative ion. Note the time required in each case (?). What is the effect of valence?

g. To the reserved portion of your colloidal arsenious sulphide from **c** add successive small amounts of colloidal ferric hydroxide from **f**. What do you observe? What do you conclude as to the

sign of the charges on the two substances in colloidal suspension?

Reference for additional work. The Ultramicroscope as a Student Project; Miller and Ketterer, Journal of Chemical Education, 11, 571, 1934.

113. How Soap Cleanses

a. Place 1 c.c. of kerosene in one test-tube and 1 c.c. of cottonseed oil in another. Add about 10 c.c. of water to each, shake vigorously and place in the rack (?). Is a permanent emulsion formed? Now add to each test-tube 2 c.c. of soap solution (ivory soap in water, 1 part to 10), shake again, and observe as before (?).

b. Boil 200 c.c. of water in a flask. Smear thoroughly the test-tube brush with ferric oxide (pulverized) suspended in cottonseed oil (6 g. : 100 c.c.) [Instructor] and push it into a test-tube. Add about 15 c.c. of the hot water, and work the brush in the tube (?). Does hot water alone remove the rust and oil?

Remove the brush, pour out the water, place 15 c.c. of hot soap solution in the test-tube, and work the brush in the tube as before (?). Remove the brush, pour the contents of the test-tube into a 100 c.c. beaker, rinse first the brush and then the test-tube with hot water, catching the rinsing-water in the beaker. Have the oil and rust been removed from the brush?

After a short time, examine the contents of the beaker (?). Where is the oil (?) and in what condition? Where is the rust (?) and is it free from oil?

Explain how soap solution removes grease or oil from a large object or a powder (?).

114. Dyeing. Dyes and Perfumes

a. Preparing the Cotton. In case the sizing has not been removed from the cotton cloth provided, boil three pieces in 50 c.c. of water containing 2 c.c. of concentrated hydrochloric acid. Rinse the goods in water, dip in 50 c.c. of cold water containing 0.5 c.c. of ammonium hydroxide, and rinse again.

b. Chrysophenin, a Direct Dye on Both Cotton and Wool.* To 20 c.c. of water in the evaporating dish add 5 c.c. of the chrysophenin suspension (shake the bottle) and 1 c.c. of sodium sulphate solution, and heat to boiling.

Place in this bath one piece each of flannel and of cotton and

* Congo-red or picric acid may be used instead of chrysophenin in this experiment, if desired.

keep them in motion with a glass rod for two minutes. Remove them and wash in running water (?). Is the dye fast to washing on both? What was the purpose of the sodium sulphate [C 515; I 842]?

Smooth out the samples on a square of glass (or a bottle) to dry, and paste them in your note-book.

c. A Lake. Take some cochineal solution, add to it a few drops of ammonium hydroxide, and shake. Then add 1 c.c. of aluminium sulphate solution, shake, and allow to stand (?).

d. Alizarin, a Non-basic, Mordant Dye. In a test-tube dilute 2 c.c. of *N* aluminium sulphate solution with 10 c.c. of water, place in it a piece of cotton cloth and boil for two minutes.

In a second test-tube dilute 1 c.c. of ammonium hydroxide with 10 c.c. of water. Wring the piece of cloth, place it in this solution and warm and shake for two minutes. Then wring the cloth, which is now mordanted with aluminium hydroxide.

In the evaporating dish put 50 c.c. of water and 5 c.c. of the alizarin suspension (5 g. of 20 per cent paste to 100 c.c. of water; shake the bottle). Place in this the piece of mordanted cloth and a piece of unmordanted cotton, and heat to boiling. Keep the pieces of cloth in motion for at least ten minutes. Finally, wash them in running water (?). Is the dye fast to washing on both? Why do they differ [C 513; I 840]?

Dry the samples on glass and paste them in the note-book.

e. Basic, Mordant Dyes. Measure into as many large test-tubes the following solutions:

(1) 2 c.c. Malachite green (0.05%).
(2) 2 c.c. Methyl violet (0.05%).
(3) 2 c.c. Tannic acid (1%).
(4) 2 c.c. Tartar emetic (1%).

Add to each 20 c.c. of distilled water, and label and number the tubes.

Place two pieces of cotton cloth in the evaporating dish, add the contents of (3), and keep at the boiling-point for five minutes. Wring the pieces of cloth and place them in (4), which is cold, and keep them in motion for five minutes. Then remove and wring the cloth, which is now mordanted with antimonyl tannate (?).

The Dye without Mordant. Place in (1) and in (2) one piece

each of unmordanted cloth, and keep each solution at the boiling-point for one minute. Wash the samples thoroughly in running water (?). Is the dye fast to washing?

The Dye with Mordant. Now place in (1) and in (2) one piece each of the mordanted cotton, boil each for one minute, allow them to cool, and then wash the cloth thoroughly (?). Is the dye fast to washing? Dry all the samples on glass and mount in the note-book.

f. Preparation of Typical Dyes. Phenolphthalein. Take 0.1 gram of phthalic anhydride (the anhydride of phthalic acid, $C_6H_4.(COOH)_2$) and 0.1 gram of phenol $C_6H_5.OH$ in a test-tube, add two drops of concentrated sulphuric acid, and heat carefully for a minute over a small flame. The mixture, which should be well shaken during the heating, will turn dark-red in color. Allow to cool, add a few c.c. of water, and then add drop by drop a dilute solution of sodium hydroxide until a pink color persists on shaking (?).

Take a portion of this solution, and test the action of phenolphthalein as an indicator by adding first dilute hydrochloric acid, then dilute sodium hydroxide [**C 263; I 389**].

g. Fluorescein. To 0.1 gram of phthalic anhydride and 0.1 gram of resorcinol $C_6H_4(OH)_2$ add 3 drops of concentrated sulphuric acid, and heat carefully for a minute. Allow to cool, add a few c.c. of water, then add sodium hydroxide until alkaline (use litmus paper as a test).

Shake up a few drops of this solution with a test-tube of water. The dye imparts to the solution a brilliant green fluorescence, hence its name.

h. Preparation of Typical Perfumes. Take 0.1 gram of beta-naphthol $C_{10}H_7.OH$ and 10 drops of methyl alcohol in a test-tube, add 2 drops of concentrated sulphuric acid, and warm gently for a few minutes. The methyl ether of beta-naphthol, which is formed, has a most powerful odor, reminiscent of acacia blossoms.

Repeat the experiment with ethyl alcohol instead of methyl alcohol. The ethyl ether of beta-naphthol is produced; its odor recalls the perfume of orange flowers.

Reference for additional work. Preparation of a Synthetic Resin; Stone, Journal of Chemical Education, 7, 1663, 1930.

CHAPTER XVIII

SILICON AND BORON

115. Silica

Mix 1 g. of finely powdered silica with 4–5 g. of anhydrous sodium carbonate. Coil the platinum wire to watch-spring form and, by alternately heating in the Bunsen flame or blast-lamp, and dipping in the mixture, obtain a large bead and heat it strongly till all action (?) seems to have ceased. Place the bead in a test-tube and make others by the same process. Dissolve the beads in a small amount of water. Add hydrochloric acid a drop at a time until the solution is strongly acid (?). Evaporate the solution to dryness on the sand bath (?). Treat the residue with warm water, wash the whole contents of the dish into a test-tube, and examine (?).

116. Analysis of a Silicate

a. Mix dry potassium carbonate with anhydrous sodium carbonate in equal proportions in a mortar. Coil the platinum wire to watch-spring form. Mix a little powdered talc (is this soluble in water? What is its common name?) with 6–7 times as much of the "fusion mixture," and hold some of the result on the platinum wire in the flame of the blast-lamp till it is completely melted and all action (?) has ceased. Repeat till several beads are obtained. Treat the beads with boiling water in a test-tube until they are completely disintegrated. Filter through a small filter paper and wash the precipitate with water. Preserve this filter paper and precipitate for use later. Acidify the filtrate with concentrated hydrochloric acid and proceed as in **115**, last two sentences (?).

b. Make a hole in the paper and wash the precipitate obtained above into a test-tube. Add dilute hydrochloric acid, and warm

(?). Filter, if necessary, and add ammonium hydroxide to alkaline reaction (?). The precipitate is aluminium hydroxide. Boil and filter. To the filtrate add a few drops of ammonium hydroxide, some ammonium chloride solution, and some sodium phosphate solution, and stir with a glass rod (?). Compare **93 c.**

117. Silicon Tetrafluoride

Mix intimately 1 g. of pulverized calcium fluoride with an equal weight of sand, place in a test-tube, and moisten the mixture with concentrated sulphuric acid. Apply a gentle heat (?). Hold a glass rod, with a drop of water at its lower end, in the gas and examine the rod (?).

118. Boric Acid

a. Pulverize some borax and make a concentrated solution in boiling water. Add concentrated hydrochloric acid until the solution is strongly acid, and set aside to cool (?). Filter off the crystals, wash with a few drops of cold water, and dry. Dissolve the crystals in the smallest possible amount of boiling water, and set the solution aside (?). Filter, and wash the crystals as before.

b. Dissolve a part of the crystals in hot distilled water. Test this solution, and a sample of the distilled water, simultaneously with litmus paper (?). Dip a strip of turmeric paper in the same solution, wrap it round the upper part of the test-tube, and boil the solution until the paper is dry (?). Touch the paper with a glass rod dipped in sodium hydroxide solution (?). This is a test for boric acid.

Treat the rest of the crystals with cold sodium hydroxide solution (?).

c. Place on separate parts of a watch-glass a drop of concentrated sulphuric acid, a drop of glycerine, and a very little pulverized borax. Rub the end of a platinum wire in each of these. Bring the end of the wire slowly up to the outer edge near the bottom of a small Bunsen flame. How is the flame colored? This is a test for a borate.

d. An alternative method: Dissolve a small crystal of borax in 1–2 c.c. of water in a test-tube. Add a drop or two of concentrated sulphuric acid and then 2–3 c.c. of alcohol. Heat the mixture and set fire to the vapor of the alcohol (?).

Reference for additional work. Preparation of boron from borax; Thurston, Journal of Chemical Education, 6, 550, 1929.

119. Borates

a. Dissolve 1 g. of borax in distilled water. Test both this solution, and the distilled water, with litmus paper (?).

Put two drops of the solution into a test-tube and dilute with water till the tube is two-thirds full. To the remainder add silver nitrate solution (?). Add silver nitrate solution to the very dilute solution also (?). The difference is more marked if the dilute solution is first warmed. For comparison, add silver nitrate solution to an exactly equally diluted sodium hydroxide solution (?). What conclusion do you draw in regard to the action of water on borax? Write the equation, and explain.

b. Heat a straight platinum wire in the Bunsen flame, and, while yet glowing, dip it into a small quantity of borax. Return the wire to the flame and observe the changes in the substance (?) until it forms a bead. Try borax beads, as directed in **2 g**, **h**, and **i**, with cupric oxide (?), manganese dioxide (?), and ferric oxide (?), separately.

120. Identifying an Unknown Substance*

a. Obtain [Instructor] a single unknown solid substance. It will contain one of the following negative radicals:

orthophosphate	carbonate	acetate
metaphosphate	bicarbonate	borate
pyrophosphate		

The positive radical may be (NH_4), (K), (Na), or (Ca).

Limit yourself to identifying the negative radical and (NH_4). Record immediately the result of each observation. Record negative results also.

b. External Examination. Record the state (?), crystalline form (?), color (?), and odor (?).

c. Solubility and Reaction of the Solution. With a few particles, try the solubility in water and, if in doubt, use the method in Exercise **21 a** (?). Test the solution on litmus papers (?).

d. Effect of Heating. Heat 0.5 g. in a dry test-tube. Does it melt (?), char (?), or otherwise change (?), and does it give off gas or vapor? Odor?

*See footnote to Exercise **89**.

If WATER VAPOR is given off (?), the substance may be a hydrate, acid salt, carbohydrate, or calcium hydroxide. Incline the mouth of the tube downwards, drive all the water off, dry out the tube with filter-paper, and continue heating. Does it now char (?), change (?), or give off gas or vapor?

A SUBLIMATE indicates a salt of NH_4. Test **82 e.**

A COLORLESS GAS with NO ODOR may be carbon dioxide (test?).

A COLORLESS GAS with AN ODOR may be ammonia or sulphur dioxide (tests?).

e. Action of Concentrated Sulphuric Acid. To 0.5 g. add 2–3 drops (not more) of concentrated sulphuric acid (?). If necessary, warm gently (?).

A COLORLESS, ODORLESS GAS may be carbon dioxide (test?).

A GAS with an ODOR may be acetic acid (test?).

If there is NO GAS (no bubbling), the substance may be a phosphate or a borate (test?).

f. Report. State your conclusion, with the reasons therefor (?).

g. Obtain a second unknown and proceed as before (?).

h. Obtain a third unknown, involving **89** as well as **120** (?).

CHAPTER XIX

THE ALKALI METALS

121. Potassium Hydroxide

a. Dissolve about 30 g. of potassium carbonate in 200–300 c.c. of water in a large beaker, and heat on a wire gauze to boiling. Slake 15–20 g. of quicklime in a beaker (?), using heat if necessary to start the action, and make the product into a very thin paste with water. Add this gradually, and with constant stirring, to the boiling solution (?). Continue boiling for a few minutes (why?). Let the mixture settle, and, when it is cold, decant the clear liquid (or filter rapidly). Use the solution in **b**, **c**, and **d**.

Is calcium hydroxide appreciably soluble [**C** and **I**, inside front cover]? Is calcium carbonate more or less soluble than is the hydroxide? Formulate the action and explain why it went to completion. What kind of hydroxides alone can be made by this method? Which hydroxides are of this kind [**C** and **I**, inside front cover]?

b. Find the concentration of the solution made in **a** by titration (alkalimetry). To do this, place a carefully measured volume (about 10 c.c.) of the clear solution in a small flask. Dilute with about four times its volume of water, as the concentrated solution is apt to decompose the indicator. Fill a burette to the very tip of the nozzle with "normal" [**C** 160; **I** 221] hydrochloric acid.* Add some phenolphthalein solution to the alkali and run in the acid cautiously until the red color just disappears. Note the volume of acid used (?). Calculate the concentration of potassium hydroxide in terms of a normal solution as unity (?).

c. (Two students working together.) If the alkaline solution

* Or normal oxalic acid may be prepared (two students working together), and used here. Calculate the weight of pure crystalline oxalic acid ($H_2C_2O_4$),$2H_2O$ required to make 500 c.c. of normal oxalic acid solution. Weigh out [quant.] this amount on glazed paper and transfer it to a 500 c.c. graduated flask [Storeroom]. Dissolve the acid in distilled water and then fill up the flask to the mark.

is above normal, calculate the volume of the solution required to make 100 c.c. of normal alkali. Place the necessary amount of the solution in a 100 c.c. graduated flask [Storeroom] and fill to the mark with water. (If the solution is less than normal, calculate and use the amount required for 200 c.c. of semi-normal alkali.)

Measure (burette) 5 c.c. of acetic acid into a flask and dilute with about 20 c.c. of water (or take 25 c.c. of commercial vinegar), add phenolphthalein, titrate with the normal (or semi-normal) alkali, and calculate the normality of the acetic acid (or vinegar) used (?). Calculate also the percentage of acetic acid present (?).

d. Place very small quantities of the following solutions in separate test-tubes, dilute with water, and add excess of the solution of potassium hydroxide from **a** to each; ferric chloride (?); cupric sulphate (?); mercuric chloride (?). Describe the color and structure of the precipitates.* Boil the contents of each test-tube (?). Do the precipitates dissolve or change in any way?

What kind of hydroxides can be made by this method? Do any metals fail entirely to form hydroxides [C 546; I 685]?

e. Pulverize a small piece of potassium hydroxide and leave it exposed to the air on a watch-glass for 24 hours, or more (?). To a part of the product add dilute hydrochloric acid (?). Simultaneously, expose a small piece of sodium hydroxide and treat it in exactly the same way (?). Compare the results and explain.

122. Potassium Nitrate

a. Dissolve 22 g. of potassium chloride in 45 c.c. of boiling water in a large test-tube (or small beaker).

Boil 20 c.c. of water in a beaker (set on the wire gauze) and add 25 g. of sodium nitrate. When this has dissolved, add the boiling solution of potassium chloride and continue heating for a minute or so (?). Then allow the mixture to settle and immediately pour the hot liquid off the crystalline residue into another clean beaker. Examine the two products in **b** and **c** respectively.

b. Pour a few c.c. of hot water on to the crystalline residue, stir with a rod to wash the residue and drain away the liquid.

* The structure of a precipitate may be described as gelatinous, flocculent, curdy, pulverulent, granular, or crystalline. What circumstances will determine the structure of a precipitate? Hereafter, describe every precipitate by terms like these.

Taste the residue (?). Dissolve a part in a very little hot water, pour several drops on a watch-glass and examine the crystals, when they appear, with a lens (?). Draw two of them (?). What is the substance?

c. When it is cold, examine the liquid that was poured off into the beaker in **a** (?). What form do most of the crystals show? Are there any cubical crystals (lens)? Pour away the liquid. Dissolve the crystals in a very little boiling water and set aside. Examine the final crystals and draw two of them (?).

d. Write the equation for the action (?). Tabulate [**C 164; I 226**] the solubilities of potassium chloride, sodium nitrate, potassium nitrate and sodium chloride at 20° and at 100° respectively. (Extrapolate to approximate values if necessary.)

Which is the least soluble of the four salts at 20°, and which at 100°? Why was sodium chloride the substance precipitated in the hot mixture? Why did potassium nitrate remain dissolved? Why did it come out so copiously when the liquid cooled? Why were there a few crystals of sodium chloride mixed with it?

Explain why purer potassium nitrate can be obtained by crystallizing the product once more from water.

e. Mix intimately in the mortar 5 g. of finely pulverized potassium nitrate with 2 g. of charcoal, and drop the mixture in small portions into a red-hot crucible (?). What gases are evolved? What is the residue (test with an acid)?

f. Pulverize 5 g. of potassium nitrate and mix on paper [CAUTION!] intimately with 2 g. of flowers of sulphur. Throw the mixture [HOOD] in small portions into a red-hot crucible (?). What gases are evolved? Dissolve the residue and add barium chloride solution (?). Explain the explosive power of gunpowder (?).

123. Reactions of Potassium Salts

a. Heat the tip of a clean platinum wire and quickly touch some powdered potassium nitrate with it. Hold the wire with adhering particles in the lower part of the outer blue layer of the Bunsen flame. Notice the color of the flame and examine with the spectroscope. Make a diagram showing the position of the lines with reference to the D line (in the yellow), which, on account of the sodium present, is shown by all flames in the laboratory.

b. Using sodium and potassium chlorides separately in turn,

view the flames given by each of these salts through a piece of cobalt glass. Which tint of light is absorbed by the glass, and does not reach the eye (?), and which tint passes through and is visible?

Mix the two chlorides intimately, and observe the flame with the eye (?). Which color is visible? Why is the other invisible? Now view the flame of the mixture through cobalt glass (?). (If you do not get good results with one piece of cobalt glass, try *two* thicknesses, one behind the other). Which metal can you recognize thus?

c. Saturate 10 c.c. of warm water (40°) with potassium nitrate. Add this solution to an equal volume of tartaric acid solution in a beaker (?). Agitate and cool in a stream of water (?). Note, also, the effect of rubbing the inside of the vessel with a glass rod. Describe the product [footnote to **121 d**]. Filter, and wash the precipitate with a little alcohol.

d. Dissolve a few particles of the precipitate from **b** in a drop or two of warm water and test with litmus (?). Remembering that tartaric acid $H_2C_4H_4O_6$ is a dibasic acid, what sort of salt must the product be?

To a few particles of the precipitate add dilute hydrochloric acid (?).

To a part of the precipitate add drop by drop potassium hydroxide solution (shake between drops), using as little of the base as possible (?). To the resulting solution add concentrated hydrochloric acid a drop at a time. No effect can be expected until after the mixture becomes acid (test?). Stir vigorously with a glass rod, and cool in running water between drops (?). Finally, try the effect of excess of the acid (?).

e. Heat the rest of the precipitate strongly in an open porcelain crucible (?). Extract with hot water, filter, and add any acid to the filtrate (?). The ignition of all potassium or sodium salts of organic acids gives the same result.

f. Take 2–3 c.c. potassium chloride solution and, in another test-tube, dilute a few drops of it with 10 c.c. of water. Then add some picric acid solution to each portion (?). Explain the difference in behavior (?).

What substance is shown to be present in a solution when we get the tests in **c** and **f**?

124. Ammonium Salts

a. What is a common effect of heating ammonium salts (**82 d**)? Heat 1 g. of ammonium phosphate in a hard glass test-tube (?). Dissolve the residue in water and test with litmus paper (?).

Do all salts of ammonium give ammonia when heated (**80 a**; **87 a**)? Is simple heating a test for an ammonium salt? Observe the odors of all the salts of ammonium (solids and solutions) in your kit, or upon the side-shelf (?), and explain.

b. Do ammonium salts impart color to the flame?

c. Take a solution of any ammonium salt and divide it into three portions. To one add excess of tartaric acid solution, and shake (?). To the second add picric acid solution (?). Compare these results with **123 c** and **f**. To the third add sodium hydroxide solution and note the odor (?). How should you distinguish ammonium-ion from any other ionic substance? Why is heating the salt not a sufficient test (**82 e**)?

d. Test ammonium chloride solution with litmus (?). Do you infer that ammonium hydroxide is a very weak base [**C 406**; **I 709**]?

125. Sodium Bicarbonate

a. Measure 24 c.c. of ammonium hydroxide solution and 12 c.c. of water into a large test-tube, add 8 g. of powdered ammonium carbonate, cork the tube and shake until the salt is dissolved. Add solid, powdered sodium chloride in excess and shake vigorously until the liquid is saturated.

Decant the clear liquid into another test-tube, and lead into it carbon dioxide (made as in Exercise **96 b**; be careful not to allow acid spray to be carried over [?]) until a copious precipitate (?) has appeared. While this is going on, proceed with **c**.

Filter, and dry the precipitate by pressing between filter-papers. Note the appearance (?) and taste (?).

Write ionic equations for the reactions involved.

b. Dissolve in water a little of the solid from **a**, which must have ceased to smell of ammonia (why?), and test the reaction of the solution with litmus (?). If the solution is not acid, explain why it is not so.

To part of the solid add any dilute mineral acid (?).

c. Effect of Heating the Bicarbonate. Place some sodium bicarbonate in a test-tube, fitted with 1-hole stopper and L-tube, so that the mouth is inclined slightly downwards, with the L-tube dipping into limewater. Warm the bicarbonate gently with a small flame. What gas is given off? What is deposited in the cool part of the tube? Taste the residue when cold (?). Dissolve in a very little water, test the reaction of the solution with litmus paper (?), and set it aside to crystallize in an open dish (?). Explain the reaction with litmus (?). Dry the crystals, and ascertain the effects upon them of (a) addition of an acid (?), and (b) of exposure on a watch-glass (?).

Compare the solubilities of the carbonate [C and I, inside front cover] and bicarbonate of sodium [C 568; I 717], and explain why, in the Solvay process, the bicarbonate is made first and then the carbonate from it.

126. Reactions of Sodium Salts

a. Take some salt of sodium and try the flame test, and examine the flame with the spectroscope as in 123 **a**. Take a solution of some salt of sodium, and add to one portion picric acid solution (?), and to the other tartaric acid solution (?). Compare all the results with those obtained in 123 and 124 **b** and **c**.

b. How could you distinguish sodium, potassium, and ammonium salts from one another? How could you demonstrate positively the presence both of a potassium and of an ammonium salt in a mixture of the two without the aid of the flame test or spectroscope?

c. Which salts of potassium, ammonium, and sodium are least soluble?

CHAPTER XX

THE ALKALINE EARTH METALS

127. Calcium Oxide and Hydroxide

a. Select two small chips of marble. Place one on the wire gauze and heat with the full flame for 10 minutes (meanwhile proceed with **c** and **d**). Examine it and compare its appearance with that of the unheated fragment (?). Write the equation for the change (?).

b. Place two strips of red litmus paper in two watch-glasses. Lay on one the heated fragment from **a**, and on the other the unheated fragment, and moisten each with water carried on a glass rod (?). What has been formed by the action of the water? Write the equation (?). What sort of oxide is calcium oxide [C 135; I 181]?

How may the decomposition of the marble be arrested (?) and reversed (?) without altering the temperature? What conditions permitted complete decomposition to take place here?

c. Place a lump of quicklime in the evaporating dish, add a little water (only enough to wet the lower quarter of the lump) and warm gently (?). Write the equation (?).

d. Place about 1 c.c. of powdered fresh quicklime in a test-tube, add dilute hydrochloric acid, shake, and warm if necessary (?). Write the equation (?).

For comparison, take a chip of marble and cover it with dilute hydrochloric acid (?). Write the equation (?). What is the reason for the difference?

128. Reactions of Calcium Salts

a. Try the flame test with a particle of solid calcium chloride and examine with the spectroscope (see that the platinum wire is clean).* Make a sketch of the spectrum showing the positions of the lines with reference to the sodium and potassium lines.

* After use, the platinum wire should always be cleaned immediately. Form upon it a borax bead, and cause the molten bead to traverse the

b. To one portion of a diluted solution * of calcium chloride add ammonium carbonate solution (?). Warm, if necessary. Filter, divide the precipitate and treat parts of it with hydrochloric acid (?) and much diluted acetic acid (?), respectively. Explain the result (?).

c. To a second portion of the solution add excess of dilute sulphuric acid (?). Filter. Pierce the filter-paper and wash a small part of the precipitate into a test-tube. Add some concentrated hydrochloric acid (?). Explain the change, if any occurs (?).

d. To a portion of the filtrate from **c** add a little sodium carbonate solution (?). Is the carbonate or the sulphate of calcium more soluble? What are their actual solubilities? How may permanent hardness be removed?

129. Hard Water

a. Soft Water. To about 10 c.c. of distilled water add soap solution (12 g. per 1 liter), drop by drop, shaking between drops. Count the number of drops required before a "permanent" lather or froth is obtained (?). A "permanent" froth is defined as one which persists for three minutes.

Give the name and formula of one typical component of soap.

b. Temporary Hardness. Take 5 c.c. of freshly made, saturated limewater (1.7 g. $Ca(OH)_2$ per liter) and add an equal volume of distilled water. Pass carbon dioxide (made as in Exercise **96 b**) through the half-saturated limewater steadily until two changes (?) have occurred. Write two equations, one for each change (?). What substance is present in the final clear liquid?

To 2 c.c. (measured) of this add soap solution (a few drops at a time) and shake until a "permanent" lather is obtained (?). The precipitate is a calcium soap. Write the formula of a typical component of this soap (?). Write the equation and name each substance (?).

c. To a second 2 c.c. (measured) of the clear product from **b**,

wire from end to end several times. Throw off the bead. Heat the wire persistently in the Bunsen flame, dipping it from time to time in hydrochloric acid (why?), until the wire no longer colors the flame. If much corroded, the wire may be boiled in nitric acid before being heated.

* In this and all following paragraphs headed "reactions," where "diluted" solutions are spoken of, the solutions must be diluted with 3–4 volumes of distilled water to secure good results.

add 1 c.c. (measured) of saturated limewater and shake (?). What is the precipitate [C 578; I 733]? Now add a few drops of soap solution, noting how much is required to form a "permanent" lather? Was the amount required as great as in **c**, or was it nearer the amount used in **a**?

d. Boil a third 2 c.c. (measured) of the clear product from **b** (?). What is the precipitate? When the liquid is cold, add soap solution as in **c**, to determine whether the hardness has changed (?).

e. Permanent Hardness. Dissolve a crystal of magnesium chloride in 10 c.c. of water, add soap solution and shake (?). Write the equation (?) and name each substance (?).

f. Test the city water with soap solution (?).

130. Reactions of Strontium Salts

a. Same as **128 a**, using a particle of strontium chloride. Use diluted strontium chloride solution for **b**, **c**, and **d**.

b. Add ammonium carbonate solution and heat (?).

c. Add dilute sulphuric acid (?).

d. Add a clear solution of calcium sulphate (made by shaking a little of the pulverized salt with distilled water and filtering until clear) (?). The precipitate may come slowly. Explain.

131. Reactions of Barium Salts

a, b, c. Same as **130 a**, **b**, and **c**, using barium chloride.

d. Add to a diluted solution of barium chloride a clear solution of strontium sulphate (made by shaking the salt with distilled water and filtering) (?). Explain. Now add concentrated hydrochloric acid (?). Why does the precipitate not behave like that in **128 c**?

Compare with **130 d**, and arrange the sulphates of these three metals in the order of solubility. Give two methods of distinguishing the compounds of the elements in this family. Examine the table of solubilities [**C** and **I**, inside front cover] and suggest other ways of distinguishing calcium-ion and barium-ion, respectively, from the other two. How could you tell a solution containing the ions of a member of this family from one containing those of the members of the previous family?

132. Identification of Unknown Substances

a. Take three dry test-tubes, apply to the instructor for three "unknown" substances, and ascertain what each is. Record negative as well as positive results (?).

b. Study: (1) Physical appearance (?), (2) Odor (?), (3) Solubility in distilled water and reaction of the solution toward litmus (?). After the final conclusion has been reached, reëxamine the results recorded under (1), (2), and (3), and consider if the substance found has the properties there noted. All results require checking in some such way.

c. (4) Identify first the negative radical, using the methods described in 89 and 120 (?).

Before beginning (4), make a list of all the negative radicals known to you, and place opposite to each the gases, if any, which salts containing that radical, when heated, might be expected to give off. Consider also the means of recognizing these gases, if formed.

Before heating with a drop or two of concentrated sulphuric acid make a list of the reactions of sulphuric acid with salts containing each of the negative radicals. Consider also the means of recognizing such of the possible products as are volatile.

d. (5) Dissolve the substance in distilled water (if insoluble, try dilute hydrochloric acid). Identify now the positive radical, using the reactions for the metallic ions just studied in Exercises 123–131 (?).

e. (6) Write out the experiments and reasoning carefully in your note-book, and make sure that they prove the substance to be the one you finally decide that it is, and exclude the possibility of its being any other. See (3), above (?). Report the result to the instructor.

CHAPTER XXI

MAGNESIUM AND ZINC. IONIC EQUILIBRIA. ALUMINIUM

133. Magnesium

a. Mix thoroughly in a mortar equal bulks of magnesium powder and powdered calcium carbonate. Put the mixture in a test-tube (it should fill about half an inch of the tube), fix the tube in a clamp on the stand, and heat the top layer in the Bunsen flame until the reaction begins. [CAUTION! Be careful to keep the tube directed away from the face during the heating.] Allow the test-tube to cool, add a little water, and then, slowly, an excess of concentrated hydrochloric acid (?). (If the tube has been broken, place the contents with the acid in a beaker.) Note the odor (?). What effect will the acid have upon any excess of either of the ingredients? The acid will also dissolve the oxides of magnesium and calcium formed by the action. When all action has ceased, filter and wash the black residue (?) with water. After drying this on the radiator or water bath, prove that it is carbon.

b. This may be done by placing some of it in a dry test-tube, adding a pinch of potassium chlorate, heating in the Bunsen flame, and pouring the gas when it has cooled (close the tube with the thumb while waiting for this) into a test-tube containing 2 c.c. of limewater, and shaking (?).

What is the reducing agent in this action?

c. Examine the test-tube used in **a** (?) and explain [**C** 522; **I** 658].

134. Properties of Magnesium Compounds

a. Try whether magnesium chloride dissolves completely in water (?). Test the solution with litmus and draw an inference (?).

Heat some of the crystals strongly in a dry test-tube (?). Test the reaction towards litmus paper of the water which condenses in the tube (?), and then remove the liquid from the sides of the tube with a piece of filter paper. Does the residue dissolve completely in water? Explain (?).

b. To some diluted magnesium sulphate solution add ammonium hydroxide (?).

Now mix with some ammonium hydroxide several times its volume of ammonium chloride solution (what effect will this have on the ionization of ammonium hydroxide? Would ammonium sulphate answer as well?), and then add the mixture to a new portion of magnesium sulphate solution (?).

To this combination of three solutions add now some sodium phosphate solution (see **93 c**) (?). Explain the exact purpose of each ingredient.

c. To a fresh portion of the diluted magnesium sulphate solution add ammonium carbonate solution, and warm (?). Repeat, adding excess of ammonium chloride solution to the magnesium sulphate solution before using the carbonate (?).

Calcium-ion (**128 b**), strontium-ion (**130 b**), and barium-ion (**131 b**) were also precipitated by ammonium carbonate. Repeat **c** with one of them, adding first excess of ammonium chloride solution (?). If you had a salt of magnesium mixed with a salt of one of those other metals, how should you proceed so as to precipitate a compound of the alkaline earth metal first and one of magnesium afterwards?

d. Add two drops of hydrochloric acid (why?) to about 250 c.c. of the city water, evaporate to small bulk, and test it for calcium-ion and magnesium-ion.

e. Pass hydrogen sulphide through magnesium sulphate solution (?).

135. Reactions of Zinc Salts

a. Test a diluted solution of zinc sulphate with litmus paper (?). Explain (?).

b. To a part of it add sodium carbonate solution (?). Bring the contents of the tube to the boiling-point, filter, and wash the precipitate with water. To a portion of the precipitate add an acid (?). Dry the rest of the precipitate for **c**.

c. Heat the dried, basic zinc carbonate from **b** in a porcelain crucible to redness for a few minutes. Remove a small portion of the product and try the action of an acid upon it (?). If it effervesces, ignite for a longer time. What is the color of the final product when hot, and when cold? Reserve for **d**.

d. Moisten the residue from **c** with a drop of cobalt chloride solution and heat again (?).

e. To another part of the zinc sulphate solution add a very little sodium hydroxide solution, and shake (?). Filter, suspend the precipitate in water, and divide into three parts.

To one add an excess of sodium hydroxide solution (?). Does this show zinc hydroxide to be basic, or acidic?

To the second portion add dilute hydrochloric acid (?). What sort of hydroxide does it now seem to be? Explain [**C 593; I 802**] (?).

To the third portion add ammonium hydroxide (?). What complex ion is formed [**C 593; I 802**]?

f. To a third portion of zinc sulphate solution add ammonium sulphide solution (?). Filter, and wash the precipitate and filter-paper with water until no odor of hydrogen sulphide remains. To a part of the precipitate add a drop of hydrochloric acid (?). Odor? Preserve the rest of the precipitate for **g**.

g. Roll up a small part of the filter paper from **f** (or **b**) into a ball, and coil the platinum wire tightly round it. Roast the whole in the Bunsen flame (?). Moisten the ash with cobalt chloride solution and heat again (?).

136. Reactions of Cadmium Salts

a. Same as **135 e**, using diluted cadmium sulphate solution. Answer the same questions.

b. Saturate another part of the solution with hydrogen sulphide (?). Is the action easily reversible? Add dilute hydrochloric acid (?).

By what reactions could you distinguish between salts of magnesium, zinc, and cadmium?

c. Apply to the instructor for three unknown substances. To identify the anions, follow the outline of work in **132**. To identify the cations, employ the scheme commonly used in analysis [**C 725; I 995**]. Present to the instructor a logical and coherent, written report, as directed in **132** (?).

137. Ionic Equilibrium and the Ion-Product Constant

a. Dilute a few drops of methyl orange solution [**C 263; I 389**] with much distilled water. Add a few drops of an acid (?) and

then excess of a base (?). What colors does this indicator show in neutral, acid, and alkaline solution, respectively? What ionic substance is present in the acid, and practically absent from the other solutions?

b. Take some distilled water in a beaker and add to it 2–3 drops of methyl orange solution, and divide the liquid between three test-tubes. To the first two add a little acetic acid (?), to the third a drop of hydrochloric acid (?). To the first add now some solid ammonium chloride, and shake (?). To the second add some solid ammonium acetate, and shake (?). What ionic substance has disappeared? Explain the difference in behavior [C 596; I 809]. To the third add solid ammonium chloride, and shake (?). Explain the absence of effect.

c. Repeat **a**, using phenolphthalein instead of methyl orange. What ionic substance is present in the alkaline, and practically absent from the other solutions?

d. Take some distilled water in a beaker and add to it 2–3 drops of phenolphthalein solution, and divide the liquid between three test-tubes. To the first two add just enough dilute ammonium hydroxide, and to the third just enough dilute potassium hydroxide solution to turn the liquid a pale red in each case (?). To the first add now some solid potassium nitrate, and shake (?). To the second add some solid ammonium nitrate, and shake (?). To the third add solid potassium nitrate, and shake (?). Answer the same questions as in **b**.

e. Take three portions of a saturated solution of potassium chlorate in as many test-tubes. (If there is any deposit in the bottles, this and the following solutions must be shaken before use to insure saturation.) To the first add saturated sodium chloride solution (?), to the second saturated potassium chloride solution (?), to the third saturated sodium chlorate solution (?). What are the approximate concentrations of each of the four original solutions [C and I, inside front cover]? Allow the three mixtures to stand for a minute or two (?) before drawing any conclusion. Explain [C 599; I 815]. The experiments will fail if all the solutions are not saturated.

f. To 1–2 c.c. of concentrated hydrochloric acid add concentrated sulphuric acid carefully drop by drop (?). Explain [C 600; I 816].

138. Purification of Sodium Chloride

a. Prepare about 150 c.c. of a cold saturated solution of common salt by grinding the salt for some time in a mortar with the water. If crude salt is used, it must first be washed with water. Place the solution in a beaker, and pass hydrogen chloride into the solution. Prepare this gas by placing a handful of common salt in a generating-flask (Fig. 19, Exercise 36), covering it with concentrated hydrochloric acid, and allowing concentrated sulphuric acid to fall into it from a dropping-funnel. The hydrochloric acid prevents frothing and steadies the stream of gas (why?). Deliver the gas into the solution through a thistle-tube with the mouth downward (?). When considerable precipitation has occurred, filter by putting a clean silver coin with milled edges in a funnel, pouring the liquid and crystals upon it, and pressing with a spatula.

Why is the thistle-tube preferable to ordinary tubing?

b. Explain why, in **a**, the salt is precipitated. If the crude salt had contained other salts, which of them would have been affected by the introduction of hydrogen chloride, and which not? Specifically, would sodium sulphate or magnesium chloride have been affected, and how? If either of these would be affected and had been present, under what circumstances might it have entered into the precipitate [**C** and **I**, inside front cover]? Within what limits, then, does the process give a means of purification?

139. Relative Activity of Several Acids

a. In clean test-tubes place equal volumes of (1) zinc chloride, (2) zinc sulphate, and (3) zinc acetate solutions. Compare their reactions towards litmus and towards Congo red paper [**C** 263; **I** 389] (?).

b. Into each pass hydrogen sulphide to saturation (?). Are actions like this reversible, theoretically? The reverse action consists in the action of what acid upon what insoluble salt in each case? Will it be equal with different acids [**C** 604; **I** 820]? If not, the most active acid will have kept the most zinc in solution and the least active the least.

c. To ascertain how much zinc remains in each solution, filter the mixtures separately and, after testing with Congo red paper (?), add ammonium hydroxide to each (?). The precipitates are

zinc sulphide (why?). Compare the amounts (?). Infer the relative activities of the acids (?).

Why was ammonium sulphide used in **135 f**?

140. Ionic Equilibrium Again

a. Take a larger amount of zinc sulphate solution, and add dilute sulphuric acid to it cautiously (only a few drops are required) until a sample just ceases to give any precipitate with hydrogen sulphide. Explain (?). To half of the mixture add much powdered, anhydrous sodium sulphate, stir until it has dissolved, and test a part with hydrogen sulphide again (?). What effect must the great addition of sulphate-ion have upon the hydrogen-ion introduced by the sulphuric acid? Why is zinc sulphide now precipitated?

b. To the other half of the mixture, add solid sodium acetate and shake until the latter has dissolved. Now lead hydrogen sulphide into the liquid (?). Explain why zinc sulphide is now precipitated (?).

141. Aluminium

a. Record here the action of aluminium on hydrochloric acid (**16 a**) and its degree of activity (?). Try the action of the metal on dilute sulphuric (?) and dilute nitric acids? Compare and explain (?).

b. Place some aluminium turnings with sodium hydroxide solution in a beaker (?). To ascertain whether anything has gone into solution, neutralize one-half of the liquid very carefully with dilute hydrochloric acid (?). Test the precipitate by **142 f** (?).

c. Divide the rest of the liquid from **b** into three parts. To these add solutions of calcium chloride (?), magnesium chloride (?) and zinc chloride (?) respectively. Write the general equation.

142. Reactions of Aluminium Salts

a. Test a diluted solution of aluminium sulphate with litmus paper (?). Explain (?). Use successive portions of this solution in **b**, **c**, and **d**.

b. Add ammonium sulphide solution (?). Filter off the precipitate, wash it until odorless (why?), and ascertain whether it is a sulphide or not (?). Preserve a part of it for **f**.

c. Add sodium carbonate solution (?). Filter off the precipitate, wash it until free from sodium carbonate (why?), and ascertain whether it is a carbonate or not (?).

d. Add a little sodium hydroxide solution (?). Proceed exactly as in **135 e**, and answer the same questions (?). Explain the difference in behavior observed (?).

e. To a small portion of the suspension from **d** add sufficient sodium hydroxide solution to redissolve the precipitate. Then add excess of ammonium chloride solution, and boil (?). Explain (?).

f. Proceed as in **135 g** with a small part of the filter paper from **b** (?) (or use the method in **135 d**).

g. Ammonium Alum — a Double Salt. Calculate what weight of ammonium sulphate $(NH_4)_2SO_4$ is required to give equimolecular proportions with 10 g. of aluminium sulphate crystals, which consist of the hydrated salt $Al_2(SO_4)_3{,}18H_2O$ (?). Weigh out the required quantities of the two salts and dissolve them separately, each in the smallest possible amount of hot water.

Then mix the clear solutions, suspend a thread tied to a glass rod in the mixture, and set it aside to crystallize. Note the form (?), color (?), and taste (?) of the crystals. What is their formula [**C 614; I 834**]?

h. Coagulation. Take 100 c.c. of water with clay in suspension, add 1 c.c. of aluminium sulphate solution, stir vigorously, and then add 15 c.c. of limewater. Observe the water after it has stood for some time (?). Explain [**C 615; I 834**] (?).

143. Analysis of a Baking Powder

Baking powders (see Exercise **110 f**) contain (1) sodium bicarbonate, (2) a substance which is acid (or becomes so on being heated), and (3) starch to delay interaction. The object is to learn what radicals are present in a given sample.

a. Preparatory. Place about 4 c.c. of the baking powder in a large test-tube, add 20 c.c. of water, and shake vigorously for several minutes. Test the gas that is given off by means of a glass rod dipped in limewater. Filter the liquid and test the clear filtrate as in **c, d, e,** and **f.**

b. Starch (see Exercise **101**). Perforate the filter-paper and with water wash some of the residue into a test-tube. Boil this suspension, and then cool it and fill the test-tube up with water.

With a glass rod, add to the suspension one drop of the iodine solution (?). A blue color indicates starch.

c. Tartrate Radical. Place 4 c.c. of the filtrate (**a**) in an evaporating dish with 5 drops of concentrated sulphuric acid and evaporate to dryness over a small flame. Charring and an odor of burnt sugar indicate a tartrate.

d. Phosphate Radical (see Exercise **92 c**). Take 1 c.c. of the filtrate (**a**) and acidify with 1 c.c. of dilute nitric acid. To 5 c.c. of ammonium molybdate solution add 3 drops of this mixture, warm, and set in the rack (?). Phosphates give a yellow precipitate.

e. Sulphate Radical (see Exercise **72 b**). Acidify about 5 c.c. of the filtrate (**a**) with 5 c.c. of dilute hydrochloric acid and add barium chloride solution (?). What is the precipitate (if any)?

f. Ammonium Radical (Exercise **82 e**). To 5 c.c. of the filtrate (**a**) add 5 c.c. of sodium hydroxide solution. Heat to boiling and note the odor (?) and reaction of the vapor (not the liquid) towards moist red litmus paper (?). What is the gas (if any)?

g. Calcium Radical. Shake about 0.5 c.c. of the baking powder with 5 c.c. of dilute hydrochloric acid. Filter and to the filtrate add ammonium hydroxide until the liquid is alkaline to litmus. Now add acetic acid until the solution is acid to litmus, boil, and filter if the liquid is not clear. Add ammonium oxalate solution. The precipitate, if any, is calcium oxalate [**C 581**; **I 736**].

h. Aluminium Radical. Wrap a few particles of the powder tightly in a small piece of filter-paper, and wind the platinum wire spirally round the mass. Char the little ball in the Bunsen flame, moisten it with cobalt chloride solution, applied with a glass rod, and heat again (?). The blue color of the ash is characteristic of aluminium.

i. Sodium and Potassium Radicals. Use the flame test, with and without cobalt glass, as in Exercise **123 a**.

j. Report. Summarize, stating which radicals were present and which absent (?).

CHAPTER XXII

COPPER, MERCURY, SILVER

144. Cuprous Chloride

a. Dissolve about 2 g. of cupric chloride in 15 c.c. of water in a small flask. Add 2–3 c.c. of pure, concentrated hydrochloric acid and about 5 g. of metallic copper, and boil [Hood] until the green tint is no longer perceptible in the dirty yellowish-brown color of the product. If a few drops added to a test-tube full of water, previously boiled to remove dissolved oxygen, confer a blue tinge upon the water, the action is still incomplete. What ion confers the blue tinge? What change do the cupric ions undergo? Is the change an oxidation or a reduction of cupric chloride?

b. To a small part of the solution, when cold, add excess of sodium hydroxide solution (?). Why is so much of this required? Preserve the mixture in a corked test-tube for use in **145.**

c. Pour the rest of the solution from **a** into a large amount of water in a beaker (?). Expose some of the solid product, while covered with water, to the sunlight (?).

d. To the rest of the solid product from **c** add concentrated hydrochloric acid, and shake (?). What is the complex negative ion here formed [**C 625; I 859**]? Does it give a greater or a less concentration of cuprous-ion than does the insoluble cuprous chloride? Upon this basis explain the process of solution here observed. Pour a little of the solution into much water (?).

e. To the rest of the solution made in **d** add a little chlorine-water (?). What ionic substance is shown by its color to be present? Pour this solution into much water (?).

Define this form of oxidation, and the form of reduction in **a,** in terms of ions.

f. Cuprous Iodide. Dilute a few drops of cupric sulphate solution and add potassium iodide solution (?). Filter. Wash the precipitate thoroughly (?). What is the color (?) of the precipitate, and what is it? Add part of the filtrate to some starch

emulsion (?). Shake the rest with some chloroform (?). Read the footnote on p. 22.

145. Cuprous Oxide

a. Divide the mixture from **144 b**, containing a precipitate of hydrated cuprous oxide, into three parts. Shake one persistently with air in a bottle, admitting fresh air from time to time (?).

b. Boil the second portion (?).

c. To the third portion add ammonium hydroxide (?). What is the color of the mixture? What complex ion is formed [**C 623**; **I 857**]? Why is cuprous oxide dissolved by ammonium hydroxide solution?

Shake this solution with air. What ion is formed? Is the action more or less rapid than in **a**, and why?

146. Cupric Hydroxide

a. To 1–2 c.c. of diluted cupric sulphate solution add excess of sodium hydroxide solution (?). Take one-third of this mixture and boil it (?).

b. Boil 1 g. of sugar dissolved in water (or use diluted glucose syrup) with a few drops of dilute sulphuric acid for several minutes (?). This gives glucose and fructose [**C 472**; **I 750**]. Add this glucose solution to another portion of the mixture from **a**, warm gently (?), and note all changes. Make no equation for the action of the glucose.

c. To the remainder of the mixture from **a** add ammonium hydroxide, and shake (?). What complex ion possesses this blue color [**C 622**; **I 857**]? Does this ion give a greater or a less concentration of cupric-ion than does the insoluble hydroxide? Upon this basis explain the process of solution here observed.

d. Cupric Bromide. Examine a solution of potassium bromide. What is the color of bromide-ion? Take 0.5 g. of cupric bromide (color?) in a dry test-tube. Add two drops of water and agitate for some time (?). Then add more water, a drop or two at a time, agitating vigorously, and giving the substance time to dissolve, if it can, after each addition. Continue the addition of water cautiously until the substance has all dissolved, and afterward until the change in color is complete, and then stop. What is the color of a concentrated cupric bromide solution? What is the color of

cupric-ion? Compare the color with that of cupric sulphate solution (?) and explain [C 623]. Formulate the change which has been witnessed (?).

e. Now take a fresh portion of cupric bromide and repeat the experiment as in **d**, stopping the addition of water at the green stage. Divide the mixture into two parts. To one add 2–3 g. of solid potassium bromide and shake vigorously (?). To the other portion add 4–5 g. of solid cupric chloride (?). Interpret the results.

147. Reactions of Cupric Salts

a. Use diluted cupric sulphate solution. What is the color of cupric sulphate itself? To what is the color of the solution due? Test the reaction of the solution with litmus paper (?) and explain [C 319; I 469]. Is copper an active metallic element?

b. Pass hydrogen sulphide through one portion (?). Is this action reversible, theoretically? Add dilute sulphuric acid (?). Do dilute acids act upon any sulphides (64 c)? Why not upon this one [C 605; I 822]?

c. To another portion add potassium ferrocyanide solution [C 627; I 863] (?).

d. Note here the interaction (44 a) of zinc with cupric-ion (?).

e. Make a borax bead and heat with it a minute particle of cupric oxide in the oxidizing (?) and in the reducing (?) flame, as in 2 g and h. The latter requires patience. If cupric sulphate had been used here, what reaction would have taken place [C 338; I 493]?

f. Prepare a match (or splinter of wood) as in 76. Place on the end a moistened mixture of any copper salt with anhydrous sodium carbonate and heat in the reducing region of a small Bunsen flame. Break up the charred stick in water in a mortar, wash away the lighter particles, and rub the residue hard with the pestle (?).

148. Ammonio-cupric Compounds

a. To a diluted solution of cupric sulphate add ammonium hydroxide (?), first a drop (?), then in excess (?). Of what ion does the copper now form a part? Do other compounds of copper yield the same ion (146 c)?

b. Try with the blue solution the tests in 147 b, c, and d (?). Are the concentrations of cupric ion given by cupric sulphide (?),

cupric ferrocyanide (?), cupric sulphate (?), and cupric hydroxide (?), larger or smaller than the concentration of free cupric-ion given by ammonio-cupric-ion? Which of these compounds would be dissolved by ammonium hydroxide solution, and which not?

c. Which action of all those in **147** and **148** should you hold to give the most delicate test for cupric-ion?

149. Cuprocyanides

a. To 3 c.c. of a diluted solution of cupric sulphate add potassium cyanide solution [CARE! POISON], first a drop (?), then in excess (?). Does the solution show the color of cupric-ion? In what form of combination is the copper [C 627; I 863]?

b. Divide the solution into three parts and try the tests for cupric-ion given in **147 b** and **d**, using in **d** a piece of granulated zinc (?). Would cuprous sulphide dissolve in potassium cyanide solution? Explain your answer. Does cuprous sulphide (?) give larger or smaller concentrations of free copper ions than does the cuprocyanide? Would potassium cuprocyanide give the bead test (**147 e**) or the match test (**147 f**)?

150. Double Salts (Potassium-cupric Sulphate)

a. Saturate water at 70° with 5 g. of finely powdered potassium sulphate (about 25 c.c. will be required). Calculate the weight of crystallized cupric sulphate which must be taken to get an equimolecular proportion, and dissolve it in its own weight of hot water. Mix the two solutions, taking care not to allow any undissolved fragments of either salt to get into the mixture, and set the result aside to crystallize (?). Examine the form of the crystals and compare with those of blue vitriol (?). Dissolve a part of the crystals in water and use portions of the solution for **b**.

b. With the solution try tests in **147 b**, **c**, and **d** (?). Is cupric-ion present? To another portion add ammonium hydroxide (?).

How do double salts differ (a) from complex compounds like potassium cuprocyanide and ammonio-cupric sulphate and (b) from simple salts like cupric sulphate?

151. Equivalent of Copper

a. Take a small rod of pure zinc, smooth the ends with a file, and weigh carefully. Place in a beaker an exactly known weight

of crystallized cupric sulphate (about 2 g.), and dissolve in distilled water. Put the zinc in this solution, and allow them to remain in contact until the latter is completely decolorized. Remove the zinc, free it carefully from the brown deposit (?), and dry and weigh it. What weight of zinc has gone into solution?

b. To avoid weighing the precipitate of copper, which it would be difficult to do exactly, calculate from the formula what quantity of copper was contained in the amount of blue vitriol taken (?). Calculate from your data the weight of copper displaced by the equivalent weight of zinc found in **19 b**, or, if this experiment was not performed, assume the latter to be 32.7. This weight of copper will be the equivalent (that of oxygen being 8). Look up the specific heat of copper [**C 40**], and use this and the equivalent observed to find the atomic weight (?).

c. What other atomic weights could be measured on this plan?

152. Mercurous and Mercuric Salts

a. Mercurous Nitrate. Place about 10 g. of mercury with 15 c.c. of diluted (1 : 1) nitric acid in a small beaker, and let the action go on for an hour. Stirring will cause crystallization. Dissolve the crystals in water to which a few drops of nitric acid have been added (why?). Use this solution in **c**.

b. Mercuric Nitrate. Boil some mercury or mercurous nitrate with excess of concentrated nitric acid. Evaporate [Hood] the solution on a water bath, moisten with nitric acid, and dry.

c. Reactions of Salts of Mercury. Use diluted portions of mercurous nitrate solution and of a diluted solution of any mercuric salt, and add to each the following reagents. Compare the results in each case.

(1) Litmus paper (?). Explain (?).

(2) Dilute hydrochloric acid (?). Treat the precipitate, if there is any, with ammonium hydroxide [**C 633; I 872**] (?).

(3) Sodium hydroxide solution [**C 632; I 870**] (?).

(4) Ammonium hydroxide [**C 633; I 872**] (?).

(5) Hydrogen sulphide to saturation [**C 632; I 871**] (?).

(6) Potassium iodide solution (shake), until there is no further change (?). What complex ion is formed? Using this solution, try an experiment to show that mercuric sulphide gives an even

smaller concentration of mercuric-ion than does this complex ion (?).

(7) Stannous chloride till there is no further change [C 631; I 869] (?).

(8) A clean piece of copper (?). Determine whether any copper goes into solution (?). Explain [C 634; I 873].

(9) Heat a little of a salt of mercury in a dry test-tube (?).

d. How could you distinguish a solution of a mercurous and of a mercuric salt, respectively, from salts of silver, copper, magnesium, zinc, and cadmium?

153. Reactions of Silver Salts

a. Take 1–2 c.c. of silver nitrate solution. Test its reaction towards litmus [C 636; I 876] (?). Is silver more or less active as a metallic element than copper?

Add dilute hydrochloric acid until no further precipitation occurs (?). Filter, wash the precipitate with water, and place a small part of it in the sunlight (?). Reserve the rest for **b**, **c**, and **d**.

Place a drop of silver nitrate solution on the skin, and examine after an hour (?).

b. To a small part of the precipitate from **a** add ammonium hydroxide (?). What complex ion is formed? Now add dilute nitric acid in excess (?). Formulate the action of this acid (?).

c. To another small part add sodium thiosulphate solution (?). Pass hydrogen sulphide (see **f**) through the mixture (?). Explain both actions (?).

d. Place the rest of the precipitate in a porcelain crucible, put on it a piece of granulated zinc, and fill up with dilute sulphuric acid. Stir from time to time (?). After an hour or two pour off the acid, take out any unchanged zinc, wash the precipitate with water by decantation, add ammonium hydroxide, and filter. Find out whether any silver chloride had remained unchanged and so passed into the filtrate (see **b** above) (?). When the filter paper is dry, place the dark powder in a hollow on a stick of charcoal and melt it with the flame of the blast-lamp directed downward upon it (?).

e. Dilute a few drops of silver nitrate solution and divide into two parts. To one add potassium bromide solution (?), and to the other potassium iodide solution (?). Add to each some ammonium

hydroxide (?). Compare the rates of action with that on silver chloride (?). Arrange the three salts and ammonio-argentic-ion in the order of decreasing ability to give argentic-ion (?). Relate this order to that of solubility [C and I, inside front cover].

f. Dilute 2–3 drops of silver nitrate solution and lead in hydrogen sulphide (?). Is this action reversible, theoretically? Divide the product into two parts, and to one add dilute nitric acid (?).

To the other part add potassium cyanide solution [CAUTION! POISON] (?). What is formed? Could silver chloride be precipitated from this solution? Explain (?).

g. Touch Congo red paper [C 263; I 389] with a dilute acid (?) and with a dilute solution of a base (?).

To 1 c.c. of silver nitrate solution add a few drops of potassium dichromate solution (?). Test the solutions before (?) and after mixing (?) with Congo red paper. (If the color of the dichromate obscures that of the Congo red, wash the test-paper with distilled water.) What product does this show? Make the equation accordingly (?).

Note that chromic acid solution is deep red in color, and as an acid is too feeble to affect this indicator.

CHAPTER XXIII

TIN AND LEAD. ELECTROMOTIVE CHEMISTRY

154. Tin

a. Place some tin (gran.) in a test-tube with diluted nitric acid (1 acid : 10 water) and set aside. After **155**, examine portions of the solution. Determine whether it contains a salt of ammonium (?), and explain. Determine whether it contains stannic-ion or stannous-ion (?). How does tin behave with concentrated nitric acid (**86 d**)? Explain the difference (?).

b. Stannous Halide. Heat about 1 g. of tin with pure, concentrated hydrochloric acid (see **16 a**) (?). Let the action go on until the acid is nearly exhausted. Warm, to hasten the action, and make sure that an excess of tin is always present. Use the solution in **c**, and in **155**. Proceed with later experiments until it is ready.

c. Stannic Halide. [HOOD.] To one-half of the solution from **b** add bromine-water until the color ceases to be destroyed, and drive off the excess of bromine by warming (?). Use this liquid in **155**.

155. Reactions of Stannous and Stannic Salts

a. In **a**, **b**, and **c** use a portion of each of the solutions from **154**, after dilution, with each reagent. Compare the two results in each case. Saturate (test?) each portion with hydrogen sulphide (?). To part of each product add dilute hydrochloric acid, to learn whether the action is easily reversible (?). Filter the remainder of each product, and treat the precipitates, separately, with warm yellow ammonium sulphide solution [**C 562**; **I 711**] (?). To the resulting liquids add dilute hydrochloric acid (?). Explain why both give the same product (?). What is the gas evolved?

b. Add mercuric chloride solution, at first a little and then in excess, first to the stannic (?) and then to the stannous solution (?). When the changes (two) in the latter are complete, boil, let the precipitate settle, filter the clear part of the liquid, and deter-

mine whether the tin in the filtrate is now stannous or stannic by adding a drop or two of bromine-water (see **154 c**).

c. Add to each portion a little sodium hydroxide solution (?). Proceed exactly as in **135 e** and answer the same questions (?). Explain the difference, if any, in behavior observed. What other hydroxide resembles those of tin and zinc?

d. Boil a small portion of the stannic solution with tin (gran.) for several minutes. Now add mercuric chloride solution (?) and compare with the results in **b** (?). Account for the change in the stannic-ion (?). What kind of chemical change was this?

e. Unknowns. Apply to the instructor for two unknown substances. Identify them, and report the result, as directed in **132.**

Reference for additional work. Crystallization of a Metal from a Solution of its Salt; Kiplinger, Journal of Chemical Education, 5, 964, 1928.

156. Lead

a. Dissolve 1 g. of lead acetate in 20 c.c. of water, place in it several pieces of granulated zinc, and set aside for a time. After **c** has been done, devise a way of precipitating any remaining lead-ion and showing the presence of zinc-ion in the solution (?).

b. Wash some of the lead from **a** with distilled water on a filter, and see whether it is possible to get washings which show no reaction for lead-ion with hydrogen sulphide (?). Account for what you observe (?).

c. Reactions of Lead Salts. Use successive portions of a diluted solution of lead nitrate.

(1) Test with litmus paper (?).

(2) Saturate (test?) with hydrogen sulphide (?). Is the action easily reversed?

(3) Add dilute hydrochloric acid (?). Filter, dilute the filtrate with 5–10 volumes of water, and saturate with hydrogen sulphide (?). Explain (?). What other chlorides are "insoluble"?

(4) Add sodium hydroxide very gradually (?), first a little, then in excess (?). What other hydroxides resemble this one?

(5) Add potassium iodide solution (?). Boil, filter, and examine the filtrate (?). Infer a property of lead iodide (?).

(6) Add potassium dichromate solution (?). Proceed as in **153 g** (?).

(7) Add dilute sulphuric acid (?). What sulphates are insoluble?

157. Lead Dioxide

a. Warm and agitate 1 g. of minium with 5–6 c.c. of dilute nitric acid until it no longer changes in color (?). Dilute with water, and filter. Reserve the precipitate for **b** and **c**. Show by tests selected from **156 c** that lead-ion is present in the filtrate. What theory of the nature of red lead is suggested by this action [C 657; I 903].

b. Treat a part of the precipitate from **a** with sodium hydroxide solution (?). To another part add a little concentrated hydrochloric acid (?), and explain (?).

c. Allow the rest of the precipitate from **a** to dry, place it in an evaporating dish, and direct upon it a stream of hydrogen sulphide (?). Explain (?).

d. Do aluminium, tin, and lead exhibit the properties of typical metallic elements [C 543; I 681]? Explain.

158. Displacement of Metals. Couples

a. Clean the surface of the metal sheets supplied to you [Instructor] with sandpaper, and cut from them five strips (5×30 mm.) of copper foil, six strips of sheet zinc and three strips of sheet lead. Attach to each, with the exception of one piece of zinc (reserved for **f**), a piece of copper wire 20 cm. long.

b. Zinc. In five test-tubes take 5 c.c. each of solutions of the nitrates of lead, mercury and silver and of cupric sulphate and dilute sulphuric acid. Label them, noting on the label the name, formula, and positive ion in each case. Place a strip of zinc halfway into each solution and examine from time to time (?). Tabulate the results, and keep the strips of zinc for use again in **f**.

c. Lead. In three test-tubes take 5 c.c. each of solutions of mercurous nitrate, silver nitrate and cupric sulphate and label them as in **b**. Place a strip of lead halfway into each solution and examine later (?).

d. Copper. Repeat **b**, using 5 strips of copper (?). Record negative as well as positive results.

e. For each positive result write an ordinary equation, and also an ionic equation [C 663; I 911] (?). When the result is negative, explain why it is so (?).

f. A Couple. Place 5 c.c. of dilute sulphuric acid in each of

five test-tubes. Take the sixth strip of zinc (with no wire) and the four strips of zinc which in b have been immersed in the salts (not the one placed in the acid), and immerse each of them as completely as possible in a portion of sulphuric acid (?). Do you observe any difference in the behavior of the clean strip and those partly coated with metal? Those coated with a foreign metal are called "couples." Which metal of the couple is attacked — the more active or the less active one?

Galvanized iron and tin plate are couples [C 671; I 921]. Name the pair of metals in each (?). When each is corroded by the chemical action of water or acids, which of the two metals in each case goes into combination? In your everyday experience, which is more apt to rust, galvanized iron or tinned iron (tin plate)? Give the reason for what you have observed (?).

g. Concentration Cell. Suspend a rod of tin about 60 mm. long by a thread from one end, and hang it near the bottom of the graduated cylinder. Pour in through the dropping-funnel, which must reach the bottom of the cylinder, first water containing 5 drops of dilute hydrochloric acid and then diluted (1 : 1) stannous chloride solution. Perform the operation with care in such a way that the solutions do not mix, the dilute acid being finally uppermost, and that the surface at which they meet is near the middle of the rod of tin. If the second solution is permitted to carry air bubbles with it, mixing will inevitably occur. Place the arrangement where it will not be disturbed, and examine from time to time (?). Explain [C 672; I 922].

References for additional work. Lead Tree; Stone, Journal of Chemical Education, 6, 365, 1929. Experiment on Chromium Plating; Fine, Journal of Chemical Education, 8, 933, 1931.

CHAPTER XXIV

ARSENIC, ANTIMONY, BISMUTH

159. Arsenic

a. Heat one particle of arsenic in a hard glass test-tube (?).

b. Roast a particle of arsenic on a crucible lid (?). Note the behavior and odor (?).

c. Mix a pinch of pulverized arsenic trioxide with wood charcoal (pulv.). Heat the mixture strongly in a dry test-tube (?). Compare results with **a** (?).

d. Boil 0.5 g. of arsenic (pulv.) with excess of nitric acid [HOOD] (?). Compare with **92 b.** Use the solution for **161 c.**

160. Arsenic Trioxide and Arsenious Chloride

a. Boil 0.5 g. of arsenic trioxide with water (?). Test the mixture with litmus (?). Now add sodium hydroxide solution, and boil (?). To what class of oxides does the trioxide appear to belong? Formulate the whole change.

b. Boil 1 g. of the trioxide with 2–3 c.c. of concentrated hydrochloric acid (?). To what class of oxides does it appear now to belong? Formulate this change (?). Set aside and examine later (?). What are the crystals [**C 679; I 936**]? Is this action reversible? Use the solution for **c** and **162.**

Is arsenic a typical metallic element? Is it a metallic element at all? Give reasons taken from **a** and **b.**

c. Take a small part of the solution from **b** (setting aside the rest), dilute with water, and saturate with hydrogen sulphide (?). Divide into two parts. With one, try whether the action is easily reversible (?). Filter the other and heat the precipitate with yellow ammonium sulphide solution (?). What other sulphide behaved in this way? Now add dilute hydrochloric acid to the liquid (?). Explain (?). What is the gas evolved?

161. Arsenites and Arsenates

a. Arsenites. Use successive portions of diluted potassium arsenite solution.

(1) Add silver nitrate solution (?), then ammonium hydroxide (?).

(2) Add cupric sulphate solution [I 863] (?).

(3) Test the solution with litmus (?). What substances must be present? Saturate with hydrogen sulphide (?).

b. Arsenic Acid and Arsenates. Use successive portions of diluted potassium arsenate solution.

(1) Add silver nitrate solution (?). Add now ammonium hydroxide (?).

(2) Add magnesia mixture (93 c) (?). Compare with 134 b (?).

(3) Add to ammonium molybdate solution as in 92 c (?).

(4) Add 2–3 drops of dilute hydrochloric acid (?) and saturate with hydrogen sulphide (?). Now add excess of concentrated hydrochloric acid and saturate again (?), heating to assist the action (?). Explain (?).

c. Neutralize the solution from 159 d with ammonium hydroxide, avoiding excess, and use tests selected from **b.**

162. Arsine

a. [HOOD. CARE! POISONOUS GAS *]. Arrange a side-neck test-tube (or small flask), with safety and straight delivery tubes and nozzle, to generate and burn hydrogen. Place in it a piece of chemically pure zinc, and add pure hydrochloric acid. When the air has been displaced (CARE! Test?), light the gas and hold a crucible lid in the flame (?). If there is no deposit, add a drop of the solution of arsenic trichloride (160 b), observe the appearance of the flame, and obtain a deposit on the crucible lid (?). What kind of chemical change takes place in the flame (see 64 b)? Heat the tube, through which the gas passes to the nozzle, with a Bunsen flame (?) [C 678; I 936]. When these experiments are completed, fill the test-tube with water to stop the action.

b. Apply bleaching powder solution (fresh) to the deposit (?).

* This experiment should not be performed by large classes; it is better reserved for lecture demonstration or for selected students.

Can arsine be made according to the general method considered in **100 b**? What other hydrides behave like arsine when heated?

163. Antimony

a. Proceed as in **159 a** and **b**, using antimony (?).

b. Heat 2–3 g. of pulverized antimony with concentrated nitric acid in a small flask [HOOD] (?). Dilute, filter, wash the precipitate well, dry, and use in **c**, **d**, and **e**. Use a small part to determine whether the product is a nitrate or not (?). What metal behaved similarly when treated with nitric acid? Compare with arsenic (**159 d** and **161 c**) (?).

c. Boil a small part with water (?). Add sodium hydroxide solution, and boil (?). What kind of oxide is it?

d. Boil a small part with hydrochloric acid (?). What kind of oxide is it?

e. Boil a part with an equal amount of potassium-hydrogen tartrate in 5–6 c.c. of water (?). Filter, and set the filtrate aside (?). What are the crystals? To answer this question, dissolve some potassium-hydrogen tartrate and test the solution with litmus (?). Later, dissolve some of the crystalline product in warm water and test with litmus (?). Inference (?).

f. Treat about 0.5 g. of antimony trichloride with water (?), and test the liquid with litmus paper (?). Add more water, warm, and ascertain whether the action is reversible by adding drop by drop (shake between drops) concentrated hydrochloric acid (?). When the liquid has become clear add a large amount of water (?). What law is illustrated? Finally, add concentrated hydrochloric acid again (?), and use the solution in **g**.

How does this action differ from that of water upon phosphorus trichloride (**94 b**) and upon arsenic trichloride [**C 683**; **I 941**]? What is the significance of this difference?

g. Dilute the liquid from **f**, saturate with hydrogen sulphide (?), and proceed as in **160 c** (?). Answer the same questions (?).

h. Stibine. Repeat **162**, using antimony trichloride (?).

164. Bismuth

a. Prepare a match (or splinter of wood) as in **76**, and proceed as in **147 f**, using any bismuth salt (?). What metals are obtain-

able in this precise way? Could zinc, mercury, silver, and aluminium be so obtained? Explain (?).

b. Warm about 1 g. of bismuth with 8–10 c.c. of diluted (1 : 1) nitric acid (?). Concentrate to 3 c.c. and set aside [C 685; I 944] (?). Compare this result with arsenic (**159 d**) and antimony (**163 b**) and interpret (?).

c. Proceed as in **163 f**, using bismuth nitrate (or the product from **b**) and nitric acid, instead of the salt and acid there employed (?).

d. Take 1–2 c.c. of bismuth nitrate solution, dilute it, and clear up with nitric acid if necessary. Saturate a part with hydrogen sulphide (?), and proceed as in **160 c** (?). Compare with the sulphides of arsenic and antimony (?).

e. To the remainder of the solution of bismuth nitrate add sodium hydroxide (?), at first a little, and then in excess (?). Compare this hydroxide with the oxides of arsenic (**160 a**) (?) and of antimony (**163 c**) (?).

Filter off the precipitate, ignite it in a porcelain crucible, and note the color when hot (?) and when cold (?).

f. Do arsenic, antimony, and bismuth exhibit the properties of typical metallic elements? If not, in what respects do they fail to do so?

g. Unknowns. Apply to the instructor for two unknown substances. Identify them as directed in **132** and [C 724; I 995], and report the result. Do not use Marsh's test (**162 a**) for arsenic.

Reference for additional work. The Preparation and Properties of an Alloy (Wood's Metal); Bachman, Journal of Chemical Education, 10, 241, 1933.

CHAPTER XXV

CHROMIUM AND MANGANESE

165. Chromates and Dichromates

a. Melt 5 g. of potassium carbonate with equal amounts of potassium hydroxide (omit this from the equation) and potassium nitrate (include only oxygen, from this, in the equation) at a low temperature in an iron crucible [Storeroom] and stir in (use the reverse end of a file) 5 g. of powdered chromite. Heat strongly [Blast-lamp] for several minutes (?). When the mass has cooled dissolve it in a little boiling water. Filter, and add dilute nitric acid to the solution until it is acid (?). Note the change in color (?).

b. Take some potassium dichromate solution and run into it potassium hydroxide solution from a burette till the change in color is complete. A test-tube trial will show the tint to be reached. Concentrate the solution and allow it to crystallize (?). What kind of salt (neutral, acid, basic, double, or complex) is potassium dichromate, essentially? What are the colors of dichromate-ion and of chromate-ion?

c. Use successive portions of diluted potassium chromate solution. What are the ions in this solution?

(1) Acidify a part of the solution with dilute sulphuric acid (?). Concentrate and set aside to crystallize (?).

(2) Recall the actions of hydrogen sulphide (**64 h**), of sulphurous acid (**69 f**), and of hydrogen peroxide (**57 e**), on such an acid solution (?).

(3) Add lead nitrate and barium chloride solutions to separate portions (?).

d. Repeat **c** (3) with potassium dichromate solution (?). Compare the results and explain (?).

e. Chromic Anhydride. Make a cold saturated solution of **5 g.** of sodium dichromate, add to it two volumes of concentrated sul-

phuric acid in a beaker, and cool (?). Filter through a small plug of asbestos, and dry the precipitate by smearing it on a piece of broken bisque plate [Storeroom].

166. Chromic Salts

a. Pulverize potassium dichromate (10 g.) thoroughly with one-fifth its weight of sulphur, and heat with the blast-lamp in a porcelain crucible for fifteen minutes. Grind up the resulting mass in a mortar with water, filter, wash the green residue thoroughly (?), and dry it on a radiator for use in **c**. Test the filtrate for potassium sulphate (?).

b. Make a borax bead, dissolve a particle of chromic oxide in it, and note the effects of the oxidizing and reducing flames upon it (?). All chromium compounds give the same result. If chromic sulphate had been used, what would have been the nature of the chemical action?

c. Chromic Chloride. Mix the chromic oxide, prepared in **a**, with one-third its weight of pulverized wood charcoal, make into a stiff paste with some starch, and mold the mixture into little pellets of the size of peas. Cover these completely with a layer of charcoal powder (why?) in a closed crucible, dry them by heating gently with the Bunsen flame, and let them cool before exposing them to the air (why?). Place them in a piece of hard glass tubing. Then connect with a chlorine apparatus and, when the chlorine gas has reached the pellets and completely displaced the air (why?), heat strongly with a blast-lamp. Conduct any superfluous chlorine into a test-tube filled with sodium hydroxide. Describe the substance which is formed, and try its solubility in water and acids (?).

d. Chrome-Alum. Dissolve 10 g. potassium dichromate in water, add the amount (calculated) of sulphuric acid necessary to form potassium sulphate and chromium sulphate, warm and add alcohol (7–10 c.c.), a little at a time, until the yellow color has entirely given place to a pure, bright green. The action takes some time to reach completion. Note the odor (?). Set the greater part of the solution aside to evaporate spontaneously. Concentrate the smaller portion on the water bath until crystals appear. Examine the form and color of the crystals from both portions (?). What is the color of their solution in water? What is the color of chromic-ion?

e. Reactions of Chromic Salts. Make a solution of chrome-alum. What are the ions in the solution?

(1) Boil a portion for some time [**C 694; I 958**].

(2) To another portion add sodium hydroxide solution, at first a little (?), then in excess (?). Boil [**C 693; I 957**] (?).

(3) Add ammonium sulphide (?). Filter off the precipitate, wash it until odorless, and determine whether it is a sulphide (?).

(4) Add excess of sodium hydroxide solution and then a large volume of bromine-water, and heat (?). Try another portion, using lead dioxide instead of bromine (?). Infer the nature of the action from the change in color (?).

Reference for additional work. The Preparation and Preservation of Large Crystals of Chrome Alum; Fliedner, Journal of Chemical Education, 9, 1453, 1932.

167. Manganates and Permanganates

a. Fuse a mixture of 5 g. of potassium hydroxide, 2.5 g. potassium chlorate (include only the oxygen, from this, in the equation), and 5 g. finely powdered manganese dioxide, at a red heat, in an iron crucible [Storeroom], stirring with the reverse end of a file, until effervescence ceases (?). Add the last ingredient gradually. Treat the mass with a small amount of cold water, decant the clear liquid away from the precipitate, and use it in **b**, **c**, and **d**. What is the color of manganate-ion?

b. Dilute a part of the clear green solution with a very large amount of water in a beaker (?). If no change should occur, pass carbon dioxide into the diluted solution (?). What is the color of permanganate-ion? How does this differ from manganate-ion in respect to composition, valence, and physical properties?

c. Add to another part a few drops of alcohol, and warm (?).

d. To the rest add a boiling solution of oxalic acid (?).

e. Repeat **c** and **d** with potassium permanganate solution, acidified by adding twice its volume of dilute sulphuric acid (?).

f. Recall the actions of hydrogen peroxide (**57 f**), hydrogen sulphide (**64 i**), and sulphurous acid (**69 g**) on acidified potassium permanganate solution (?).

168. Reactions of Manganous Salts

a. Use any manganous salt. What is the color of manganous-ion? Prepare with it a borax bead in the oxidizing (?) and reducing (?) flames.

b. Prepare a bead of a mixture of sodium carbonate and sodium nitrate on a platinum wire with any manganese compound (?).

c. To a diluted solution of a manganous salt, add ammonium sulphide (?). Is the product a sulphide?

d. To another portion add sodium hydroxide (?). Divide into two parts. Shake one with air (?). To the other add bromine-water, and warm (?).

e. Unknowns. Apply to the instructor for two unknown substances. Identify them, and report the result. Identify the negative radical as in **132.**

CHAPTER XXVI

IRON, COBALT, NICKEL

169. Iron. Ferrous and Ferric Salts

a. Recall the preparation of iron from an oxide (**18**), and the action of the metal on dilute acids (**16 a**) (?).

b. Prepare a borax bead with ferric oxide in the reducing (?) and oxidizing (?) flames.

c. Recall the action of heat upon ferric sulphate (**74 b**) (?).

d. Wash some crystals of ferrous sulphate in water until the surface layer has been removed by solution. Why is this necessary? Dissolve the clean crystals in freshly boiled distilled water and allow to cool. Dilute also some ferric chloride solution [see footnote, p. 154]. Use successive portions of these two solutions, and add to each the following reagents. Compare the results in each case.

(1) Ammonium hydroxide (?). Shake with air (?).

(2) Potassium ferrocyanide solution (?).

(3) Potassium ferricyanide solution (?) and add much water (?).

(4) Ammonium thiocyanate solution (?).

e. To portions of each solution add ammonium sulphide solution (?). Ascertain in each case whether the action is easily reversible (?). Explain the behavior of the ferric chloride solution [**C 713; I 984**] (?). How could you determine whether the free sulphur was formed before or after the acidification?

f. To portions of each solution add potassium iodide solution (?). To a little starch emulsion add a few drops of the ferric salt-potassium iodide mixture (?).

g. Saturate (test?) a portion of the ferrous solution with hydrogen sulphide (?). Explain in terms of the ion-product constant (?). Now add ammonium hydroxide (?). Filter. Wash the precipitate until odorless, and determine whether it is a sulphide or hydroxide (?). Explain in terms of the ion-product constant (?).

h. Saturate (test?) a portion of the ferric solution with hydrogen sulphide (?). Filter. What is the precipitate (test?)? Examine the clear filtrate, and determine, by means of tests from **d**, whether ferric-ion or ferrous-ion is present (?). Formulate the action of the hydrogen sulphide (?).

i. Boil a portion of the ferric solution with excess of pulverized iron for several minutes. Filter, and at once apply to part of the clear filtrate (color?) tests selected from **d** (?). Formulate the action of the iron.

j. To 2 c.c. of potassium permanganate solution add a large excess of dilute sulphuric acid (?). Add this mixture drop by drop to 5 c.c. of a dilute solution of ferrous-ammonium sulphate until the pink color is permanent [**C 700; I 968**] (?). Apply to this liquid tests from **d** (?). Formulate the action in terms of ions alone. Which kinds of ionic chemical change have been illustrated here? How could this action be used for estimating iron?

What other oxidizing agents convert ferrous into ferric salts (see **84 g**)?

k. Hydrolysis. Dissolve 0.5 g. each of ferric sulphate and ferrous sulphate (prepared as in **d**) separately in water, and warm very slightly. Observe the tints by looking downward through the solutions at a piece of white paper (?). Test each solution with Congo red paper, compare (?), and interpret the results. Now add some pure sulphuric acid to each and observe the tints again (?). Explain (?). What are the colors of ferrous-ion and ferric-ion, respectively? Which of these forms of the element is more typically metallic?

170. Double and Complex Salts of Iron

a. Iron-Ammonium Alum. Weigh 6 g. of ferric sulphate into an evaporating dish. Weigh out an equimolecular quantity (calculate) of ammonium sulphate. Dissolve the salts separately, each in the minimum amount of boiling water, mix the solutions, and set aside (?). Describe the crystals (?). Collect them upon a filter, wash them free from the mother-liquor, and dry with filter paper.

Ascertain (see **169 d**) whether iron-alum is a double salt, or a salt of a complex acid (?).

b. Ferrocyanides and Ferricyanides. Use successive portions of diluted potassium ferrocyanide solution.

(1) Add ammonium hydroxide (?) and compare with **169 d** (?).

(2) Add ammonium sulphide solution and compare with **169 e** (?). Is ferrous-ion present?

(3) Add bromine-water (shake) in excess, and boil off the superfluous bromine. To a part of the liquid add ferric chloride solution (see **169 d**) (?).

(4) To the rest of the liquid from (3) apply the residual tests in **169 d** (?). Is ferric-ion present?

c. Blue-Prints. Dissolve 10 g. of potassium ferricyanide in 100 c.c. of water, and 13 g. of ammonium-ferric citrate in a second 100 c.c. Mix equal volumes of the two solutions and filter if there is any precipitate. Paint evenly over unsized paper with a clean camel's hair brush, dry, and keep in a dark place until required.

When dry the paper is sensitive to light. Expose a sheet to bright sunlight in a photographic printing-frame. Wash thoroughly in very dilute hydrochloric acid. Why is the paper blue? Repeat with a second sheet, placing a fern or a design cut out of paper, or a photographic negative, in front of the paper. Why is the protected part unchanged in color?

d. Removal of Ink and Rust Stains. Stains of fresh writing **ink** (ferrous tannate, colorless, and an organic dye; both soluble) can usually be washed out with water, if the latter is used at once. After the oxidation has occurred, the ferric tannate (black, insoluble) must be reduced again, by soaking the cloth for 12 hours or longer in ammonium oxalate solution, before the stain can be washed out. **Rust** stains are often rendered soluble by ammonium oxalate also.

Take a piece of white linen, stained with ink or rust, and treat with ammonium oxalate solution as above. Interpret the result.

171. Reactions of Cobalt and Nickel Salts

a. With a small crystal of cobalt chloride, prepare a borax bead in the oxidizing (?) and reducing (?) flames.

b. To successive portions of diluted cobalt chloride solution add the following:

(1) Sodium hydroxide solution, first a little (?), then in excess, and warm (?). Shake with air (?).

(2) Ammonium sulphide solution (?).

(3) Potassium cyanide solution, first two drops (?), and then in excess (?). Boil the mixture. Add bromine-water (or chlorine-water, or bleaching powder) and then sodium hydroxide solution (?). Compare this with c (3) below (?).

c. Repeat a and b, using nickel sulphate crystals and solution.

d. **Unknowns.** Apply to the instructor for two unknown substances. Identify them as directed in **132**, and report the result.

172. Separation of Lead, Mercury and Silver

a. Mix in one test-tube 2 c.c. each of solutions of lead nitrate, mercurous nitrate, and silver nitrate. Dilute with water and add dilute hydrochloric acid until the precipitation is complete. Filter, and wash the precipitate with a little cold water.

b. To separate the **lead** pour 50 c.c. of boiling water through the filter, taking care to pour it over every part of the precipitate. Which compound will dissolve? Test the filtrate for the presence of this compound (?).

c. Next, to separate the **silver**, dilute 5 c.c. of ammonium hydroxide with water, place a clean vessel under the funnel, and pour the solution over the precipitate (?). What do you observe? Which compound is now dissolved (?) and which remains upon the filter?

To the filtrate, add concentrated nitric acid, until the ammonium hydroxide is neutralized (test on litmus papers) (?). Name the precipitate, and summarize the properties by which it may be recognized: Color (?), crystalline or amorphous (?), behavior towards ammonium hydroxide (?), towards light (?).

d. Finally, to get the residue on the filter into solution for the purpose of testing it for **mercury**, make a little *aqua regia* by adding 1 c.c. of concentrated hydrochloric acid to 0.5 c.c. of nitric acid, warm the mixture, and pour it on to the residue. Catch the filtrate in a clean test-tube. Dilute the filtrate with 5 c.c. of water and put into it a small strip of clean copper foil. After a few minutes, wash the foil, rub it gently, and examine [**C 634; I 873**] (?).

e. Devise confirmatory tests for each of the three metals, and apply them to the various portions separated in **b**, **c**, and **d**.

173. Identification of an Unknown Substance. Metallic Radicals *

a. Obtain [Instructor] an unknown solid substance.

b. External Examination. Record the state (?), color (?), luster, if any (?), crystalline form (?), odor (?).

c. Solubility and Reaction of the Solution [C 724; I 995]. Repeat **120 c** (?).

d. If the unknown is soluble in water, proceed at once as in **e** below. If it is **insoluble in water,** try to bring it into solution by boiling successively with dilute nitric acid (?), concentrated nitric acid (?), and *aqua regia* (?). In case it dissolves, evaporate off the excess of acid and proceed as in **e.** The only common substances which are still insoluble are: the sulphates of lead, strontium and barium; some silicates; calcium fluoride; silver chloride (soluble in ammonia).

Fuse with sodium carbonate in a crucible, cool, extract with water, and filter. The residue contains the positive radical of the unknown as carbonate, and may be analyzed for this as in **e,** after dissolving in dilute nitric acid.

e. To a portion of the solution of the unknown add dilute hydrochloric acid. If a precipitate is obtained, examine as in **C 725; I 996** (Group I).

f. If no precipitate is obtained with dilute hydrochloric acid, pass hydrogen sulphide through the same portion of the solution. If a precipitate is now obtained, examine as in **C 725–6; I 996** (Group II).

g. If no precipitate is obtained with hydrogen sulphide, boil the solution to expel all hydrogen sulphide, and add a few drops of concentrated nitric acid to oxidize any ferrous salt to the ferric state. Then proceed as in **C 726; I 997** (Groups IIIa and IIIb).

h. If still no precipitate has been obtained, proceed as in **C 726–7; I 997** (Groups IV and V).

* The systematic **identification of unknowns** demands a clear understanding of the subject-matter of Chapter LIII, keen observation and (most important of all) a certain amount of common-sense. Always be wary about reporting upon a substance as the result of a single test for either radical. If possible, devise one or more confirmatory tests to check up upon your result. Above all, make sure that your report is not directly contradicted by the physical properties of the substance or by its reaction in aqueous solution **[C 724; I 995].**

i. Report. State your conclusion, with the reason therefor (?). Also, show that the conclusion is in harmony with the observations recorded under **b** and **c** (?).

j. The Negative Radical in the unknown should now be identified by the plan outlined and detailed in **89** and **120**. Report as in **i**.

174. Analysis of a Coin

a. Weigh a new 10 cent piece to the nearest centigram (0.01 g.). Weigh also a filter-paper. Take 25 c.c. of concentrated nitric acid in the graduated cylinder, pour it into an equal volume of water in a beaker, and mix by stirring with a glass rod. Place the coin in a small beaker, and add the acid. If the action becomes vigorous, cover the beaker with a watch glass (?). Later on, when the action subsides, warm the solution and, if necessary, add more acid until the metal is all dissolved. Note the color of the solution (?).

b. Dilute the solution with 50 c.c. of water and keep it warm by heating on a wire gauze over a low flame. Add dilute hydrochloric acid, a few c.c. at a time (?). Stir well after each addition until the precipitate settles and leaves the solution clear. When further addition of hydrochloric acid causes no more precipitation, continue with **c**.

c. Place the filter-paper (weighed in **a**) in a glass funnel. Stir the solution in **b** thoroughly, and with the help of the stirring rod pour it, a few c.c. at a time, on to the filter-paper, taking care that the funnel never becomes too full (?). Try to get as much of the precipitate as possible out of the beaker on to the filter-paper in this part of the process. Now complete the transfer by means of the wash-bottle, wash the precipitate several times with distilled water (?), and set it aside until the next period to dry.

d. Weigh the filter-paper and the silver chloride precipitate on the balance to the nearest centigram. Tabulate your results as follows:

Weight of filter-paper	g.
Weight of filter-paper + silver chloride	g.
Weight of silver chloride	g.

e. Use the atomic weight table to calculate the weight of silver in the silver chloride precipitate (?). Tabulate your results now as follows:

Weight of coin	g.
Weight of silver	g.
Percentage of silver in coin	%

f. Devise a means of completing the analysis by determining the weight of copper contained in the filtrate from **c**. Before proceeding to carry out this determination, however, submit your plan to the instructor for criticism and approval.

g. Using the results of Exercise **173** and of previous exercises on the particular metals present, devise a scheme for (1) the qualitative, and (2) the quantitative analysis of a nickel coin. Submit your plan to the instructor for criticism and approval.

APPENDIX

I. Tension of Aqueous Vapor

Temp. C.	Press. mm.	Temp. C.	Press. mm.	Temp. C.	Press. mm.
10	9.2	18	15.4	26	25.1
11	9.8	19	16.3	27	26.5
12	10.5	20	17.4	28	28.1
13	11.2	21	18.5	29	29.8
14	11.9	22	19.7	30	31.5
15	12.7	23	20.9	31	33.4
16	13.5	24	22.2	32	35.4
17	14.4	25	23.6	.....	.....

II. Approximate Atomic Weights of the More Important Elements

Aluminium	Al	27	Manganese	Mn	55
Bromine	Br	80	Mercury	Hg	200.6
Calcium	Ca	40	Nitrogen	N	14
Carbon	C	12	Oxygen	O	16
Chlorine	Cl	35.5	Phosphorus	P	31
Chromium	Cr	52	Potassium	K	39
Copper	Cu	63.6	Silicon	Si	28.3
Fluorine	F	19	Silver	Ag	108
Hydrogen	H	1	Sodium	Na	23
Iodine	I	127	Sulphur	S	32
Iron	Fe	55.8	Tin	Sn	118.7
Lead	Pb	207	Zinc	Zn	65.4
Magnesium	Mg	24.3			

III. Lists of Apparatus

1. Equipment of Laboratory. These articles are for common use. Those marked * should be fixed in their places, so that they cannot be removed. The articles in this list, for the care of which no individual is responsible, should be as few as possible.

Balances[1]
*Barometer (with thermometer)
*Blast-lamps and bellows (or air supply)
*Burners, fish-tail
*Cork-press
*Iron mortar and pestle
Jars for refuse
*Lens (on light chain) or microscope
*Magnet
Radiators or drying oven
*Roll of paper, smooth, colored[2]
*Scales and weights[3]
Spectroscope (Browning's, direct vision, English make) [Instructor]
*Tripod for each blast-lamp

2. Supply Room. These articles are given out at the supply room when needed. The student who obtains one of them leaves a signed receipt, and is held responsible for the safe return of the article.

Supply of all apparatus in Lists 3 and 4, to replace breakage.
Articles, if any, which may be omitted from Lists 3 and 4
Apparatus for making sulphuric acid, *viz.*, distilling flask with bent neck, Chapman pump, rubber connections and screw clamp
Bisque plates
Bottles, square, 50 c.c.
Bottles, narrow mouth, 500 c.c.
Condensers, with rubber tubing and universal clamp and holder
Distilling flasks, 30 c.c.
Electrolytic cells
Graduated flasks (100 c.c., 500 c.c.)
Iron crucibles
Lead dishes
Retorts, 100 c.c.
Round bottom flasks, 250 c.c.
Screw clamps
U-tubes, 155 mm.

3. Individual Outfit: Non-returnable. A copy of this list accompanies each outfit and is checked by the student.

1 Clay triangle
Copper wire, No. 22, 10 ft.
Copper wire, No. 30, 20 ft.
25 Corks, assorted, small
1 File, rat-tail, 6 in.
1 File, triangular, 6 in.
Filter-paper, pkg., 11 cm.
Gas tubing, 2 ft.
Glass rod, 4 mm., 2.5 ft.
Glass tubing, 6 mm., 5 ft.[4]
1 Horn-pan balance, 6.5 in. beam
1 Litmus paper, box, both colors, 100 strips
1 Medicine Dropper
Parchment paper, pkg., 100 sheets[5]
1 Platinum wire, 3 in., No. 28

[1] Student balance, Varsity model.
[2] To prevent use for writing.
[3] Harvard trip scales, with rider (0–5 g.) to avoid loss of small weights, and weights (5 g.–1000 g.). A small platform spring balance (letter balance form), 0–100 g. grad. in ½ g., for measuring chemicals, in case horn-pan balances are not included in the individual outfits (see below).
[4] Stems of dropping funnel, thistle tube, and thermometer are of same diameter (6 mm.). This saves boring fresh corks, and thus avoids waste of time and supplies.
[5] Substitute for paper in list No. 1.

2 Rubber stoppers, 1-hole, No. 0
1 Rubber stopper, 2-hole, No. 6
Rubber tubing, 1 ft. 3/16 in.
1 Sand bath, 5 in.
1 Sponge
1 Test-tube brush, small
1 Test-tube holder
1 Towel (or muslin)
1 Weights, set, 10 mg. to 50 g.
1 Wire gauze, 4 × 4 in.

4. Individual Outfit: Returnable. A copy of this list accompanies each outfit and is checked by the student. A receipt for the outfit is left at the supply room, and the student is then held responsible for the return or replacement of every article upon the list. Articles marked * may be transferred to List II or even to List I.

1 Boat, porc., 6 cm.
1 Bridge, galv. iron[1]
1 Bunsen burner
1 Burette clamp
1 Cork borer, with rod, 5 mm.[2]
1 Crucible tongs
1 Deflagrating spoon, 13 mm. bowl
1 Funnel support, two holes
1 Iron stand, small
2 Iron rings, two sizes
1 Mortar, 10 cm., and pestle
1 *Pneumatic trough[1]
1 Sink tube, brass[1]
1 Pinch clamp
1 Spatula (horn or glass)
1 Test-tube rack
1 Wing top for burner
5 Beakers, nest, tall form, no lip, Nos. 0, 1, 2, 3, 4
1 Bottle, special, 32 oz.[3]
1 Bottle, special, 4 oz.[3]
2 Bottles, wide mouth, 250 c.c.
2 Bottles, wide mouth, 100 c.c.
1 Burette, plain, 50 c.c.
1 Crucible, porcelain, No. 6
1 Cylinder, graduated, 100 c.c.
1 Dropping funnel, 60 c.c. stem, 6 mm.
1 Evaporating dish, 5.5 cm.
1 Evaporating dish, 7 cm.
1 Evaporating dish, 8 cm.
1 Flask, wide mouth, 125 c.c.
1 Flask, wide mouth, 250 c.c.
1 Flask, 500 c.c., with cork
1 Flask, 1000 c.c., with cork
2 Funnels, 7.5 cm., short stem
4 Glass squares, 5 × 5 cm.
12 Test-tubes, 4 × 0.5 ins.
12 Test-tubes, 6 × 0.67 ins.
1 Test-tube, 6 × 1 ins.
2 Test-tubes, hard glass, 7 × 0.67 ins.
1 Test-tube, side-neck
1 *Thermometer, stem 6 mm.
1 Thistle safety tube, stem 6 mm.
1 Tube, hard glass, 1 × 0.67 in.
1 U-tube, with side tubes, 6 ins.
1 Watch-glass, 2 ins.
1 Watch-glass, 3.75 ins.
1 Watch-glass, 4.5 ins.

[1] Earthenware vessels, ¾ gallon milk pans, for which bridges of galvanized iron can be made, are inexpensive and last longer than tin troughs. The sink, if in the desk, can be provided with a tube to slip over the exit, and be used for collecting gases.

[2] Cork borers, if supplied for common use, are abused and soon become worthless. One size suffices.

[3] Mouth to fit No. 6 stopper.

IV. List of Chemicals

All chemically pure, excepting where otherwise stated.

After omissions, if any have been determined upon, the substances (excepting those marked **Cal.**) **are numbered consecutively** and, if a side-shelf is used, their bottles and places on the shelves are numbered to correspond.

(Spec.) indicates a small amount, or **specimen,** of the dry substance. These substances are *used* only in solution.

Cal. indicates one of the substances in the **calendar** which are set out only when needed, and then on a special shelf. This mark appears also upon the bottle, taking the place of the serial number.

Concentration, in case of a solution, is given as N, $\frac{1}{2}$ N, etc., to assist students in using suitable proportions in a rational way. The number in parenthesis following the concentration is the weight of the substance required, with water, to make one liter of the solution. Sat. = saturated. Excepting where a formula is given, the calculation assumes the use of the commonest form, often a hydrated one.

* **Rubber stoppers,** the rest glass.

The labels should bear the name of the substance and all the data mentioned above. Thus both the student and the person who prepares the solution are fully informed as to the nature of the contents.

Solids

1. Acid, boric (spec.)
2. oxalic, com'l.
   oxalic, **Cal.**
3. tartaric (spec.)
   Almonds, crushed, **Cal.**
   Apple, slices, **Cal.**
4. Aluminium, filings
5. oxide, purif.
6. sulphate, hydrated
7. Ammonium carbonate
8. chloride, com'l.
9. nitrate
10. molybdate (spec.)
11. oxalate (spec.)
12. phosphate
13. sulphate
14. thiocyanate (spec.)
15. Antimony, com'l.
16. trichloride
17. Arsenic, gran.
18. trioxide, pulv., com'l.
    Asbestos, long fiber, **Cal.**
19. short fiber
    Baking powder, **Cal.**
20. Barium chloride, com'l.
21. hydroxide (spec.)
22. oxide, purif.
23. peroxide, anhyd.
24. Bismuth, com'l.
25. nitrate
26. Bleaching powder
27. Cadmium sulphate (spec.)

Solids—*Continued*

28. Calcium carbide
29. Calcium carbonate, purif., pulv.
30. Calcium carbonate [Marble], gran. 4 mm.
31. Calcium chloride, gran.
32. fluoride, pulv.
33. oxide [Quicklime]
34. phosphide
35. sulphate, pulv.
36. sulphate [Gypsum], transp. cryst.
37. Calico, colored
38. Charcoal, animal, pulv.
39. wood, pulv.
40. wood, splinters 6 × 6 × 50 mm.
41. Chromite, pulv.
42. Chromium-potassium sulphate [Chrome-alum]

Cloth, cheese, **Cal.**
cotton, white, **Cal.**
woolen, **Cal.**

43. Coal, bituminous
44. Cobalt chloride
45. Cochineal (spec.)
46. Congo red paper
47. Copper, foil
48. turnings
49. Cupric bromide
50. chloride
51. oxide, pulv.
52. sulphate, hydrated
53. Fat, tallow
54. Ferric chloride (spec.)
55. Ferric oxide, com'l.
56. Ferric sulphate
57. Ferrous-ammonium sulphate (or ferrous sulphate)
58. Ferrous sulphide, gran. 4 mm.

Flour, **Cal.**

59. Gelatine
60. Gunpowder
61. Iodine
62. Iron, filings
63. Iron, nails washed with gasoline
64. Iron, pulv.
65. Iron pyrites, gran. 4 mm.

Iron, wire, **Cal.**

66. Labels, paper

Lactose, **Cal.**

67. Lead, gran., purif.

Lead, ½ g. pieces, **Cal.**
Lead, sheet, **Cal.**

68. acetate
69. dioxide, purif.
70. monoxide
71. nitrate, com'l.
72. oxide, red [Minium]
73. Magnesite, gran.
74. Magnesium, pulv.
75. Magnesium, wire, size No. 16
76. chloride
77. sulphate, hydrated
78. Manganese dioxide, pulv., com'l
79. Manganous chloride (spec.)

Meat, **Cal.**

80. Mercuric chloride
81. Mercurous nitrate

Mercury, **Cal.** [with dropper]
Naphthol (beta), **Cal.**
Nickel, "reduced," **Cal.**

82. sulphate
83. Paraffin

Phenol, **Cal.**
Phthalic anhydride, **Cal.**

84. Phosphorus, red

iodide, **Cal.**
pentachloride, **Cal.**
pentoxide, **Cal.**

85. Potassium bromate (spec.)
86. bromide
87. carbonate, purif.
88. chlorate, com'l.
89. chloride
90. chromate (spec.)
91. cyanide, 98% (spec.)
92. dichromate, pulv., com'l.
93. ferricyanide (spec.)
94. ferrocyanide (spec.)
95. -hydrogen sulphate (spec.)
96. -hydrogen tartrate
97. hydroxide, purif.

Solids—*Continued*

98. Potassium iodide
99. nitrate, com'l.
100. perchlorate
101. permanganate, com'l.
102. sulphate
Resorcinol, **Cal.**
103. Rosin
104. Sand, for sand baths
105. Sawdust
106. Silica, pulv., com'l.
Silver foil, **Cal.**
107. Silver nitrate (spec.)
108. sulphate (spec.)
109. Soda-lime
Sodium, **Cal.**
110. Sodium acetate, fused
111. -ammonium phosphate [Microcosmic salt]
112. carbonate, anhyd.
113. carbonate, hydrated
114. chlorate (spec.)
115. chloride [Common salt]
116. dichromate, com'l.
117. -hydrogen carbonate
118. -hydrogen sulphite, com'l.
119. hydroxide, purif.
120. nitrate
121. nitrite, com'l.
122. peroxide
123. phosphate
124. sulphate, anhyd.
125. sulphate, hydrated
126. sulphide, com'l.
127. sulphite
128. tetraborate [Borax], pulv.
129. thiosulphate, com'l.
130. Starch
131. Stannous chloride
132. Strontium chloride
133. sulphate, pulv.
134. Sugar, com'l.
135. Sulphur, flowers
136. roll
137. Talc [Talcum], pulv.
138. Tin, gran., com'l.
Tin, rod, 60 mm., **Cal.**
139. Turmeric paper
140. Vaseline
Wood splinters, 16 cm., **Cal.**
141. Wool yarn, white
Yeast, **Cal.**
142. Zinc, gran., com'l.
143. Zinc, pulv.
Zinc I, 2 g. pieces, **Cal.**
Zinc I, rod 30 to 40 mm., **Cal.**
Zinc I, sheet, **Cal.**
144. acetate (spec.)
145. chloride (spec.)
146. sulphate

Liquids and Solutions

147. Acid, acetic, 6 *N* (420 c.c., 80%)
148. boric (½ sat., 35) [for burns and cuts]
149. hydrochloric, conc., 13 *N*
150. hydrochloric, dil., 6 *N* (467 c.c.)
hydrochloric, normal, **Cal.**, *N*
151. nitric, conc., 16 *N*
152. nitric, dil., 6 *N* (382 c.c.)
153. oxalic, 2 *N* (sat., 126)
154. picric (20 + 100 c.c. alcohol)
155. phosphoric, 1.73 sp. gr., 46 *N*
pyrogallic, **Cal.** (278)
156. sulphuric, conc., 36 *N*
157. sulphuric, dil., 6 *N* (167 c.c.)
sulphuric, normal, **Cal.**, *N*
tartaric, **Cal.**, *N* (75)
Alcohol, 95%, **Cal.**
158. Alizarin, 20% paste (50)
159. Aluminium sulphate, *N* (111)
160. Ammonium carbonate, 2 *N* (78.5 + 300 c.c. NH_4OH)
161. chloride, 4 *N* (213.5)
162. hydroxide, com'l., 7 *N* *
163. molybdate + HNO_3 (70 + 180 c.c. HNO_3)

Liquids and Solutions—*Continued*

164. Ammonium oxalate, *N* (71)
165. sulphide, yellow (NH_4HS + S)
166. thiocyanate, *N* (76)
167. Amyl alcohol
168. Barium chloride, *N* (122)
169. Barium hydroxide [Baryta water], ½ *N* (sat., 79)
170. Benzene
171. Bismuth nitrate, *N* (161 + 80 c.c. HNO_3)
Bleaching powder, fresh, **Cal.** (sat.)
Bromine, **Cal.**
172. Bromine water, ⅓ *N* (sat.)
173. Cadmium sulphate, *N* (140)
174. Calcium chloride, 2 *N* (219)
175. hydroxide [Limewater], 0.04 *N* (sat.)
176. Carbon disulphide, com'l.
177. tetrachloride
Chlorine water, **Cal.** (sat.)
178. Chloroform
Chrysophenin, **Cal.** (10)
179. Cobalt chloride, *N* (118.5)
180. Cochineal solution
Cotton-seed oil, **Cal.**
181. Cupric sulphate, *N* (125)
Ether, **Cal.**
Fehling's sol., **Cal.**
182. Ferric chloride, *N* (90)
Formaldehyde, **Cal.** (10)
Gasoline (petrol), **Cal.**
Glucose syrup, com'l., **Cal.**
183. Glycerine, com'l.
184. Hydrogen chloride, sol. in toluene, com'l. (+ solid $CaCl_2$, for drying)
Indigo solution, **Cal.** (1 g. indigo-carmine)
Kerosene, **Cal.**
185. Lead nitrate, *N* (165)
186. Litmus solution, neutral
187. Magnesium sulphate, *N* (123)
Malachite green, **Cal.** (0.5)
188. Manganous chloride, *N* (99)
189. Mercuric chloride, ½ *N* (sat. 68)
190. Mercurous nitrate, ¼ *N* (70 + 4 c.c. HNO_3 + Hg)
Methyl acetate, **Cal.**
191. Methyl orange (1)
violet **Cal.** (0.5)
Milk, **Cal.**
sugar, **Cal.**
192. Nickel sulphate *N* (131.5)
Petrol, see gasoline
193. Phenolphthalein (1 + 500 c.c. alcohol)
Phosphorus trichloride, **Cal.**
194. Potassium arsenate [KH_2AsO_4], 2 *N* (120)
195. arsenite [$KAsO_2$ + H_3AsO_3 (90)]
196. bromate, ⅓ *N* (59)
197. bromide, *N* (119)
198. chlorate, saturated, ½ *N* (sat., 161)
199. chloride, saturated, 4 *N* (sat., 320)
200. chromate, *N* (97)
201. cyanide, *N* (65)*
202. dichromate, com'l., ½ *N* (74)
203. ferricyanide, ½ *N* (55)
204. ferrocyanide, ½ *N* (53)
hydroxide, **Cal.** (840)*
205. iodide, ½ *N* (83)
206. permanganate, ½ *N* (79)
207. Silver nitrate, ¼ *N* (42.5)
208. sulphate, 1/25 *N* (sat., 5.5)
209. Sodium acetate, *N* (136)
210. carbonate, 2 *N* (106 Na_2CO_3)*
chlorate, sat., **Cal.**, 6½ *N* (sat., 692)
chloride, sat., **Cal.**, 5½ *N* (sat., 322)
211. -hydrogen sulphate, saturated, com'l.
212. hydroxide, 2 *N* (80)*
213. phosphate, *N* (119)
214. thiosulphate, *N* (124)
215. Stannous chloride, *N* (112.5 + 500 c.c. HCl + Sn)

Liquids and Solutions—*Continued*

216. Starch emulsion
217. Strontium chloride, *N* (133)
Tannic acid, Cal. (10)
Tartar emetic, Cal. (10)
218. Toluene, com'l.
219. Zinc acetate, ½ *N* (59)
220. chloride, ½ *N* (34 $ZnCl_2$)
221. sulphate, ½ *N* (72)