SYNTHETIC INORGANIC CHEMISTRY

A COURSE OF LABORATORY AND CLASSROOM STUDY FOR FIRST YEAR COLLEGE STUDENTS

BY

ARTHUR A. BLANCHARD, Ph.D.
Professor of Inorganic Chemistry

AND

JOSEPH W. PHELAN, S.B.
Late Professor of Inorganic Chemistry

AND

ARTHUR R. DAVIS, Ph.D.
Assistant Professor of Chemistry
at the Massachusetts Institute of Technology

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PREFACE TO FIFTH EDITION

Six years have elapsed since the appearance of the Fourth Edition of this book. The general plan and purposes of the course therein outlined have continued to meet satisfactorily the problem of first-year college students in chemistry, yet the number of improvements and supplementary preparations and exercises that the present authors have accumulated and in part used in planograph form has so increased that a new edition seems to be in order.

A very considerable portion of the text has been wholly rewritten, and the entire text has been subjected to a revision and rearrangement. Specific new exercises and discussions which have been introduced include such topics as the determinations of vapor density and molecular weight, the standardization of acids and the titration of acids and bases, Faraday's law, and the use of the *p*H scale of hydrogen-ion concentration. Several new preparations have been introduced, and a few of the old ones have been discontinued. A complete list of apparatus and chemicals required in the course has been added to the Appendix.

The purpose of this, as well as of the former editions, may be indicated by a brief statement of the manner in which it is used with the large freshman class at the Massachusetts Institute of Technology. The entire year's work for both laboratory and class room is outlined in this book. Each year a list of experiments and preparations is made out and posted. All students are supposed to perform these exercises (thirty laboratory periods of three hours each in the course), and the class room exercises (sixty hours) are built around the methods and principles of this work. The lectures in chemistry (sixty hours) follow approximately the order in which the elements are taken up in the book, but no attempt is made to keep in exact step. The historical, industrial, and economic aspects of chemistry are left largely to the lectures, whereas the discussion of problems, both numerical and manipulative, is left for class room and laboratory.

The students of barely passing grade may not complete more than the posted exercises, but to the enthusiastic student is open a free choice of the other preparations, subject of course to the laboratory facilities. Indeed, except that he must not forget that class room quizzes and examinations are based on the posted preparations, the better student may be allowed to substitute others for posted ones.

All students entering the Massachusetts Institute of Technology should have met an entrance requirement in chemistry. It is very discouraging to such students to be set at once to reviewing what they have already had, however much they may need the review. The nature, and the considerable freedom in the choice, of laboratory work solves this situation in a very satisfactory manner. A review of preparatory school work is of course necessary, but by bringing this in incidentally the sting of it is removed.

The chapters of the book are divided into two parts, part one containing the directions for laboratory work, and part two the discussion of principles, review of previous work, and problems. Except for Chapters I and III the first part contains the directions for preparations involving the elements with which the chapter is concerned. Part two of these chapters contains directions for short experiments, many of which will be familiar from secondary school work or will have been shown in the lecture; the facts observed in the experiments, however, are stated, and the significance of the facts is discussed in the text. The student is privileged to perform as many of these experiments as he elects, but he is not required to perform any. He is required, however, to study and understand the experiments. In this way the necessary review is achieved while at the same time adding considerably to the student's previous knowledge and comprehension. These chapters end with a set of general questions which require a good deal of thinking and looking up of data. Written discussions of these questions are to be handed in by all students.

Chapter I is devoted to the quantitative measurements of chemistry — combining ratios, densities, and so forth. Part one may be actually performed in the laboratory or it may be handled with part two entirely in the class room; the laboratory work may start with the preparations of Chapters II and IV. Chapter III deals with the ionic theory. The preparation work is interrupted after about the fifth week and the short experiments in ionization are performed in the laboratory. Part two of Chapter III is simultaneously handled in the class room.

Students are required to prepare a preliminary report on each preparation before they are given an order card for the raw materials at the stock room. When the preparation is completed, the final report, which includes answers to questions and incidental experiments, is to be written. The preparation of these reports should be done as far as possible outside of laboratory time. The final report and the preparation are to be submitted together during laboratory time to the instructor. When both are satisfactory the preparation is accepted and taken to the recording office.

The preparations are attacked by the students with the same enthusiasm that research workers feel. For all that, the directions have been made very explicit, for the reason that if the inexperienced student were asked to devise his own directions his successes would not be frequent enough to maintain his courage. Difficulties enough are sure to arise, even with good directions, to develop originality and resourcefulness. The laboratory work develops a valuable technique, but the comprehension of chemistry comes from the effort put into preparing the reports. Note writing is very easy to neglect in the enthusiasm for getting ahead in the laboratory work. The preparation of reports might come to be regarded as irksome if a system were not firmly maintained from the start. With such a system the reports are prepared cheerfully and the desired progress in gaining a comprehension of chemistry is made.

A. A. BLANCHARD
A. R. DAVIS

CAMBRIDGE, MASS.
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SYNTHETIC INORGANIC CHEMISTRY

DIRECTIONS FOR WORK

The course outlined in this book is an experimental study of chemistry. Chapters I and III deal with general principles. The first part of each of these two chapters gives directions for experiments which are to be performed by the student. Records of these experiments are to be kept in the laboratory note book as follows: the experimental facts and measurements are to be recorded on the left-hand page as the note book lies open; opposite these statements, on the right-hand page, calculations are to be made, equations for the chemical reactions are to be written, and final conclusions are to be drawn. The second part of each of these chapters is devoted to notes discussing the principles that the experiments illustrate, and problems for home work.

The other nine chapters are devoted to preparations and experiments which reveal the properties of the various classes of the chemical elements and their compounds.

Preliminary Reports on the Preparations. Before beginning work on a preparation the student should have a clear knowledge of the whole procedure and should understand the reactions as well as the application of chemical principles to these reactions.

To that end study carefully the general discussion of the preparation as well as the procedure. On the left-hand page of the note book (1) write a brief discussion of the fundamental principles involved in the preparation; (2) write equations for all reactions; and (3) starting with the given amount of the principal raw material, calculate what amounts of the other substances are necessary to satisfy the equations. When the amount specified in the directions is different from that calculated, state the reason for the difference. Calculate also on the basis of the equations the amount of the main product as well as of any important intermediate products or by-products.

Present this preliminary report to an instructor and obtain his approval before beginning operations.

Manipulation. All references from the procedure to the general notes on laboratory manipulation (pp. 4–22) should have been studied before making the preliminary report. Indeed the instructor will probably make sure by a quiz that this has been done before he accepts the preliminary report.

Laboratory Record. The working directions, in the section entitled *procedure*, are to be kept at hand while carrying out the manipulations. These directions do not need to be copied in the laboratory note book; but it is essential, nevertheless, to keep a laboratory record in which are entered all important observations and data, such, for example, as appearance of solutions (color, turbidity); appearance of precipitates or crystals (color, size of grains, crystalline form); results of all weighings or measurements; number of recrystallizations; results of test for purity of materials and products, etc.

Questions on the Preparations. The sections under this title give suggestions for study, which involves laboratory experiments, consultation of reference books, and reasoning.

The answers to the questions should be written in the laboratory note book following the entries for the exercise, and this book should be submitted at the same time as the preparation for the approval of an instructor.

Use of Time in Laboratory. In preparation work it is frequently necessary to wait for considerable periods of time for evaporations, crystallizations, etc., to take place. This time may be utilized for work upon the study questions and experiments, but even then it is advisable to have usually more than a single preparation under way. Thus no time need be wasted by the energetic student who plans his work well. A program of work should be made out in advance of the laboratory exercise.

Yield of Product. Where possible the methods employed in these preparations resemble those actually used on an industrial scale; where this is impossible on the limited scale of the laboratory, mention is made of the fact, with reasons therefor. On account of the limitations connected with work on a laboratory scale, it is of course impossible to get as high percentage yields as could be obtained on a commercial scale. The weight of each preparation is to be determined and recorded, but the chief stress is to be laid upon the excellence of the product rather than upon its quantity.

Experiments. The second part of each of the nine chapters, of which the preparations comprise the first part, is devoted to short experiments. Not only are the directions for these experiments given, but the results to be observed are stated, and the meaning of the results is discussed. Thus this experimental part may be studied, and the experiments may or may not be actually performed, according to the discretion of the student, or the advice of the instructor. The study of this part should be made by every student as a preparation for the *Report* which he is expected to write on the chemistry of the elements dealt with in the chapter.

General Questions. These questions which appear at the end of each of the nine chapters are to serve as the basis of the written report referred to in the preceding paragraph.

Number of Preparations. A certain number of the preparations will be designated each term as "required," which means that they will be discussed in detail in the class room and that detailed knowledge of them will be assumed when examination questions are made out. Besides the required preparations, students will be able to make a number of others of their own selection — this selection of course being subject to the instructor's approval.

NOTES ON LABORATORY MANIPULATION

These notes are intended to help the student in foreseeing and in overcoming some of the difficulties that arise in experimental work. They by no means make it unnecessary for him to exercise ingenuity and originality in planning and carrying out the details of laboratory work. At the outset these notes should be read through carefully; then, when in the later work references to specific notes are made, their general bearing will be better appreciated.

1. PRECIPITATION; CRYSTALLIZATION

In the majority of chemical processes which are carried out in the *wet way*, separations are accomplished by taking advantage of differences in solubility. If a certain product is extremely insoluble and is formed almost instantaneously when solutions containing the requisite components are mixed, the process is called *precipitation* and the insoluble substance is called the *precipitate*. If the product to be formed is less insoluble, so that it separates more slowly, or only after evaporating away a part of the solvent, the process is called *crystallization*.

In some cases the precipitate, or the crystals, constitute the desired product; in others, a product which it is necessary to remove from the solution before the desired product can be obtained pure. In either case it is necessary to make as complete a separation as possible of the solid from the liquid. This involves the manipulations described under Notes 2, 3 and 4.

2. POURING

In pouring a liquid from a vessel, either into a filter or into another vessel, care must be taken not to slop the liquid or to allow it to run down the outside of the vessel from which it is poured. To this end touch a stirring rod to the lip of the dish or beaker (Fig. 1) and allow the liquid to run down the rod.

3. TRANSFERRING PRECIPITATES OR CRYSTALS

If large crystals have separated from a liquid they may be picked out, or the liquid may be poured off.

If a precipitate or a crystalline meal has formed it must be drained in a filter funnel. First pour off the liquid (see Note 2) — through the filter if necessary, so as to save any floating particles of the solid — then pour the main part of the damp solid into the filter. A considerable part of the solid will adhere to the dish; most of this may be scraped out by means of a spatula, but the last of it is most easily *rinsed* into the filter. For rinsing, a jet of water from the wash bottle (Fig. 2) may be used if the solid is very insoluble. If the solid is soluble in water, some of the saturated solution may be poured back into the dish from out of the filter bottle, and by means of this the last of the solid may be removed to the filter.

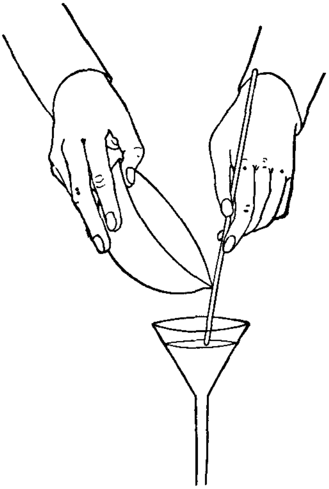


FIG. 1

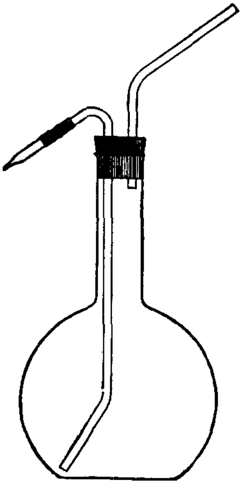


FIG. 2

4. FILTERING; COLLECTING PRECIPITATES

(*a*) *A coarse-grained crystal meal* can best be collected in a filter funnel in which a perforated porcelain plate is placed, and the mother liquor clinging to the crystals can best be removed with the aid of suction (see next paragraph).

(*b*) *Filtering with Suction.* With a fine-grained crystal meal, or a precipitate which is not of such a slimy character as to clog the pores of the filter paper, a suction filter is most advantageously used. A 5-inch filter funnel should be fitted tightly by means of a rubber stopper into the neck of a 500-cc. filter bottle (Fig. 3). Place a 1½-inch perforated filter plate in the funnel and on this a disk of filter paper cut so that its edges will turn up about 3 mm. on the side of the funnel all the way around. Hold the disk of dry paper in the right position, wet it with a jet from the wash bottle, draw it firmly down against the filter plate by applying the suction, and press the edges firmly against the side of the funnel, so that no free channel shall remain. In pouring the liquid, direct it with a stirring rod (Note 2) on to the middle of the filter; do not allow it to run down the side of the funnel, as this might turn up the edge of the paper and allow some of the precipitate to pass by. After all the solid has been brought upon the filter it may be freed from a large part of the adhering liquid by means of the suction, and it may then be purified by washing with a suitable liquid (see Note 5).

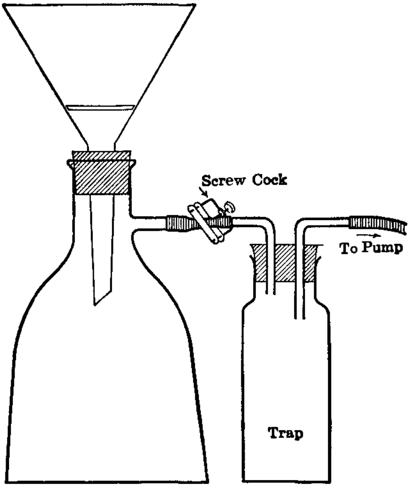


FIG. 3

The suction filter is very generally useful for the purpose of separating a solid product from a liquid. If the liquid runs slowly, the rate of filtration can be increased by using a larger filter plate or still better a Büchner funnel and thereby increasing the filtering area. The student should, however, avoid using the suction indiscriminately, for in many cases, as explained in paragraph (*c*), it is a positive disadvantage.

Suction. The most convenient source of suction is the Richards water pump, which can be attached directly to the water tap. If the water is supplied at a pressure of somewhat over one atmosphere (34 feet of water), a vacuum of very nearly an atmosphere can be obtained. If the pressure is insufficient, an equally good vacuum can be obtained by means of the suction of the escaping water. To this end the escape pipe must be prolonged by a tube sufficiently constricted to prevent the sections of the descending water column from breaking and thus allowing air to enter from the bottom.

To keep the suction pump working continuously, however, is extravagant of water as well as being a nuisance in the laboratory on account of the unnecessary noise. Consequently this rule is made and must be observed:

The suction pump must never be kept in operation more than two minutes at one time.

If suction must be applied for more than that length of time, the vacuum which is produced inside of the two minutes may be maintained in the suction bottle by closing the screw cock. (See Fig. 3.) Thus, if all the joints of the bottle are tight, a slimy precipitate may be left filtering under suction over night, or even longer.

Trap. The use of the trap shown in the diagram is always necessary, as otherwise dirty water may be sucked back accidentally and contaminate the solution in the filter bottle.

(*c*) *Filtering without Suction.* A slimy or gelatinous precipitate can be collected much better without suction. Suction drags the solid matter so completely into the pores of the filter that in most cases the liquid nearly ceases to run. A filter funnel and filter should be chosen large enough to hold the entire precipitate. The filter paper should be folded twice and then opened out in the form of a cone and fitted into the funnel. The upper edge of the filter should come about $\frac{1}{2}$ inch below the rim of the funnel. It is best to fit the paper carefully into the funnel, to wet it and press it up against the glass all around, so that there will be no air channels.

For slow-running liquids, if a large filter is used, it may be filled at intervals and left to take care of itself while other work is being done.

If a considerable weight of liquid is to come on the point of the filter, this may be reënforced by means of a piece of linen cloth, which should be placed under the middle of the filter paper before it is folded, and should then be folded in with it so as to strengthen the point.

After the precipitate is collected in the filter and drained, it should if necessary be washed (see Note 5).

Both filtration and washing take place much more rapidly if the liquid is hot. Time can also usually be saved if the precipitate is allowed to settle as completely as possible before commencing to filter. The clear liquid can then be decanted off, or if necessary poured rapidly through the filter before the latter becomes clogged with the main part of the precipitate.

(*d*) *Filtering Corrosive Liquids.* Solutions of very strong oxidizing agents, concentrated solutions of the strong acids and bases, and concentrated solutions of a few salts of the heavy metals — notably zinc chloride and stannous chloride — attack filter paper. Ordinary paper is thus unserviceable for filtration, but a *felt* made of asbestos fibers is frequently very useful. Shredded asbestos, which has been purified by boiling with hydrochloric acid and subsequent washing, is suspended in water; the suspension is poured onto a perforated plate placed in a filter funnel; and suction is applied whereby the water is removed and the fibers are drawn together to form a compact felt over the filter plate. Enough asbestos should be used to make a felt 1 to 3 mm. thick, and care must be taken to see that it is of uniform thickness and that no free channels are left through which solid matter may be drawn. Before it is ready for use a considerable amount of water should be drawn through the filter, and the loose fibers should be rinsed out of the filter bottle. Before pouring the liquid onto the filter the suction should be started gently, and the liquid should be directed by means of a stirring rod (Note 2) onto the middle of the filter. If these precautions are not observed the felt may become turned up in places, so that the precipitate will pass through.

A wad of glass wool in the bottom of a glass funnel may sometimes be used to filter corrosive liquids. Another method which can be used in separating crystals from a corrosive liquid consists in putting a glass marble into a funnel. The crystals form a mat in the small space between the marble and the sides of the funnel and the liquid can be removed by suction.

(*e*) *Cloudy Filtrates.* When a filtrate at first comes through cloudy, it is usually sufficient to pour the first portion through the filter a second time. The pores of the filter soon become partially closed with the precipitate, so that even the finest particles are retained. With some very fine-grained precipitates, repeatedly pouring the filtrate through the same filter will finally give a clear filtrate.

Special kinds of filter paper are made to retain very fine precipitates, but they allow the liquid to pass much more slowly than ordinary filters, and their use is not essential in any of the following preparations.

Particles of colloidal size may be removed by boiling the liquid with a little bone charcoal and subsequent filtration.

(*f*) *To Keep Liquids Hot during Filtration.* When liquids must be kept hot during a slow filtration, as, for example, when cooling would cause a separation of crystals that would clog the filter, it sometimes becomes necessary to surround the funnel with a jacket which is heated with steam or boiling water. In the following preparations the use of such a device will not be necessary, although there are several instances where it is necessary to work quickly to avoid clogging the filter. It helps to keep the funnel covered with a watch glass.

(*g*) *Cloth Filters.* In preparations made on a small scale, paper filters placed in ordinary filter funnels are invariably used if the liquid is not too corrosive. On a larger scale or in commercial practice, cloth is much used for filters, and it can be made in the shape of bags or it can be stretched over wooden frames. The cloth or other filtering medium (asbestos, paper pulp, sand, etc.) has to be chosen in each case with reference to the nature of the precipitate and the corrosiveness of the liquid.

Many of the preparations in this book, if carried out on a larger scale than given in the directions, would require the use of such cloth filters. It is often advantageous to tack one piece of cloth permanently across a wooden support and on top of this to lay a second cloth. The precipitate can then be easily removed together with the unfastened cloth.

For devices for rapid filtration and filtration in general on a large scale, a work on industrial chemistry should be consulted.

5. WASHING PRECIPITATES

(*a*) *Washing on the Filter.* Precipitates and crystals are washed to remove the impurities contained in the mother liquor which clings to them. Pure water is used for washing provided the solid is not too soluble or is not decomposed (hydrolyzed) by it. Special directions will be given when it is necessary to use wash liquids other than pure water.

First, the solid is allowed to drain as completely as possible, then the wash liquid is applied, preferably from the jet of a wash bottle, so as to wet the whole mass and to rinse down the sides of the filter. If suction is used, suck the solid as dry as possible, then stop the suction while applying the washing liquid; after the solid is thoroughly wet, suck out the liquid and repeat the washing.

A little thought will make it clear that the washing is much more effective if the liquid is removed as completely as possible each time before applying fresh wash liquid, and that a number of washings with a small amount of liquid each time is more effective than fewer washings with much greater quantities of wash liquid. It is, of course, evident that with each washing the liquid should penetrate to all parts of the solid material.

(*b*) *Washing by Decantation.* A very insoluble precipitate can be washed most thoroughly and quickly by decantation. The solid is allowed to settle in a deep vessel and then the clear liquid is poured (decanted) or siphoned off. Following this the precipitate is stirred up with fresh water and allowed to settle, and the liquid is again decanted off. By a sufficient number of repetitions of this process, the precipitate may be washed entirely free from any soluble impurity, after which it may be transferred to a filter, drained, and then dried.

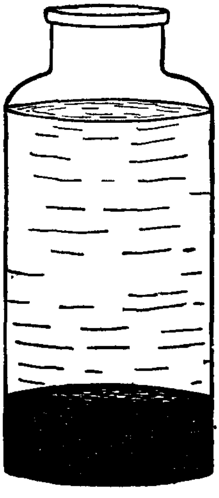


FIG. 4

Most precipitates, even after they have settled as completely as possible in the liquid from which they were thrown down, are very bulky, and their apparent volume is very large as compared with the actual volume of the solid matter itself. For example, a precipitate of basic zinc carbonate (Prep. 31), after it has settled as completely as possible in a deep jar (Fig. 4), may still occupy a volume of 400 cc. When this bulky precipitate is dried, however, it shrivels up into a few small lumps whose total volume is not more than 4 or 5 cc.

If a precipitate, which is at first uniformly suspended in a liquid, is allowed to settle in a tall jar until it occupies but one-fifth of the original volume of the mixture (Fig. 4), any soluble substances will still remain uniformly distributed throughout the whole volume. If now the upper four-fifths, consisting of the clear solution, is drawn away, it follows that practically one-fifth of the solution, containing one-fifth of the soluble impurities, remains with the precipitate. By stirring up the solid again with pure water, the soluble impurities become uniformly distributed through the larger volume, and on letting the precipitate settle and drawing off four-fifths of the liquid, as before, there will remain with the wet precipitate only $\frac{1}{5} \times \frac{1}{5} = \frac{1}{25}$ of the original soluble matter. After the third decantation the remaining suspension will contain $\frac{1}{5} \times \frac{1}{25} = \frac{1}{125}$ of the original impurities, and so on.

6. EVAPORATION

(*a*) When it is necessary to remove a part of the solvent from a solution, as when a dissolved substance is to be crystallized from it, the solution is evaporated. In some cases, where the dissolved substance is volatile or is decomposed by heat, the evaporation must take place at room temperature, but ordinarily the liquid may be boiled. The concentration of a solution should always be carried out in a porcelain dish of such size that at the outset it is well filled with the liquid. The flame should be applied directly under the middle of the dish where the liquid is deepest; the part of the dish against which the flame plays directly should be protected with wire gauze. Under no circumstances should the flame be allowed to play up over the sides of the dish: first, because, by heating the dish where it is only partly cooled by liquid, there is great danger of breakage; second, because, by heating the sides, the film of liquid which creeps up is evaporated and the solid deposited becomes baked hard and in some cases is decomposed. To prevent the formation of a solid crust around the edges, which even at best will take place to some extent, the dish should occasionally be tilted back and forth a little, so that the crust may be dissolved, or loosened, and washed back into the middle of the dish.

While evaporating a solution over a flame it should be carefully watched, for if it should be allowed to evaporate to dryness the dish would probably break and the product be spoiled. If a precipitate or crystals separate from the liquid and collect in a layer at the bottom, the dish may break, because where the solid prevents a free circulation of the liquid the dish becomes superheated, and then when in any one place the liquid does penetrate, the sudden cooling causes the porcelain to crack. Usually when a solid begins to separate from a boiling liquid the evaporation should be stopped and the liquid left to crystallize. After that the mother liquor may be evaporated further in a smaller dish.

(*b*) *Evaporating to Dryness.* The only circumstances under which a direct flame may be used to evaporate to dryness are that the dish shall be held in the hand all the time and the contents rotated to keep the sides of the dish wet.

Steam Bath. Laboratories are sometimes equipped with general steam baths, which are copper or soapstone chests kept filled with steam, and provided with round openings in the top into which evaporating dishes may be set.

Each student, however, may set up a steam bath, as shown in Fig. 5, at his own desk. After the water in the beaker reaches the boiling point a very small flame is all that should be used, because the steam that escapes around the sides of the dish is wasted; only as much as will condense on the bottom of the dish is effective. With such a steam bath there is no danger of spattering or of decomposing the solid product while evaporating a solution to dryness.

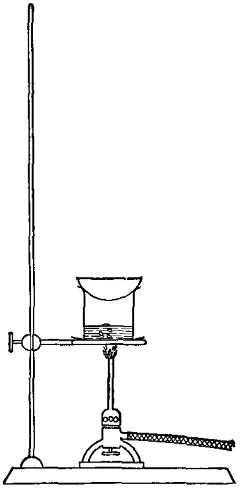


FIG. 5. Steam Bath for Evaporating to Dryness. Note 6 (*b*)

Hot Plate. A large, thick iron plate kept hot with a burner or with steam coils is useful for drying certain damp preparations.

7. DISSOLVING SOLID SUBSTANCES

The process of dissolving solid substances is hastened, first by powdering the substance as finely as possible, and second by raising the temperature. The solid and solvent should be heated together in a porcelain dish (not in a beaker), and care should be taken to keep the mixture well stirred, for if the solid should settle in a layer on the bottom, that part of the dish would become superheated and would be likely to break (see last paragraph in Note 6 (*a*)).

The finer particles of the solid dissolve first; as the solution becomes more concentrated the rate of solution grows slower, and it takes a very long time to dissolve the remaining coarser particles. Hence when a limited amount of solvent or reagent is used, as for example when copper is to be dissolved in a minimum amount of nitric acid, it is best to hold in reserve perhaps one-tenth of the reagent; when the nine-tenths are almost exhausted and the reaction with the coarser particles has almost stopped, pour off the solution already obtained, and treat the small residue with the fresh acid held in reserve.

8. CRYSTALLIZATION

(*a*) A great number of pure substances are capable of assuming the crystalline condition when in the solid form. Crystals are bounded by plane surfaces, which make definite and characteristic angles with each other and with the so-called axes of the crystals.

The external form of a crystal reflects in some manner the shape or structure of the individual molecules of the substance, for the crystal must be regarded as being built up by the deposition of layer on layer of molecules, all of which are placed in the same definite spatial relation to the neighboring molecules.

When a substance takes on the solid form very rapidly (as when melted glass or wax cools) its molecules do not have an opportunity to arrange themselves in a regular order, and consequently the solid body is *amorphous*. The axes of the individual molecules point in every direction without regularity, and consequently the solid body possesses no crystalline axes or planes.

It is evident from the above that the essential condition favoring the formation of perfect crystals is that the solid shall be built up very slowly. This is the only general rule which can be given in regard to the formation of perfect crystals.

The excellence of a chemical preparation is judged largely from its appearance. The more uniform and perfect the crystals, the better appearance the preparation presents.

In the following preparations sometimes a pure melted substance is allowed to crystallize by simply cooling; the cooling should then take place slowly. More often crystals are formed by the separation of a dissolved substance from a saturated solution. Perfect crystals can best be obtained in this case by keeping the solution at a constant temperature and allowing it to evaporate very slowly. This is easily accomplished in industrial works where large vats of solution can be kept at a uniform temperature with steam coils and allowed to evaporate day and night. On the laboratory scale it is almost impossible, first on account of variations in temperature, and next on account of dust which inevitably falls into an uncovered dish.

The majority of substances are more soluble at higher temperatures than at lower. If a solution just saturated at a high temperature is allowed to cool very slowly, it is possible for the solid to separate so slowly as to build up perfect crystals. This is an expedient that can be adopted to advantage in several of the preparations. In many cases, however, when a saturated solution cools it becomes *supersaturated*, sometimes to a high degree. Then when crystallization is once induced it occurs with such rapidity that a mass of minute crystals, instead of a few large, perfect ones, is produced. To avoid this supersaturation a few *seed crystals* (*i.e.*, very small crystals of the kind desired) may be placed in the solution before it has cooled quite to the saturation point. These form nuclei on which large crystals can be built up, and when they are present it is impossible for the solution to remain supersaturated.

In carrying out the following preparations the principles just stated should be kept carefully in mind; but in many instances specific suggestions will be given as to the easiest method for obtaining good crystals of any particular substance.

Large crystals, it is true, present a pleasing appearance, but oftentimes they contain a considerable quantity of the mother liquor inclosed between their crystal layers. Hence if purity of product is the sole requisite, it is often more desirable to obtain a *meal* of very fine crystals. Such a meal is obtained by crystallizing rapidly and stirring while crystallizing. Some substances are so difficult to obtain in large crystals that it is more satisfactory to try only to obtain a uniform crystal meal.

(*b*) *Purification by Recrystallization.* When a given substance crystallizes from a solution, it generally separates in a pure condition irrespective of any other dissolved substances the solution may contain. Thus a substance can be obtained in an approximate state of purity by a single crystallization. Portions of the mother liquor (containing dissolved impurities) are, however, usually entrapped between the layers of the single crystals, not to mention the liquid which adheres to the crystal surfaces. By dissolving the crystals, the small amount of impurity likewise passes into the solution, but only a small fraction of this impurity is later entrapped by the crystals when they separate from this mother liquor. By several recrystallizations, then, a substance can be obtained in a very high state of purity.

9. DRYING

(*a*) A preparation that is not affected by the atmosphere can be dried by being spread in a thin layer, allowing the liquid adhering to the grains or crystals to evaporate. Paper towels are extremely useful in drying preparations because a great deal of the moisture is absorbed into the pores. When a corrosive liquid, for example nitric acid, clings to the product, the latter is best spread on an unglazed earthenware dish, which absorbs the liquid without being attacked by it. During the drying the material should occasionally be turned over with a spatula.

If the material is not decomposed by heat it can be dried much more rapidly in a warm place, as on a steam-heated iron plate (steam table); but *a product containing water of crystallization should never be dried at an elevated temperature.* During the drying the preparation must, of course, be carefully protected from dust.

(*b*) *Efflorescent crystals and crystals which absorb carbon dioxide* should be quickly pressed between paper towels until as much as possible of the liquid is soaked up, and then they should be wrapped in a tight package in several layers of fresh paper towels and left in the cupboard for not more than 24 hours. The liquid is drawn by capillarity into the paper and evaporates from the outer surface, but the paper so impedes the circulation of air that water vapor does not escape, and the crystals will not effloresce unless left for more than a day. With preparations that react with carbon dioxide (such as barium hydroxide) the solution which soaks into the paper retains all the carbon dioxide which might otherwise contaminate the product.

(*c*) *Substances which decompose on standing exposed to the air* may be quickly dried if they are first rinsed with alcohol, or with alcohol and then ether. Rinsing with alcohol removes nearly all the adhering water, and a further rinsing with ether removes the alcohol. Alcohol evaporates more rapidly than water, but ether evaporates so rapidly that a preparation wet with it may be dried by a very few minutes' exposure to the air.

Alcohol and ether are both expensive and should be used sparingly. They can be used most effectively as follows: After all the water possible has been drained from the preparation, transfer the latter to an evaporating dish and pour over it enough alcohol to moisten it thoroughly; stir it with a spatula until the alcohol has penetrated to every space between the crystal grains, then pour off, or drain off, the alcohol and treat the preparation in like manner with another portion of fresh alcohol. After that wash it once or twice with ether in exactly the same way. If the preparation is washed on the filter, drain off the water as thoroughly as possible, stop the suction, add just enough alcohol to moisten the whole mass, and after letting it stand a few moments drain off the liquid completely. Apply a second portion of alcohol and portions of ether in the same manner.

10. PULVERIZING

In chemical reactions in which solid substances are involved the action is limited to the surface of the solid, and for this reason it is evident that it must be much slower than reactions which take place between dissolved substances; it is also evident that, the more finely powdered a solid substance, the greater is its surface, and therefore the more rapidly it will react.

For grinding any quantity of a substance a large porcelain mortar (say 8 inches in diameter) with a heavy pestle is preferable to the small mortars usually supplied in the desks. One or more such mortars is placed in the laboratory for general use.

If a hard substance can be obtained only in large pieces, it should first be broken with a hammer, then crushed into small particles in an iron or steel mortar, after which it should be ground in the porcelain mortar. In the final grinding it is often advisable to sift the fairly fine from the coarser particles, then to finish grinding the former by itself and to crush and grind the coarser particles apart.

11. NEUTRALIZING

Various indicators are used to determine whether a solution is acidic or basic. For example, litmus is red in the presence of acid, blue in the presence of a base, and of an intermediate purple tint in pure water or a neutral salt solution. When a solution which is acid must be rendered exactly neutral, base is added until the solution gives the neutral tint to litmus. If the contamination will do no harm, a drop or two of the litmus solution is added directly to the liquid; otherwise, a drop of the liquid must be withdrawn on a stirring rod and touched to a piece of litmus paper.

It is a tedious operation exactly to neutralize a solution in this way, but the process is greatly facilitated if a fraction of the liquid to be neutralized is held in reserve in another vessel. The reagent may be added rather freely to the main portion until the neutral point is not only reached but overstepped. Then a part of the reserve may be added and the reagent again added, but more cautiously this time, and so on until the whole solution is exactly neutralized.

The procedure outlined in the last paragraph is a general one to follow whenever adding a reagent which must be used in exactly the right amount and not in excess: always hold a fraction of the original material in reserve before adding the reagent to the main portion.

12. DRY REACTIONS; FURNACES

Dry solid substances do not react appreciably with each other at ordinary temperature. Reactions are made possible in two ways: first, the *wet way*, in which the substances are dissolved and thus brought into most intimate contact. In many cases solution also produces ionization, which, as is known, greatly increases chemical activity.

Reactions in the *dry way* are rendered possible by heat. Heat alone increases the rapidity of a chemical reaction, it being a general law that the speed is increased from two to three times for every increase of 10°C. in temperature. If one or more of the reacting substances are melted by the heat, the same sort of intimate contact is brought about as in solutions. Fusion is likewise a means of producing electrolytic dissociation, and on this account also it increases chemical activity.

In some of the furnace reactions in which none of the substances are melted, as, for example, in the reduction of strontium sulphate to strontium sulphide by means of charcoal (see Preparation 20), the process probably takes place by virtue of a certain amount of gas which is continuously regenerated. A little of the hot charcoal is oxidized to carbon monoxide, which then reduces some of the strontium sulphate, it being itself changed to carbon dioxide thereby; the latter gas comes in contact with incandescent charcoal, and carbon monoxide is again produced.

Reactions in the dry way are usually carried out in crucibles of iron, clay, or graphite, according to which one is least attacked by the reagents. For rather moderate temperatures the crucible may be heated over a flame; otherwise the requisite temperature can be obtained in a furnace.

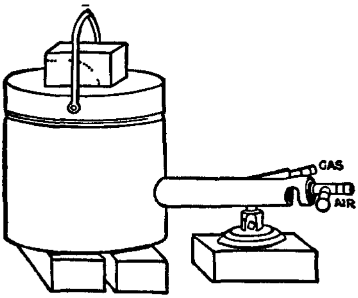


Fig. 6

The form of furnace to be recommended for this work is represented in Fig. 6. It consists of a cylinder of fire clay, 7 inches high and 7½ inches in external diameter, which is surrounded by a sheet-iron casing. It is heated, as shown, by a blast lamp introduced through an opening in the lower part of one side. If a suitable air blast is not available, a gasoline blow torch (such as is commonly used by plumbers) is serviceable.

When such a furnace as that described is heated as hot as possible with a well-regulated mixture of gas and air, a temperature of about 1,450°C. can be obtained. For carrying out ordinary chemical preparation work an accurate enough measure of the temperature is given by the color of the glowing interior of the furnace, and the approximate centigrade values corresponding to different colors are as follows:

Incipient red heat	550°
Dull red heat	650°
Red heat	800°
Bright red heat	1,000°
Yellow heat	1,200°
White heat	1,350°

13 GAS GENERATORS

(*a*) *Carbon Dioxide, Hydrogen, and Hydrogen Sulphide.* The simplest form of generator for these gases in shown in Fig. 7. The solid material, cracked marble for carbon dioxide, feathered zinc for hydrogen, and ferrous sulphide for hydrogen sulphide, is placed in the 300-cc. thick-walled generator bottle. The tubes are fitted as shown, and in the drying tube is placed a plug of cotton wool to strain the acid spray out of the gas, or if the gas is to be dried, granulated calcium chloride held in place with a plug of cotton wool on either side. Enough water is poured in through the thistle tube to cover its lower end and then about 5 cc. of 6N HCl. The gas begins to generate rather slowly, but if one is impatient and adds more acid at once the action will soon become so violent as to drive foam out through the delivery tube. After a few minutes add more acid, 1 cc. at a time, in order to keep up the evolution of gas at the desired rate.

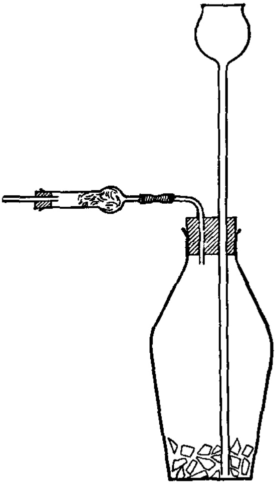


FIG. 7

(*b*) *Oxygen and Acetylene.* The apparatus shown in Fig. 8 is more suited for generating these gases, which are produced by allowing water to drip respectively on sodium peroxide and calcium carbide. Remove the fittings from the flask and place in it the required amount of dry material. The sodium peroxide to be used comes under the trade name of "Oxone"; it has been fused and then cracked into good-sized lumps which are so hard that they do not react with too much violence with water. With the fittings still removed from the flask, fill the thistle tube with water, open the pinch cock and allow the vertical tube to become completely filled, then close the pinch cock. Replace the fittings in the flask. Open the pinch cock cautiously to let a single drop of water fall on the material. Note the effect,

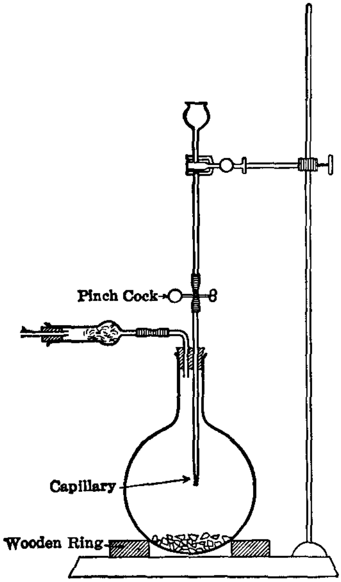


FIG. 8

and thereafter let the water in, a single drop at a time, to obtain the desired flow of gas.

(*c*) *Automatic Gas Generator for Carbon Dioxide, Hydrogen and Hydrogen Sulphide.* The apparatus shown in Fig. 9 is based on the principle of the familiar Kipp generator, and it is especially applicable if a solution is to be saturated with the gas in question, as, for example, when an ammoniacal solution of common salt is to be saturated with carbon dioxide in the preparation of sodium bicarbonate by the Solvay process.

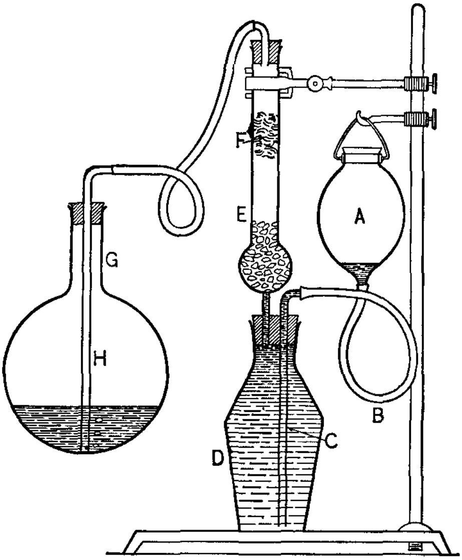


Fig. 9

Assemble the apparatus as shown in the diagram. The stem of the generator tube *E* should reach flush with the bottom of the stopper but not below. The delivery tube *C* should reach nearly to the bottom of the generator bottle *D*. Place the requisite amount of calcium carbonate (or zinc, or ferrous sulphide) in the generator tube. Then insert a loose plug of glass wool *F* about 1½ inches long so that it will stand about midway between the top of the solid material and the stopper in the mouth of the tube, and act as a gas filter (to remove acid spray). Pour the requisite amount of acid into the reservoir *A*; clamp the reservoir at just the same height as the generator tube, and pour in water cautiously until the acid rises and barely touches the solid in the generator tube. The generation of gas will now begin and proceed automatically as fast as the gas is allowed to flow from the delivery tube *H*.

Place the solution to be saturated with the gas in the flask *G*, insert the stopper and delivery tube, but let the stopper remain loose until the air is entirely expelled. Then make the stopper tight; the gas will pass in as rapidly as it can be absorbed by the solution. Shaking the receiving flask will greatly increase the rapidity of absorption, but this should be done with a good deal of caution at first, because if the undiluted acid is drawn too suddenly up in the tube *E*, the violence of the reaction may either blow out the stoppers or drive foam through the glass wool filter *F* and into the delivery tube *H*. After the solution is partly saturated the flask may be shaken continuously and the reservoir *A* raised to a higher level.

14. WEIGHING

Two types of balances are available for weighing:

1. *Rough Balances or Platform Scales.* These are to be used for weighing out materials approximately for preparations and qualitative experiments and for weighing heavy objects of more than 100 grams.

2. *Analytical balances,* which will weigh accurately to a centigram. These balances are enclosed in glass cases. They are not as sensitive as the best analytical balances, which weigh to one-tenth of a milligram, but they are sufficiently accurate to do some kinds of work extremely well and are so sensitive that they require careful and intelligent handling. *Hence before using one of these balances apply to an instructor for individual instruction as to its manipulation. The balances must not be used until permission is obtained.* The following general rules must always be observed:

1. No load of more than 100 grams should be put on the sensitive balances. No object heavier than this will need to be weighed with a greater precision than can be obtained on the platform scales.

2. The material to be weighed, unless it is in a single, clean, dry piece, should never be placed directly on the scale pan.

Usually powdered solids are weighed in a small vial or on a piece of paper. The object to be weighed should be placed on the left-hand pan, the weights on the right.

3. To be accurate the weights must be kept clean. Never touch them with the hands, but use the forceps.

4. When altering the load or weights, the scale pans must rest on the floor of the balance case. Never leave the lever raised except in taking the final swing after the weights are adjusted. During the swing the balance door must be closed, and before it is opened the pans must again be lowered.

5. The same balance and set of weights must be used throughout any one experiment in order that possible errors in the weights or balances may cancel in the successive weighings.

CHAPTER I

THE QUANTITATIVE ASPECTS OF CHEMISTRY

So many things happen when substances undergo a chemical change that it is no wonder the student is astonished and even bewildered by his observations. He soon learns that there is an entire change in physical properties of the reacting substances and finds that this phenomenon is usually the easiest to observe. Also he is able to discover the transformations of energy which always accompany a chemical change, although this is usually confined to observations of the evolution of heat.

He learns, usually from the text book, that no mass is lost or gained during a chemical change and that the total weight of the substances before and after is the same. This rule is known as the law of the conservation of matter, and it is more difficult for the student to convince himself of the truth of this characteristic of chemical change by direct observation because the experiments must be quantitative and require apparatus for measuring and weighing.

When hydrogen combines with oxygen to form water it is easily observed that a great deal of heat is given off, also that a liquid substance is formed and that the gases taken decrease in volume and in fact entirely disappear when exactly the right mixture is used. When measuring tubes are used it is observed that, when 2 volumes of hydrogen and 1 volume of oxygen are mixed, the gases entirely disappear after the reaction has taken place. When more than 2 volumes of hydrogen are taken to 1 of oxygen, the excess of hydrogen over the 2 volumes is found to remain unaffected; and likewise when more than 1 volume of oxygen is taken to 2 volumes of hydrogen, the excess of oxygen over the 1 volume is found to remain unchanged after the reaction. However, to determine that 1.008 parts by weight of hydrogen combine with exactly 8.00 parts by weight of oxygen requires elaborate apparatus and very painstaking measurements. This proportion, 1.008 : 8.00, is known as the combining ratio. Similar exact ratios exist in all chemical changes. When oxygen and zinc combine to form zinc oxide the ratio is found to be 1.00 of oxygen to 4.09 of zinc. No matter how much zinc or oxygen is used, the amount of the one or the other in excess of this ratio will be left over after combination has taken place.

Some substances do not combine with each other but each may combine with a third. Under such conditions a ratio may be calculated between the two substances that did not combine. Fluorine will not combine directly with oxygen, but each of these elements will combine with hydrogen. In hydrofluoric acid the ratio by weight is 1.008 of hydrogen to 19.00 of fluorine. In water the ratio by weight is 1.008 of hydrogen to 8.00 of oxygen. The combining ratio of oxygen to fluorine might be expected to be 8 : 19 or 1 : 2.375.

1. Determination of the Combining Ratio of Zinc and Oxygen

Zinc and zinc oxide are both substances the weights of which can be determined accurately, so that the quantity of oxygen which is combined in the oxide can be found by difference. To convert quantitatively a definite amount of zinc into the oxide by means of direct combination with oxygen would be a difficult operation; but the same result is accomplished indirectly by first treating the metal with nitric acid to obtain the nitrate and then decomposing the zinc nitrate by heat, which leaves a residue of zinc oxide.

Materials: zinc, chemically pure, about 20 mesh.
nitric acid, 6 *N*.

Apparatus: 4-inch porcelain dish.
5-inch watch glass.
600-cc. beaker.
Bunsen burner.
triangle, nichrome wire.
iron ring and ring stand.

Copy the following form on the left-hand page of your note book for recording data:

Weight of evaporating dish + zinc .... ---- grams
Weight of empty evaporating dish .... ---- grams

Weight of zinc .... ---- grams

Weight of evaporating dish + zinc oxide
after first heating............ ---- grams
second heating.......... ---- grams
third heating........... ---- grams
final weight........................... ---- grams
Weight of evaporating dish + zinc............ ---- grams
Weight of oxygen........................ ---- grams

Procedure: Weigh accurately a 4-inch porcelain evaporating dish. Place in it about 1 gram of pure zinc, and again weigh accurately. Add 5 cc. of water, and cover the dish with a 5-inch watch glass. Add 5 cc. of dilute nitric acid (6 N). Note the nature of the reaction which takes place and the color of the gas which is evolved. If the reaction stops completely before the zinc has entirely dissolved add 3 cc. more of dilute acid. When solution is complete remove the watch glass and, with a jet of water from the wash bottle, rinse the drops of liquid clinging from the under side into the dish. Place the solution on a water bath (beaker of boiling water), and leave it to evaporate (with the watch glass removed) as much as possible. When only a small amount of sirupy liquid (melted zinc nitrate) is left, take the dish to the hood, support it on a wire triangle, and heat carefully with a very small flame, holding the burner in the hand. If the liquid starts to boil, remove the flame at once, because every tiny drop that spatters out of the dish means a loss of material. Heat until the mass thickens and red fumes escape, and finally, after the mass becomes perfectly dry, heat quite strongly for a few minutes. Cool and weigh. Again heat quite strongly and weigh. The weight ought not to have decreased, but if it has, the heating must be continued until the weight becomes constant.

Calculation. From the weight of the zinc and the zinc oxide find the combining ratio of oxygen and zinc.

2. Weight of a Liter of Oxygen

Oxygen is generated by heating potassium chlorate, and its weight is determined by the loss in weight of that material. Since the gas is collected over water, under the conditions of temperature and pressure prevailing in the laboratory, the volume must be corrected to standard conditions by means of the formula on page 44.

Materials: potassium chlorate, dry, powdered.

Apparatus: wash bottle (see p. 5).
6-inch Pyrex test tube with 1-hole rubber stopper.
600-cc. beaker.
pinch cock.
2.5-inch funnel.
iron ring and ring stand.
Bunsen burner.
burette clamp.
2 feet of rubber tubing.

Data Form:

(*a*) Weight of test tube + potassium chlorate. . ------ grams
(*b*) Weight of empty test tube. . . . . ------ grams
(*c*) Weight of potassium chlorate. . . . . ------ grams
(*d*) Weight of test tube and contents after heating. . . . . ------ grams
(*e*) Weight of oxygen. . . . . ------ grams
(*f*) Weight of beaker + water. . . . . ------ grams
(*g*) Weight of beaker empty. . . . . ------ grams
(*h*) Weight of water. . . . . ------ grams
(*i*) Temperature. . . . . ------ °
(*j*) Barometric pressure. . . . . ------ mm.
(*k*) Vapor pressure (p. 353) . . . . ------ mm.

Procedure: Set up the apparatus as shown in Fig. 10. Clamp the wash bottle in an inverted position. Attach a 2-foot piece of rubber tube to the mouth piece of the wash bottle. Slip a pinch cock over the tube, and insert a small funnel in the open end. Raise the funnel to the position shown by the dotted lines in Fig. 10. Pour water through the funnel, and fill the wash bottle nearly to the top of the vertical tube. Close the pinch cock, and replace the funnel with the capillary tip from the wash bottle. Connect the other tube of the wash bottle to the Pyrex test tube by means of an elbow tube and rubber connection. Open the pinch cock and allow water to run out of the wash bottle into the beaker. If the apparatus is tight the flow of water will stop completely after a moment. Close the pinch cock, remove the Pyrex test tube, dry it, and weigh it accurately. Place in it about 2 grams of dry powdered potassium chlorate and again weigh it accurately. (The potassium chlorate must be finely powdered and thoroughly dried. Use the material which has been especially prepared for this experiment. It will be found in the balance room.) Connect the tube to the apparatus. Dip the capillary jet in a beaker of water, and raise the beaker until the surface of the water is at the same level in the beaker and in the flask. Open the cock until water has run in or out to equalize the pressure. Then close the cock. In this way the air in the apparatus at the start is at atmospheric pressure. At the end it must be brought to the same pressure, so that the two volumes are directly comparable. *Note:* It is important that the flexible rubber tube be filled completely with water; otherwise, when the levels are equalized, there will be a column of air in one part and a column of water in another part of the tube and the pressure on the gas in the flask will not be the same as that of the atmosphere on the water in the beaker. Empty the beaker and weigh it on the *platform balance* (do not use the analytical balance) without drying it. Hold the jet pointing into the beaker so that the water may be seen dripping into it, and thus the rate of the production of gas regulated. Open the pinch cock and commence heating the potassium chlorate, so that a steady, but not a rapid, stream of water runs from the jet. Heat slowly to avoid excessive pressure and to prevent the entrainment of finely divided

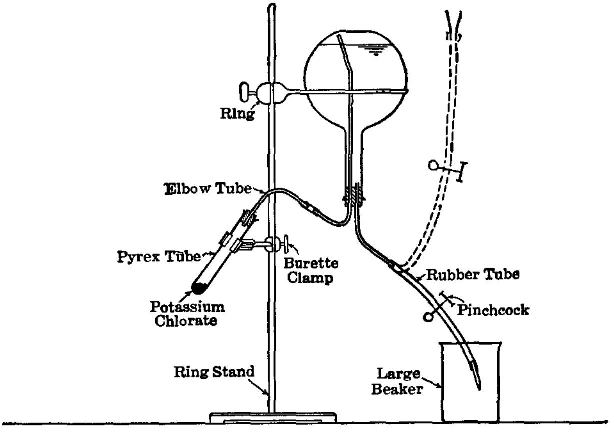


FIG. 10

solid salt in the gas stream issuing from the tube. If for any reason the heating is interrupted during the process, submerge the jet beneath the liquid, so that water, not air, will be sucked back into the tube and flask. When about 400 cc. of water have been forced over, submerge the jet and allow the ignition tube to cool to room temperature. Raise the beaker to equalize the water levels, and close the cock. Record the temperature of the laboratory and the barometer reading. Weigh the water in the beaker on the *platform balance,* which gives the actual volume of the oxygen evolved. Calculate its volume under standard conditions. Weigh the tube again, and the loss gives the weight of oxygen.

Calculation. From your data calculate the weight of 1 liter of oxygen under standard conditions.

3. DETERMINATION OF THE VOLUME OF HYDROGEN DISPLACED BY ZINC

When hydrochloric acid reacts with zinc a definite volume of hydrogen is displaced by a given weight of metal. The weight of zinc dissolved can be accurately determined, and when the volume of hydrogen liberated is corrected to standard conditions the ratio between the two is obtained.

Materials: zinc metal, rod 2.5 cm. by 0.6 cm.
hydrochloric acid, 6 *N*.

Apparatus: 4-inch drying tube and 1-hole rubber stopper.
300-cc. flask.
2.5-inch funnel.
water trough.
iron ring and ring stand.
burette clamp.
wire triangle.
pinch cock.
two 18-inch pieces of rubber tubing.
copper wire.

Data Form:

Weight of zinc before reaction .... ------grams
Weight of zinc after reaction .... ------grams
Weight of zinc consumed in the reaction .... ------grams

Weight of flask and water .... ------grams
Weight of empty flask .... ------grams
Weight of water .... ------grams
Barometric pressure .... ------mm.
Temperature .... ------°
Vapor pressure (p. 353) .... ------mm.

Arrange the apparatus as shown in Fig. 11. Clamp a drying tube in a vertical position with its larger end down. Fit this end with a stopper through which passes a short glass tube. Connect the latter by means of 18 inches of rubber tube, provided with a pinch cock, with a funnel supported upright in a considerably higher position than the drying tube. From the other end of the drying tube lead an 18-inch rubber tube to a trough. This tube should have a right angle, 3-inch glass tube, attached to its end. Inside the drying tube is to be placed the zinc. Obtain a rod of it about 2.5 cm. long and 0.6 cm. in diameter. Clean and dry it, and weigh it accurately. A short piece of twisted copper wire supports the zinc in the tube. Pour water into the funnel until the whole apparatus is filled, and close the pinch cock. When everything is ready invert a 300-cc. flask completely filled with water, over the end of the glass tube in the trough. Pour dilute hydrochloric acid (6N) into the funnel and allow it to pass the pinch cock until

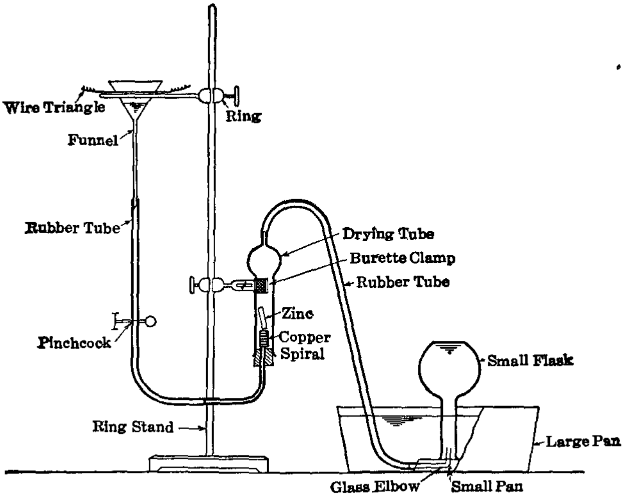


Fig. 11

hydrogen is evolved from the metal. The cone of the funnel should always be kept well filled with liquid, and care must be taken that no bubble of air is sucked into the stem. Collect the hydrogen in the flask, and when the gas has forced the level of the liquid nearly into the neck begin to wash the acid out of the apparatus by pouring water into the funnel. Have the acid completely removed, and thus the evolution of hydrogen stopped by the time the water level stands at about the middle of the neck. Equalize the level inside and outside the neck of the flask, and while in this position mark the level by means of a rubber band. Record temperature and barometric pressure. Determine on the *platform scales* the weight of water required to fill the volume occupied by the hydrogen. Dry the zinc carefully on a piece of filter paper, and weigh it accurately on the sensitive balances.

Calculation. (1) Calculate the volume of hydrogen under standard conditions equivalent to 1 gram of zinc. (2) From the combining ratio of zinc and oxygen (Experiment 1), find the volume of hydrogen equivalent to 1 gram of oxygen. (3) From the weight of 1 liter of oxygen (Experiment 2), find the volume of hydrogen equivalent to 1 liter of oxygen. Note that the calculation of the ratios (2) and (3) is based on an assumption, namely, that the quantity of hydrogen displaced by a given weight of zinc would combine with the same weight of oxygen that would combine with the given weight of zinc.

4. THE COMBINING RATIO OF HYDROGEN AND OXYGEN IN WATER

It is only with great care and refined apparatus that volumes of gases can be successfully weighed. It not being feasible to weigh hydrogen and oxygen as such in this experiment, the oxygen will be obtained from solid copper oxide, the loss of weight of which can be determined. If an excess of dry hydrogen is led over the copper oxide, the excess that does not combine with the oxygen to form water will pass on unchanged. By collecting all the water in some material which absorbs it, its weight may be found. The amount of the hydrogen combined is then given by the difference between the weight of the water and that of the oxygen.

Hydrogen gas generated from zinc and hydrochloric acid is passed through a tube containing calcium chloride to remove any water vapor, then over heated copper oxide, with the oxygen of which it combines, and then through another calcium chloride tube to absorb the water vapor formed.

Materials: copper oxide, fine wire form.
feathered zinc.
anhydrous calcium chloride.
6 *N* hydrochloric acid.

Apparatus: Pyrex combustion tube, 10 inch.
two 4-inch side arm U-tubes.
porcelain boat.
8-ounce common bottle.
thistle tube.
rubber stoppers.
Bunsen burner.
two 4-inch iron rings.
2 ring stands.
cotton.

Data Form:

Weight of boat + copper oxide before reaction. ______ grams
Weight of boat + copper after reaction...... ______ grams

Weight of oxygen .... ______ grams
Weight of U-tube after reaction .... ______ grams
Weight of U-tube before reaction .... ______ grams

Weight of water formed .... ______ grams

Procedure: While setting up the apparatus as shown in Fig. 12 heat 5 or 6 grams of copper oxide to redness in a porcelain boat so as to drive off any water it may contain. Place about 30 grams of feathered zinc in an 8-ounce bottle. Through a tight-fitting, two-hole rubber stopper pass a thistle tube reaching to the bottom and an elbow tube just entering the top of the bottle. Fill each of the U-tubes with granular calcium chloride to within 2 cm. of the side arms, and insert a loose plug of cotton on top of the calcium chloride on each side. Attach one of the U-tubes to the generator tube on one side and the combustion tube on the other. The latter should slope downward at an angle of 5° to 10°. The other end of the combustion tube is attached to the second drying tube. The two ends of the glass tubes should touch under the short rubber connector. The second calcium chloride tube should be prepared with especial care and be weighed accurately just before starting the operation. Prolong its open arm with an elbow tube whose one end, drawn out to a capillary, is turned upward. **Test the tightness of the apparatus:** This may be done by adding enough water to the generating bottle to seal the end of the thistle tube, then holding a finger on the exit tube of the apparatus and pouring more water into the thistle tube. If the top of the column of water in the thistle tube maintains its level the apparatus is tight. Pour a few cubic centimeters of 6N hydrochloric acid through the thistle tube, let hydrogen generate slowly, and fill the apparatus while preparing the rest of the material.

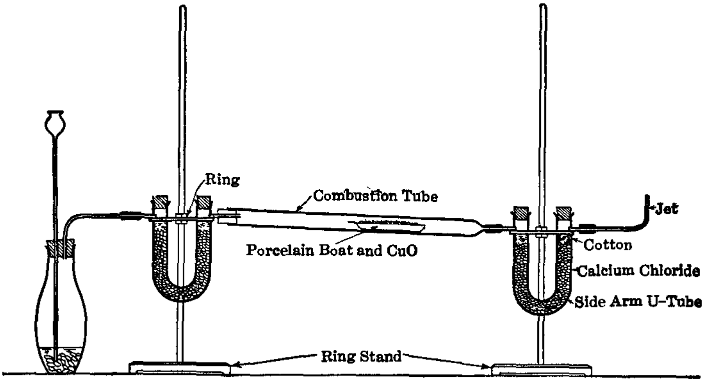


FIG. 12

After it has cooled, accurately weigh the porcelain boat filled with the copper oxide. Place the boat carefully, without spilling any of the copper oxide, in the middle of the combustion tube. Add a little more acid to the generator, and wait until the apparatus is completely filled with hydrogen before proceeding further. *Never bring a flame near the apparatus until the purity of the hydrogen escaping has been proved.* **Test the hydrogen** by holding a short test tube over the jet and carrying the tube, mouth downward, to a distant flame. If the gas does not explode, but burns quietly, quickly convey the tube, still with mouth downward, to the jet. If the hydrogen still burning in the tube ignites the jet, it is then safe to proceed with the experiment. The gas at the jet should be left burning. Increase the evolution of hydrogen a little, being careful in adding acid to pour it in a thin stream down the side of the tube so as not to drag with it bubbles of air, as this would introduce oxygen, which would be burned to water in the combustion tube. Let the hydrogen generate 3 minutes longer to sweep any last traces of oxygen from the apparatus, and then begin heating the copper oxide rather gently, using the wing-top burner. Before the experiment is ended any condensed water must be completely driven over into the calcium chloride tube by playing the flame gently over the parts of the tube where moisture is seen. When the tube has cooled to room temperature, disconnect the hydrogen generator from the drying tube and blow slowly enough air (from the lungs) through the apparatus to displace all the hydrogen. Weigh the boat to find the loss, and the calcium chloride tube to find the increase in weight.

Calculation. Calculate the combining ratio of hydrogen and oxygen, that is, how many parts by weight of oxygen combine with 1 part of hydrogen.

From this ratio and the volume ratio calculated in Experiment 3, find the weight of 1 liter of hydrogen. This involves the assumption that the quantity of hydrogen displaced by that weight of zinc which combines with a given amount of oxygen is the same as would combine directly with that amount of oxygen. By comparing the result obtained with the known weight of a liter of hydrogen (=0.090 gram) decide whether this assumption is correct.

5. Determination of the Approximate Molecular Weight of a Volatile Liquid by Dumas' Method

According to Avogadro's principle, the volume occupied by the gram molecular weights of all gases, under standard conditions, is the same. Determinations made with a large number of gases have shown that this volume is 22.4 liters. For example, 2.016 grams of hydrogen, or 32 grams of oxygen, or 71 grams of chlorine occupy a volume of 22.4 liters at 0° and 760 mm. pressure. If a new gas is discovered, its molecular weight can be determined by finding the weight that occupies a volume of 22.4 liters under standard conditions.

This method can be applied also to substances which are liquid or solid at 0° and 760 mm. pressure, provided they can be vaporized, without decomposition, at a temperature which will permit the accurate measurement of the volume occupied by a given weight of substance. If the pressure and temperature of the determination are also known, this volume can be reduced to standard conditions, and the weight, which would be required to fill 22.4 liters under standard conditions, calculated. This weight in grams is the molecular weight.

In the following experiment we shall use carbon tetrachloride as the " unknown " substance, the molecular weight of which is to be found.

Materials: pure carbon tetrachloride, 12 cc.

Apparatus: Dumas bulb (250-cc. bulb with neck drawn to a capillary).
600-cc. beaker.
250° thermometer.
2 Bunsen burners.
burette clamp.
wire holder and cover.
unglazed porcelain chips.
4-inch iron ring and ring stand.
cork stopper, split.

Data Form:

Weight of the open Dumas bulb filled with air (*a*) .... ------ grams
Weight of the sealed Dumas bulb filled with CCl_4 vapor (*b*) .... ------ grams
Weight of the Dumas bulb filled with water (*c*) .. ------ grams
Barometric pressure .... ------ mm.
Temperature of the boiling water bath .... ------ °
Room temperature .... ------ °

Procedure: Weigh accurately a clean, dry Dumas bulb. Introduce into it about 12 cc. of carbon tetrachloride by warming the bulb and allowing it to cool with the tip dipping into the liquid. Heat about 300 cc. of water to approximately 50° in a 600-cc. beaker. Drop a few pieces of porous tile into the beaker, so that the water will boil without " bumping." Immerse the bulb in the water, and hold it in this position by putting the wire holder around the neck of the bulb. Cover the beaker, and clamp the upper end of the wire holder to a ring stand. A split cork stopper will hold the wire in the jaws of the clamp. The bottom of the bulb should be about 1 cm. from the bottom of the beaker. Carry the apparatus to the hood, and heat the water with a low flame until it reaches the boiling point. Maintain the bath at this temperature until the carbon tetrachloride has entirely vaporized, and the excess vapor has escaped through the open tip. After a lighted match is no longer extinguished at the tip, wait two minutes for the vapor in the bulb to be heated to the temperature of the boiling water, and for the pressure inside the bulb to come to equilibrium with the atmosphere outside. Still keep the water boiling, and, by means of a second burner, warm the exposed stem to vaporize any carbon tetrachloride which may have condensed in it. Seal the bulb by holding the flame at the tip of the capillary. Remove the bulb from the beaker, dry it, and tip it bottom up. The condensed carbon tetrachloride will run into the stem of the bulb, and if the tip is not completely sealed bubbles of air will be drawn through the liquid into the bulb. If this happens turn the bulb right side up and immediately reheat the tip. If the seal is satisfactory allow the bulb to cool to room temperature and weigh it accurately.

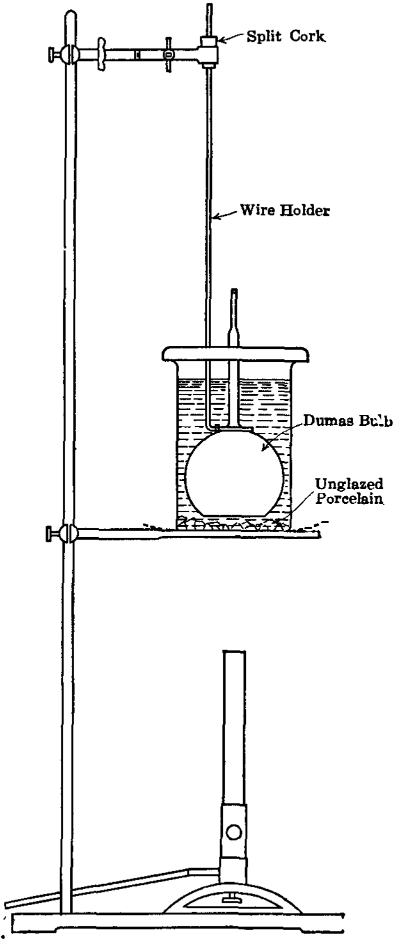


Fig. 13

After the sealed bulb has been weighed it is to be filled with water and weighed on the platform (not the analytical) balance. Water from which dissolved air has been expelled must be used to fill the bulb. To this end, while the sealed bulb is being cooled and weighed, boil about 300 cc. of distilled water in an 8-inch porcelain evaporating dish, and cool it rapidly. After the sealed bulb has been weighed, immerse the stem in the air-free water and break off the tip of the stem. Water will rush into the bulb and fill it practically completely if the preceding manipulation has been skilfully performed. If more than 3 cc. of air is found in the bulb, reject your data to this point and start the experiment again. The weight of the condensed carbon tetrachloride left in the bulb may be neglected as it is very small in comparison with that of the water.

Perform the experiment a second time, starting with a dry bulb. From your data make the following calculations for each of the duplicate determinations:

1. The volume of the bulb (*c*-*a*), neglecting the weight of air in the bulb and the coefficient of expansion of the glass.
2. Reduce to standard conditions the volume of vapor in the bulb at the recorded bath temperature and pressure (assuming that the vapor would not condense) (v_{st} CCl_4).
3. Reduce to standard conditions the volume of air in the bulb when it was weighed (v_{st} air), and find the weight of this air, using 1.293 as the weight of a liter of air (*d*).
4. The actual weight of the empty bulb (*a*-*d*) (*e*).
5. The weight of carbon tetrachloride vapor (*b*-*e*).
6. The molecular weight of carbon tetrachloride.

Notes and Problems

The law of definite proportions states that whenever two (or more) elements combine to form a definite compound the ratio by weight of the elements entering that compound is always the same.

The law of multiple proportions covers the case where two (or more) elements form more than one definite compound. The law of definite proportions applies to each of the compounds, and the law of multiple proportions says that the definite ratios for the separate compounds are to each other in the ratio of small integral numbers.

Perhaps the most easily visualized statement of the law of multiple proportions is as follows: If the same weight of one element is taken in each case the weights of the second element which combine with this definite weight of the first element to form the respective compounds are to each other in the ratio of small whole numbers.

For example, two different substances are known which contain copper and chlorine. In cuprous chloride 63.6 grams of copper are combined with 35.46 grams of chlorine; in cupric chloride 63.6 grams of copper are combined with 70.92 grams of chlorine. The weights of chlorine are in the simple integral ratio of 1.2.

The law of combining weights covers not only the behavior described by the laws of definite and multiple proportions, which apply to specific compounds and to specific pairs of elements, but it covers the combining ratios in all compounds. In the illustration above we chose apparently arbitrarily 63.6 grams of copper and found that the corresponding weights of chlorine were 35.46 and 70.92 in the respective compounds. Without stopping to inquire why we chose 63.6 grams rather than 1 gram or 100 grams, let us inspect the following tabulation of combining weights.

	Cu	Cl	Hg	O	S	H	C
Cuprous chloride	63 6	35 46					
Mercurous chloride		35 46	200 6				
Mercuric oxide			200 6	16			
Sulphur dioxide				16	16		
Cupric sulphide	31 8				16		
Hydrogen sulphide					16	1 008	
Water				8		1 008	
Carbon monoxide				8			6
Carbon tetrachloride		70 92					6
Chlorine monoxide		70 92		16			

It is obvious that the combining weights of the elements are in every case small whole multiples of recurring numbers: Cu 31.8; Cl 35.46; Hg 200.6; O 8; S 16; H 1.008; C 6. If we had taken any other weight, say 100 grams of oxygen, as a starting point it is evident that the same uniformity would be manifest, but the fundamental weight of each element would be different.

The law of combining weights may be stated as follows: For every element a combining weight may be chosen such that in all pure compound substances the ratio of the number of combining weights of the different elements is the ratio of simple integrals.

The Atomic Theory. Dalton was impressed by the significance of the facts generalized in these three laws, particularly the law of multiple proportions, and he found for them a reasonable explanation in the atomic theory (1808). According to this theory, the elements consist of atoms which were thought by Dalton to be indivisible. The atoms of the same element are all alike in weight and in all their other properties; the atoms of different elements differ in properties. When elements combine to form compounds, it is the individual atoms which are concerned.

Suppose for example one atom of element A combines with one atom of element B, to form the compound AB; then, since the weights of atoms of the same element are always alike and since whatever amount of the compound is taken it always contains an equal number of atoms of each element, the proportion by weight of the two elements must always be the same in this compound. Thus the law of definite proportions is a necessary deduction from the atomic theory. Let it be understood, however, that the law is a fact established by careful measurements. The theory is simply the best effort of the human mind to furnish an explanation of the facts.

The reasoning is similar for the law of multiple proportions. Suppose that one atom of A can combine with two atoms of B in forming an entirely different, but none the less definite, compound. Let us designate this compound AB_2. The law of definite proportions would hold for this compound as well as for the first. Furthermore, if we should take such amounts of each compound that each contained the same number of atoms of A then the second would contain twice as many atoms of B as the first. The weight of B in the second would, therefore, be exactly twice the weight of B in the first compound. Thus the law of multiple proportions is also a necessary deduction from the atomic theory.

Atomic Weights. We have found that the combining ratio of oxygen and zinc is 1:4.09. The atomic theory stipulates that the ratio of the numbers of atoms is simple, but it may be 1:1, 1:2, 1:3, 2:1, 3:1, 3:2, 2:3 or any reasonably simple ratio. Having at hand no way of telling what the real ratio is we proceed to assume one to be the correct ratio — in other words, we make a guess. Where we have nothing else to guide us we make the simplest possible guess and assume the ratio to be 1:1. If this is correct then the atom of zinc weighs 4.09 times as much as the atom of oxygen.

The weight of a single atom is so very small that it would mean little to us if we did express it exactly in arithmetical figures. What we are interested in is the ratio of the weights. When a great many million million atoms of oxygen combine with the same number of million million atoms of zinc we make the actual measurement that 1 gram of oxygen combines with 4.09 grams of zinc.

Standard of Atomic Weights, O = 16. It has been internationally agreed that it is a matter of convenience to adopt the exact number 16.000 as the atomic weight of oxygen. Exactly 16 grams is the *gram atomic weight* of oxygen. We may mention as a matter of interest that 16 grams of oxygen contains 6.06×10^{23} atoms, although this enormous figure is of no practical importance beyond the mere fact that it is enormous and has been determined accurately.

The atomic weight of zinc is therefore $4.09 \times 16 = 65.4$ if our assumption of the 1:1 ratio is correct. Therefore 65.4 grams of zinc is the gram atomic weight of this element, and it likewise contains 6.06×10^{23} actual atoms.

Of course the fact that many cases are known where two elements can combine in different proportions to form different compounds (multiple proportions) shows us at once that the atomic combining ratio cannot always be 1:1. In order to establish consistent atomic weights for all the elements on the O = 16 basis, we must either make very clever guesses as to the atomic ratios or we must have some reliable means of finding out this ratio. We shall state here that there are reliable methods of doing this, one of the most useful of which will be explained in a later section of this chapter (p. 48). In the front inside cover of this book is printed a list of all the elements with their symbols and their atomic weights. The atomic weights are obtained in many cases from the combining ratio by weight with oxygen itself, in other cases from the combining ratio with another element whose combining ratio with oxygen is known. In every instance the combining ratio by weight with oxygen must be multiplied by 16 and divided by the atomic ratio of the element to oxygen.

PROBLEMS

1. The combining ratio by weight of zinc and sulphur is 2.039 : 1. Assuming the knowledge that the atomic weight of zinc is 65.4 and that zinc and sulphur combine in the 1:1 atomic ratio, find the atomic weight of sulphur.

2. The oxide formed when 1 gram of sulphur is burned weighs exactly 2 grams. What is the combining ratio by weight of sulphur and oxygen?

3. Using the data and assumptions of the last two problems and the atomic weight of oxygen as 16, deduce the atomic ratio by which sulphur and oxygen combine. Write the formula of this compound.

4. From the atomic weights printed in the table, find the percentage composition by weight in the compounds having the atomic ratio expressed by the formulas CaO, Li_2O, Fe_2O_3, Fe_3O_4.

5. One oxide of chromium contains 52 per cent of chromium and 48 per cent of oxygen by weight; another contains 68.42 per cent of chromium and 31.58 per cent of oxygen. Prove that these compounds are in agreement with the law of multiple proportions.

6. Look up the atomic weight of chromium and find the atomic ratio in each oxide. Write the simplest formula of each oxide.

7. One gram of potassium metal burns to give 1.82 grams of an oxide. Calculate the chemical formula of the oxide.

8. The oxide obtained when iron is burned in oxygen has the composition $Fe = 72.4$; $O = 27.6$. Calculate the chemical formula of the oxide.

9. Find the formula of the substance whose composition is magnesium 25.57 per cent, chlorine 74.43 per cent.

10. Find the formula of the substance whose composition is potassium 26.585, chromium 35.390, oxygen 38.025.

Measurement of Gases. Since it is difficult to weigh a body of gas, but comparatively easy to find its volume, the amounts of gases are almost invariably estimated by measuring the volume. But the volume of a definite amount of gas is very dependent on the conditions, and to make a volume measurement have an accurate meaning it becomes necessary to know exactly the conditions of pressure, temperature, and dryness under which the measurement is made. To make the results of all measurements comparable it is customary to calculate what the measured volume would become if so-called standard conditions prevailed.

By common consent of scientific men, standard conditions have been defined as 760 mm. pressure, 0°C., and dry gas.

A remarkable uniformity has been found to exist in the behavior of all gases under changing conditions. Three simple statements, the so-called gas laws, suffice to define with a considerable degree of accuracy the volume changes with changing pressure, temperature, and water-vapor content.

Boyle's law states that at the same temperature the volume of a definite amount of a gas is inversely proportional to the pressure. The law is expressed by the equation

$$\frac{v_1}{v_2} = \frac{p_2}{p_1}$$

or

$$p_1v_1 = p_2v_2$$

Charles' law defines the change of volume with changing temperature: the volume of a definite amount of a gas under constant pressure is directly proportional to the *absolute* temperature. The absolute temperature is 273° plus the centigrade temperature; but really the determination of the absolute scale of temperature depends entirely on the behavior of gases.

The original statement of Charles' law was made in this way: For every degree rise or fall in temperature the volume of a gas increases or decreases by an amount equal to $\frac{1}{273}$ its volume at 0°C. If this law held rigidly all the way down the scale of course the volume of a gas would become zero at -273°C. This point, -273°C., would be the absolute zero below which substances could not be cooled. As different gases were studied it was found that they obeyed this law quite exactly until they approached the temperature at which they would condense to a liquid. The more difficultly condensible a gas, the further down the scale it would follow this law. Helium, which was the last gas to succumb to efforts at liquefaction, follows the law with a good deal of accuracy to within a few degrees of -273°C. Hence, since it was found that the less condensible a gas the more nearly it approximated a certain ideal behavior, an imaginary "perfect gas" was postulated which would have exactly the ideal behavior. The absolute zero then is defined as the temperature at which the volume of this perfect gas would become zero, that is -273°C.

Charles' law is expressed in the equation

$$\frac{v_1}{v_2} = \frac{T_1}{T_2}$$

when the pressure is constant and T stands for the absolute temperature; when the volume is held constant the pressure must vary as the absolute temperature, or

$$\frac{p_1}{p_2} = \frac{T_1}{T_2}$$

The equations for the laws of Boyle and Charles can be combined into one equation for use when pressure, volume, and temperature vary.

$$\frac{p_1v_1}{p_2v_2} = \frac{T_1}{T_2}$$

or

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$

Dalton's law describes the behavior of mixtures of gases as follows: When two or more gases are contained in the same vessel each one exerts the same pressure as if it occupied the whole vessel alone at that temperature. The actual measured pressure is the sum of the partial pressures of the gases present.

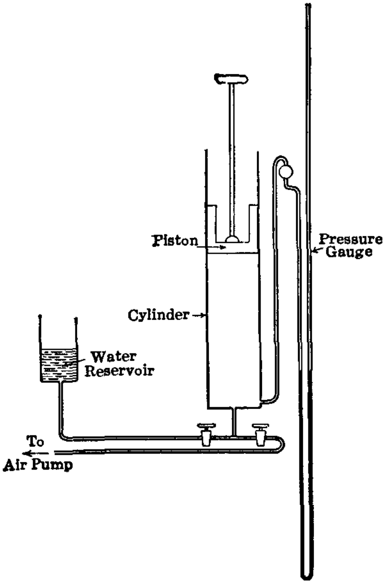


FIG. 14

Since we frequently have to measure gases which are confined over water in the measuring vessel, and are consequently mixed with water vapor, we are especially interested in applying Dalton's law to water vapor.

A gas may be mixed with any amount of water vapor up to the saturation point, and the saturation point depends solely on the temperature. We need only to be sure that the gas is saturated with water vapor in order to calculate the effect of the latter.

Saturated Water Vapor. In order to help us make clear the properties of saturated water vapor, let us make use of the somewhat idealized apparatus shown in Fig. 14.

The piston, which is assumed to be absolutely gas tight, is raised to a middle position in the cylinder and fastened there. The stop cock to the vacuum pump is opened and the cylinder evacuated until the pressure gauge reads zero. Now the cock to the pump is closed and the cock from the water reservoir is opened to let a thin layer of water run into the bottom of the cylinder. Immediately the pressure gauge jumps and shortly adjusts itself to exactly 17.4 mm. when the temperature of the apparatus is 20°C.

Now let us raise the piston to the top of the cylinder. There is a momentary depression of the gauge but it at once returns to exactly 17.4 mm. Now let us force down the piston to the bottom of the cylinder. Again there is a momentary change in the gauge level but the reading immediately becomes exactly 17.4 mm. again, if the temperature is maintained constant all the time at 20°.

Saturated water vapor is in equilibrium with liquid water. If the vapor is not saturated and any liquid water is present, enough of this evaporates to make the vapor saturated. Compressing a saturated vapor would tend to increase its concentration, which would increase its pressure. The observed fact that there is no such increase in pressure shows that the vapor does not become more concentrated, that is, that it does not become supersaturated but condenses to liquid water to maintain the exact state of saturation as the piston is pressed down. When the piston is drawn up the liquid must evaporate to maintain a saturated condition of the vapor.

At 20° the concentration of saturated water vapor is such that its pressure is 17.4 mm. At other temperatures the concentration is different, but it has an absolutely definite value for each temperature. The pressure of saturated water vapor has been carefully measured at different temperatures. The values from 0° to 100° are given in the table on page 353 in the Appendix.

If the condition of equilibrium between liquid water and water vapor is not disturbed by the presence of any other gas, then a cylinder full of oxygen and also saturated with water vapor will contain the same quantity of water vapor as a cylinder of the same size containing only saturated water vapor. Dalton's law would then require that the partial pressure of water vapor be the same in both cylinders and that the apparent pressure in the oxygen cylinder be the sum of the partial pressures of the oxygen and the water vapor.

This deduction can be verified experimentally. Let dry oxygen run into the dry cylinder until the gauge stands at 760 mm. at 20°. Then run a thin layer of water into the bottom of the cylinder. The gauge begins slowly to rise, and finally it stops at 777.4 mm. if the temperature is still 20°. Thus the partial pressure of saturated water vapor is 17.4 mm. and is not affected by the presence of the oxygen gas. It takes a much longer time to saturate the space in the cylinder when oxygen is present because the water vapor has to diffuse through the oxygen, but the final result is exactly the same. The oxygen does not diminish the capacity of the space for the water vapor.

Suppose now that we have to measure a quantity of oxygen which has been collected in a measuring tube over water in a trough. The oxygen has bubbled up through the water and we may assume that it has in this way become fully saturated with water vapor. We raise or lower the measuring tube until the level of the water is the same inside and outside the tube. On the outside surface of the water the atmosphere is exerting its pressure which is transmitted through the liquid to the gas within the tube. Let us say that the barometer reads 740 mm. Then the pressure of the gas in the tube is 740 mm. This pressure, however, is the total of two partial pressures, that of the oxygen and that of the water vapor. Let us say that the temperature is 20°; then the partial pressure of the water vapor is 17.4 mm.; and the pressure of the oxygen is $740 - 17.4 = 722.6$ mm. The volume read in the measuring tube is, say, 60 cc. We want to calculate the volume of the oxygen under standard conditions. Substituting in the general gas equation we have:

$$\frac{722.6 \times 60}{273 + 20} = \frac{760 \times V_{st}}{273}$$

or

$$V_{st} = 60 \times \frac{273}{273 + 20} \times \frac{722.6}{760}$$

The general formula for reducing to standard conditions the volume of a gas measured over water is

$$V_{st} = V_{obs} \times \frac{273}{t + 273} \times \frac{p - \text{aq. tens.}}{760}$$

V_{st} = volume of gas under standard conditions.
V_{obs} = the observed volume under conditions of experiment.
t = temperature of the gas.
p = pressure upon the moist gas.
aq. tens. = tension of saturated aqueous vapor at $t°$ (see table).

PROBLEMS

11. Reduce 125.3 cc. of gas at 725 mm. to 760 mm. pressure.

12. A cylinder of 2500-cc. capacity contains oxygen under 91.5 atmospheres pressure. Find volume in liters after the gas is run into a tank under atmospheric pressure.

13. Reduce 125.3 cc. of gas at 25.8° to 0°.

14. A sealed glass tube contains 125.3 cc. of gas at 27° and 783 mm. pressure. What will be the pressure if the tube is heated to 300° without change of volume?

15. Reduce 125.3 cc. of gas at 740 mm. and 20.7° to standard conditions.

16. Reduce 125.3 cc. of gas at 15.3 atmospheres and $-65.5°$ to standard conditions.

17. Reduce 125.3 cc. of gas measured over water at 740 mm. and 20.7° to standard conditions.

18. A certain quantity of dry hydrogen gas occupies 2,275 liters at 25° and 760 mm. If this gas were bubbled through water and collected in a vessel over water, what volume would it then occupy at the same temperature and the same barometric pressure? Assume that no hydrogen is dissolved in the water.

Gay-Lussac's Law of Combining Volumes. The measurement of the volumes of gases which enter into chemical reaction led Gay-Lussac to perceive the existence of an extremely simple relationship which is known by the above title and which may be stated as follows: The volumes of gases which react chemically are in the ratio of small whole numbers. Furthermore, if the products of the reaction are also gaseous their volumes are also in the relation of small whole numbers to each other and to the volumes of the original gases.

Gay-Lussac was unable to explain this law on the ground of any reasonable hypothesis. He tried to postulate that equal volumes of different gases must contain the same number of *atoms*, but this postulate was almost at once found to be untenable and he had nothing better to offer.

Avogadro's Principle. In 1811 Avogadro suggested the hypothesis that at the same temperature and pressure all gases contain in equal volumes an equal number of molecules. He defined the molecule as the smallest particle of a substance and drew a clear distinction between molecules and atoms; a molecule of a compound would of necessity contain two or more atoms, at least one atom of each constituent element. But the startling feature of Avogadro's hypothesis was that it demanded as a necessary deduction that the molecules of the elementary gases, oxygen, nitrogen, hydrogen, and chlorine, should consist of two atoms each. Such an idea was regarded by his contemporaries as preposterous and they would have nothing to do with his hypothesis.

It was not until 1858 that Cannizzaro showed how Avogadro's principle accounted for the reactions of gases and a great variety of chemical combinations. Since then it has come to be recognized as one of the most fundamental laws of chemistry. It has been said that modern chemistry dates from 1858.

In order to show that the molecules of oxygen, nitrogen, hydrogen and chlorine must be diatomic if Avogadro's principle is tenable, let us consider the following data which have been established by measuring combining volumes of gases and of course reducing all volumes to standard conditions:

> 2 volumes of hydrogen + 1 volume of oxygen give 2 volumes of water vapor.
>
> 1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride.
>
> 2 volumes of ammonia give 3 volumes of hydrogen + 1 volume of nitrogen.

In the first set of data let us assume that the 1 volume of oxygen contains 1 million molecules. Then the 2 volumes of water vapor according to Avogadro's principle will contain 2 million molecules of water. But the water vapor is a homogeneous substance, and, since it contains oxygen, every molecule of it must contain at least 1 atom of oxygen. Therefore, there must be at least 2 million atoms of oxygen which were derived from the 1 million molecules. Therefore, every molecule of oxygen must contain at least 2 atoms.

Following the same line of reasoning 1 million molecules of hydrogen and 1 million molecules of chlorine produce 2 million molecules of hydrogen chloride which must contain at least 2 million atoms of hydrogen and 2 million atoms of chlorine. Therefore the molecules of hydrogen and of chlorine must each contain at least 2 atoms.

Since 2 volumes of ammonia yield only 1 volume of nitrogen, the same reasoning shows that the molecule of nitrogen must contain at least 2 atoms.

Molecular Weights. The atomic weight of oxygen has been settled by convention as 16, and since there are at least 2 atoms of oxygen in a molecule, the molecular weight of oxygen must be at least 32. Let us neglect the qualification " at least " and take the molecular weight of oxygen as 32 without qualification, making this our standard from which to reckon all other molecular and atomic weights.

On this basis the molecular weight of any gaseous substance is easily calculated if we know the weight of a measured volume of that gas under any stated conditions. From this determination the weight of 1 liter of gas under standard conditions can be computed. Then, the weight of 1 liter of the gas is to the weight of 1 liter of oxygen as the molecular weight of the gas is to 32, the molecular weight of oxygen.

Gram Molecular Weight; Mole. The molecular weight is an abstract number although the molecular weights are related to each other in the same ratio as the actual weights of the molecules. The *gram molecular weight* is, however, a concrete quantity, being the molecular weight number in grams. It is a quantity that is so frequently spoken of that the name has been contracted to *mole.* A mole of oxygen is 32 grams of oxygen.

Gram Molecular Volume or Molal Volume. One mole, or 32 grams of oxygen, under standard conditions occupies a volume of 22.4 liters. According to Avogadro's principle, the same volume would contain exactly 1 mole of any other gas under standard conditions; this volume, therefore, assumes a great importance, and it is called the *gram molecular volume* or for brevity *molal volume.*

To find the molecular weight of any gaseous substance it is necessary therefore only to find the weight in grams of 22.4 liters of the gas under standard conditions. In actual practice it is not convenient to weigh containers which hold 22.4 liters. It is only necessary to know the weight of any volume and the conditions of the experiment. From these data the molecular weight can be calculated.

Avogadro's Number. The actual number of molecules of a gas in 22.4 liters under standard conditions has been determined by several different methods. The results agree very well, and the value generally accepted is 6.06×10^{23}. This quantity has been named Avogadro's number in honor of the man who first suggested the principle on which it depends. It is the number of molecules in a mole of any substance, whether gas, liquid, or solid. It is also the number of atoms in a gram atomic weight of an element.

Atomic Weights. In an earlier section (page 39) it was shown that the atomic weight of an element could be obtained by multiplying the combining ratio of the element with oxygen by 16, the atomic weight of oxygen, and dividing the result by the assumed atomic ratio. We are now in a position to verify the atomic weights so found and thus to prove whether the assumed atomic ratio was correct.

We shall start with the molecular weight of oxygen as 32 and first demonstrate that on this basis the atomic weight of oxygen is 16.

Substance	Weight in grams of 1 mole	Percentage by weight of oxygen	Weight of oxygen in 1 mole	Greatest common divisor
Water	18 016	88 81	16	1 × 16
Carbon dioxide	44	72 7	32	2 × 16
Sulphur trioxide	80	60	48	3 × 16
Acetic acid	60	53 3	32	2 × 16
Phenol	94	17 02	16	1 × 16
Nickel carbonyl	170 8	37 5	64	4 × 16
Phosphorus oxychloride	153 4	10 43	16	1 × 16
Oxygen	32	100	32	2 × 16

There are hundreds of gaseous compounds of oxygen whose densities have been measured and whose molecular weights are thus known. The molecules of these compounds can contain a small whole number of atoms of oxygen but never fractional numbers. The percentage by weight of oxygen in these compounds can be found by chemical analysis. This percentage of the molal weight will be the number of grams of oxygen in a mole of the compound, and this number must be either the atomic weight of oxygen or some small even multiple thereof. In the above table a few typical examples are selected from the data for all gaseous or volatile oxygen compounds.

The smallest number in the next to the last column is 16, and this must be the atomic weight of oxygen because it represents the smallest weight of oxygen in the molecular weight of any of its compounds. It is extremely unlikely that there would not be at least some compounds whose molecules contained but a single atom. But if such could be the case and 16 were for example twice the atomic weight, we should expect that 8 would be the greatest common divisor and that numbers equal to 3 × 8 or 5 × 8 and therefore not divisible by 16 would be found in the next to the last column. We can therefore be reasonably certain that 16 is the actual atomic weight and not a multiple of the atomic weight of oxygen.

A similar study of other elements, for example of chlorine, hydrogen, sulphur, mercury, shows that in all the gaseous or volatile compounds of these elements the smallest weight ever found in the molal volume is 35.46 grams of chlorine, 1.008 grams of hydrogen, 32.06 grams of sulphur, and 200.6 grams of mercury; furthermore, when the molal volume contains a greater weight of these elements, the weight is invariably a small even multiple of these smallest weights. Thus the atomic weights of these elements as given in the table are verified.

The following table shows selected examples from the collection of the data for all gaseous or volatile chlorine compounds.

Substance	Weight in grams of 1 mole	Percentage by weight of chlorine	Weight of chlorine in 1 mole	Greatest common divisor
Hydrogen chloride	36.5	97.22	35.5	1 × 35.5
Chlorine	70.9	100	70.9	2 × 35.5
Mercuric chloride	270.9	26.19	70.9	2 × 35.5
Arsenic trichloride	182.1	57.7	107.0	3 × 35.5
Silicon tetrachloride	170.2	83.4	142	4 × 35.5
Phosphorus pentachloride	208.3	85.2	177.5	5 × 35.5

Derivation of a Formula. Let us take for example ethyl ether. This substance is a liquid at ordinary temperature and pressure but it is easily vaporized. We must first find its molecular weight.

By measurement it is found that 1 liter of the vapor at 136.5°C. and 760 mm. weighs 2.203 grams. Reduce the volume to standard conditions:

$$V_{st} = 1.000 \times \frac{273}{273 + 136.5} = 0.6667 \text{ liter}$$

Thus 0.6667 liter under standard conditions weighs 2.203 grams. 22.4 liters will weigh

$$\frac{22.4}{0.6667} \times 2.203 = 74.02 \text{ grams}$$

Thus the molecular weight is 74.02.

Chemical analysis shows that the composition of ethyl ether is:

C, 64.87 per cent; H, 13.53 per cent; O, 21.60 per cent

The weight of each of these elements in one mole is:

$$\begin{aligned} \text{C}&: 0.6487 \times 74.02 = 48.02 = 4 \times 12.01 \text{ grams} \\ \text{H}&: 0.1353 \times 74.02 = 10.01 = 10 \times 1.008 \text{ grams} \\ \text{O}&: 0.2160 \times 74.02 = 15.99 = 1 \times 16.00 \text{ grams} \end{aligned}$$

Therefore the mole of ethyl ether contains 4 gram atomic weights of carbon, 10 gram atomic weights of hydrogen, and 1 gram atomic weight of oxygen and the formula is $C_4H_{10}O$.

PROBLEMS

19. One liter of a certain gas under standard conditions weighs 2.25 grams. Calculate the molecular weight of this gas.

20. The molecular weight of a certain volatile substance is to be determined: 0.435 gram of the substance is placed in an evacuated vessel and the whole is heated to 136.5°, at which temperature the substance is entirely converted to gas. The pressure and volume of the gas are now found to be 380 mm. and 405.6 cc., respectively. Calculate the molecular weight of the gas.

21. When a certain liquid substance is vaporized, its vapor is found to weigh 5.413 times as much as an equal volume of air under the same conditions. Assuming the average molecular weight of air to be 28.955, find the molecular weight of the substance.

22. The composition of the above substance is found by analysis to be: carbon, 45.87 per cent; hydrogen, 3.21 per cent; and bromine, 50.92 per cent. Calculate the formula of the substance.

23. A certain compound of chlorine and copper is found to have the composition: copper, 64.2 per cent; chlorine, 35.8 per cent. When 0.52 gram of this substance is heated to a sufficiently high temperature to convert it completely into a gas, it takes the place of a certain volume of air. This amount of air is found to measure 58.8 cc. under standard conditions. Calculate the molecular weight and the chemical formula of the compound.

24. A liquid substance has the composition: carbon, 12.76 per cent; hydrogen, 2.13 per cent; bromine, 85.11 per cent; and when vaporized its vapor density is 93.3 times that of hydrogen. Calculate the molecular weight and the formula of the compound.

25. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element as far as investigation of this one substance can give it?

26. Cyanogen contains 46.08 per cent carbon and 53.92 per cent nitrogen. Its density is 1.796 times that of air. Calculate its formula.

27. In a current of pure oxygen in a combustion tube 0.5000 gram of a substance is burned. The products of combustion are passed through a calcium chloride tube which weighs 36.5011 and 36.7824, respectively, before and after the experiment. Find the percentage of hydrogen in the substance.

28. The products of combustion in Problem 27 are further passed through a tube containing caustic soda, and this weighs 40.4010 and 42.1184 grams, respectively, before and after the experiment. Find the percentage of carbon in the substance.

29. The above substance is converted into a vapor at 273°, and 0.100 gram is found to occupy a volume of 34.9 cc. at 760 mm. Find the molecular weight of the substance.

30. From the results calculated in Problems 27, 28, and 29 find the formula of the substance.

CHAPTER II

WATER AND SOLUTION

Water is in many respects the most important and interesting substance on the earth's surface. By its presence in abundance the physical and chemical conditions necessary for the existence of life are maintained on the earth. By far the greater part of the chemical changes, both in nature and in industry, which have a direct bearing on human life and welfare, involve water, either as a direct participant in the change or as a solvent for the substances which are changing.

PREPARATION 1

POTASSIUM NITRATE, KNO_3, FROM SODIUM NITRATE AND POTASSIUM CHLORIDE

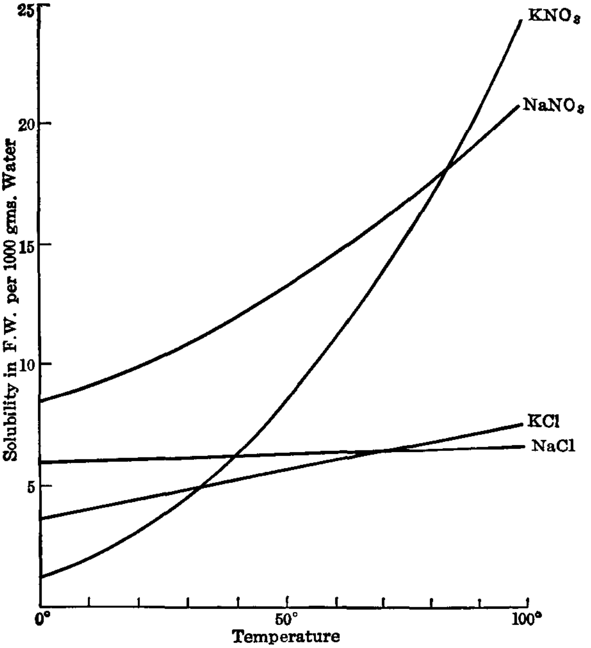
Solubility plays a controlling part in many chemical processes of which the present one is a typical example.

Salts, as well as strong acids and strong bases, exist in a peculiar state when they are in solution. This is known as the state of ionization and is more fully dealt with in Chapter III; but for our present purposes it is sufficient to know that salts consist of electrically charged radicals, the metallic radicals being positive and the non-metallic radicals negative. These radicals are held together in the compound by electrostatic attraction, which is enormous. When the salt is in solution, the electrostatic attraction still exists and prevents the negative radicals from getting away from the positive radicals, but there is a certain freedom of movement which allows radicals to exchange places easily, subject only to the condition that every negative radical must be electrically balanced at all times by some positive radical.

When sodium nitrate and potassium chloride are dissolved, the solution contains four ions, Na^+, NO_3^-, K^+, Cl^-, and from these ions not only could the two original salts be reconstructed, but also two new salts, potassium nitrate and sodium chloride, through a regrouping of the radicals. Which of the four salts will crystallize from a solution containing the four ions depends solely on their solubilities, which may vary much or little with the temperature. The following table gives the solubility at different

Grams of Salt Soluble in 100 Grams of Water

	At 10°	At 100°
KNO_3	21	246
NaCl	36	40
KCl	31	56
$NaNO_3$	81	180



Variation of Solubility with Temperature

temperatures for each salt. Thus, at 10°, 21 grams of KNO_3 are soluble in 100 grams of water. This means that, if an excess of solid potassium nitrate is shaken with pure water until no more will dissolve, the clear solution will then contain 21 grams of KNO_3 for every 100 grams of water. On the other hand, if a solution of 42 grams of KNO_3 in 100 grams of water obtained at a higher temperature is cooled to 10° and stirred until an equilibrium is attained, all but 21 grams of the salt crystallizes out, and the solution has exactly the same concentration as that obtained in the other way.

A very important fact concerning solubilities is that the solubility of a given salt is practically unaffected by the presence of another salt in the solution, provided only that the other salt does not possess one of the same ions as the first salt.

For example, suppose that sodium nitrate and potassium chloride in equivalent amounts are added to 100 grams of water at 10°, so that the total weight of K^+ and NO_3^- radicals will be 42 grams; the potassium nitrate in excess of its solubility will then crystallize out, and 21 grams of the crystals will thus be obtained. The presence of the radicals of sodium chloride in the solution is without effect on the potassium nitrate.

In the following procedure 2 *formula weights* (F.W.) of $NaNO_3$ (170 grams) and 2 F.W. of KCl (149 grams) are together treated with 210 grams of water at the boiling temperature. The 170 grams of $NaNO_3$ will dissolve in the water since this amount will not nearly saturate 210 grams of water, but from the table it is seen that it will take only 118 grams of KCl to saturate this amount of water. If this were the only consideration we should expect 118 grams to dissolve and 31 grams of KCl to remain undissolved. But we must consider the presence of the Na^+ ions also in conjunction with the Cl^- ions, and since only 84 grams of NaCl are soluble in 210 cc. of water and in all 2 F.W. or 117 grams of NaCl are available we may conclude that 33 grams will crystallize out. This removes Cl^- from the solution and upsets the equilibrium which would otherwise exist between the solid and dissolved KCl. Thus the entire KCl will dissolve and furnish the entire 2 F.W. of Cl^- ions for the 2 F.W. of NaCl. The K^+ and NO_3^- ions thus made available constitute 2 F.W. or 202 grams of KNO_3, which according to the table would be completely soluble in 210 cc. of water at 100°. Hot filtration at this point will retain a part of the NaCl as solid in the filter but allow the whole of the 2 F.W. of KNO_3 to pass into the filtrate. Cooling of the filtrate will allow a new state of equilibrium to be established corresponding to the solubilities at the lower temperature.

In preparing a preliminary report for this preparation, copy thoughtfully into the laboratory note book the flow sheet of the procedure and answer the following questions based on the flow sheet. For the purposes of the calculations one will have to assume that in every filtration a perfect separation of solution from crystals is obtained — a condition which obviously is not realized in practice.

FLOW SHEET

Heat in a covered casserole 170 grams of $NaNO_3$, 149 grams of KCl, and 210 cc of water Boil the mixture 1 minute and then filter hot Do not rinse out the casserole but use it for the second boiling

<table>
<tr><td rowspan="4"><i>On Filter</i>
NaCl, dirt, and some KNO_3 Transfer to casserole in which first boiling was made
(<i>A</i>)</td><td colspan="4"><i>Filtrate</i> (<i>B</i>) Cool to 10° and filter</td></tr>
<tr><td rowspan="3"><i>On Filter</i>
Crystals of KNO_3 impure Press and wash with 20 cc ice-cold water
(<i>C</i>)</td><td colspan="3"><i>Filtrate</i> (<i>D</i>) Saturated with KNO_3 and NaCl. Pour it into original casserole containing impure NaCl (<i>A</i>) Boil 5 minutes Filter hot</td></tr>
<tr><td rowspan="2"><i>On Filter</i>
NaCl dirt and a little KNO_3
Save temporarily
(<i>E</i>)</td><td colspan="2"><i>Filtrate</i> Cool to 10° and filter</td></tr>
<tr><td><i>On Filter</i>
KNO_3 impure Press and wash with ice-cold water
(<i>F</i>)</td><td><i>Filtrate</i> Saturated with KNO_3 and NaCl. Save temporarily in flask labelled "mother liquors"
(<i>G</i>)</td></tr>
</table>

RECRYSTALLIZATION

Unite the two lots of moist impure KNO_3, add half their weight of distilled water, and heat until solution is complete Cool to 10° and filter, pressing out as much as possible of the liquid Stop suction Pour 15 cc ice cold distilled water over the crystals and let it permeate the mass Apply suction and pressure Test for chloride If any is found repeat the washing process until the product is free from chloride Add all filtrates to the mother liquors, *G*

1. What weight of KNO_3 will be dissolved in the hot filtrate (*B*)?
2. What weight of NaCl will be dissolved in the hot filtrate (*B*)?
3. What weight of solid KNO_3 will separate when the filtrate (*B*) is cooled to 10° (*C*)?
4. What weight of solid NaCl will be obtained together with the KNO_3 in (*C*)?
5. Assume that boiling the filtrate (*D*) after adding (*A*) reduces the amount of water to 150 grams; how many grams of NaCl will be left on filter (*E*) after filtering at 100°?

6. How many grams of KNO_3 will be obtained in (*F*) after cooling the filtrate from (*E*) to 10° and filtering?

7. How many grams of NaCl will be obtained in (*F*)?

8. If (*C*) and (*F*) are now united and water added to make a total of 100 grams of water, the whole heated to 100° and then cooled to 10°, how many grams of KNO_3 will separate on cooling to 10°?

9. How many grams of NaCl will separate from the solution in Question 8 in cooling to 10°?

Materials: crude Chile saltpeter, $NaNO_3$, 170 grams = 2 F.W.
crude potassium chloride, KCl, 149 grams = 2 F.W.

Reagent: $AgNO_3$ solution.

Apparatus: 750-cc. casserole.
5-inch watch glass.
5-inch funnel.
perforated filter plate.
suction flask and trap bottle.
250° thermometer.
iron ring and ring stand.
Bunsen burner.

Procedure: Place the $NaNO_3$ and KCl in a 750-cc. casserole. Add 210 cc. of water, cover with a watch glass, and place over a low flame. While keeping watch of the casserole to see that its contents do not boil, prepare a suction filter according to Note 4 (*b*) on page 6. Then raise the flame under the casserole and watch it until boiling commences. Lower the flame, and let the mixture boil gently just 1 minute, keeping the watch glass over the casserole to retard evaporation. While it is at the boiling temperature pour (see Fig. 1, page 5) the mixture from the casserole into the suction filter. Quickly scrape most of the damp salt into the filter, and cover the funnel with a watch glass to retard cooling. Do not rinse out the casserole but reserve it with the adhering salt and to it add the batch of crystals (*A*) as soon as they have been drained from the hot liquor. Pour the filtrate (*B*) into a beaker, and cool it to 10° by setting it in a pan of cold water or ice water.

Stir the crystallizing solution so as to obtain a uniform crystal meal which is easier to handle and drain on the filter than the larger crystals that would be obtained by slow cooling. Separate the KNO_3 crystals (*C*) from the cold liquor by means of the suction filter (observing the last sentence of Note 3, page 5). Press the mass of crystals in the filter to squeeze out as much of the solution as possible. The thin layer of solution left adhering to the surfaces of the crystals is saturated with NaCl. To remove the greater part of this, stop the suction, pour carefully over the surface of the crystals 20 cc. of ice-cold distilled water, let this water penetrate into the mass of crystals for perhaps 30 seconds, then apply suction and drain these washings into the rest of the filtrate. Pour the filtrate (*D*) into the casserole in which the batch of NaCl crystals (*A*) is reserved. Bring this mixture to the boiling point and boil gently 5 minutes with the casserole uncovered, thus allowing a part of the water to escape by evaporation. Then filter at the boiling temperature exactly as in the first instance. Cool the filtrate, and collect and rinse a second crop of KNO_3 crystals (*F*) in exactly the same manner as the first crop (*C*). Reserve the filtrate in a flask labeled " mother liquors " (*G*). Add together the two crops of KNO_3 crystals (*C* and *F*), and test them for chloride by dissolving about 0.1 gram in 2 cc. of water and adding 5 drops of dilute HNO_3 acid and 1 drop of $AgNO_3$ solution. A considerable white precipitate will be seen, indicating the presence of chloride, and the crystals must be purified by recrystallization. Weigh the crystals while they are still moist, add to them in a beaker one-half this weight of distilled water, and warm until solution is complete.*

Cool the solution to 10° with stirring, and pour the mixture on to the suction filter. Some of the filtrate, which is saturated with KNO_3, may be poured back into the beaker to rinse the last of the crystals on to the filter. Drain the crystals with suction, pressing them down compactly in order to squeeze out as much of the solution as possible. Stop the suction. Pour carefully over the crystals 15 cc. of ice-cold distilled water. Let it permeate the whole mass, then again apply suction and drain and collect all the

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* If the solution is not perfectly clear at this point it must be filtered. Dilute it with 50 cc. of water so that it will not " freeze " on the filter. Pour it at the boiling temperature without suction through a filter, and then pour 20 cc. of boiling water around the upper edge of the filter, letting it run through into the filtrate to carry the last of the KNO_3. The solution will have to be evaporated to bring it back to its original volume.

filtrate and washings in the flask of "mother liquors" (*G*). Again test for presence of chloride. A trace will probably be shown. Continue the washing process, using 15-cc. portions of ice water each time until no test is shown for chloride. Transfer the crystals to white paper towels. Fold the towels over the crystals to make a compact package, and leave the package over night to dry at room temperature. Transfer the dry crystal meal to a dry 4-ounce bottle and label the preparation neatly.

If a sufficient quantity of pure product is not obtained, all the mother liquor should be boiled down in the 750-cc. casserole and used as a starting point in repeating the foregoing procedure.

Fifty grams may be regarded as a satisfactory yield.

The sequence of operations in this preparation can be readily followed on the flow sheet, page 55.

QUESTIONS

1. In the recrystallization of the potassium nitrate why is it preferable first to dissolve completely the batch of crystals in water by heating and then cool to obtain the crystals again, instead of merely washing the crystals with the same amount of cold water?

2. Define metathesis.

3. If we had barium nitrate and potassium sulphate from which to prepare potassium nitrate, make a list of the solubilities of the four salts concerned and arrange a flow sheet of a method by which pure potassium nitrate could be obtained. Which of the operations would offer the most difficulty?

PREPARATION 2

PREPARATION OF A HYDRATE

CRYSTALLIZED SODIUM CARBONATE, $Na_2CO_3 \cdot 10H_2O$, FROM ANHYDROUS SODIUM CARBONATE

Many substances, as acids, bases, salts, and even elements, when they separate from solution, or crystallize, carry water with them. Familiar examples are $(H_3AsO_4)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 8H_2O$, $CuSO_4 \cdot 5H_2O$, and $Cl_2 \cdot 8H_2O$. Such substances, when dried, show no evidence of fluidity, that is, of the property one must naturally think of as belonging to water, even sometimes when more than half the weight of the substance is water. Such substances are called hydrates, and the same substance without the water is known as the anhydrous substance. Substances containing water of this nature are crystalline, and the water is also known as water of crystallization. This fact should not lead one to think that water is necessary for the formation of a crystal, because many crystals do form that do not contain water.

Soda ash is commercial anhydrous sodium carbonate. When a solution saturated at boiling temperature is allowed to cool to below 33°, a transparent crystalline mass separates of the formula $Na_2CO_3 \cdot 10H_2O$, known commercially as *soda crystals* or *sal soda.*

If water is evaporated from the solution, saturated at 100°, a solid of the composition $Na_2CO_3 \cdot H_2O$ separates. Besides the dekahydrate and monohydrate there is at least one other well-recognized hydrate, the heptahydrate, $Na_2CO_3 \cdot 7H_2O$. This compound separates from solution only over a narrow range of temperature and concentration.

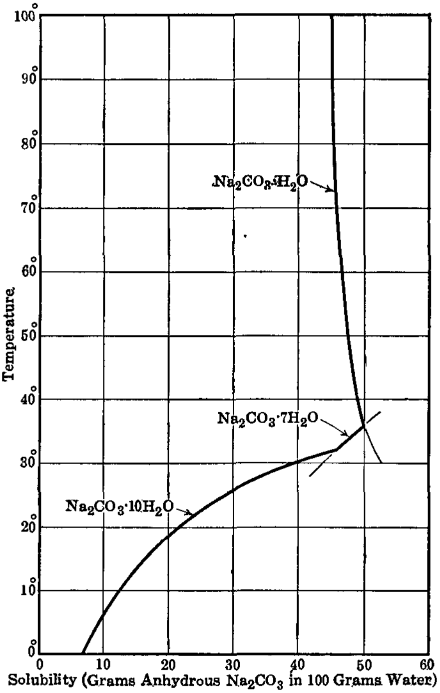

FIG. 15

The curves in Fig. 15 show the different hydrated forms which are in equilibrium with the saturated solution at different temperatures. It will be seen that the dekahydrate is the stable hydrate only below 33°. In the following preparation, if barely enough water to form the dekahydrate were added to the anhydrous soda ash and the mixture heated to 100°, a complete solution would not be obtained because some monohydrate would separate. Enough water, therefore, is taken to hold all the monohydrate in solution at the boiling point. When this solution cools to below 33° it may become highly supersaturated with the dekahydrate unless a few crystal fragments of the dekahydrate are added. It occasionally happens that if no seed crystals are added the heptahydrate is the first to separate spontaneously. However, below 33° the heptahydrate is more soluble than the dekahydrate, and, therefore, with the seed crystals added, and equilibrium established with the latter salt, the heptahydrate again dissolves.

Materials: anhydrous sodium carbonate, Na_2CO_3; 106 grams = 1 F.W.

Apparatus:
500-cc. flask.
5-inch funnel.
8-inch crystallizing dish.
8-inch glass plate to cover dish.
porcelain filter plate.
Bunsen burner.
iron ring and ring stand.

Procedure: Place the sodium carbonate and 250 cc. of water in the flask and warm it to just short of the boiling point until the salt is dissolved. See Note 7, page 13. Filter the hot solution into the crystallizing dish, keeping the dish covered with a glass plate except where the stem of the funnel enters. When the solution has cooled below 33° add a few crystal fragments of the dekahydrate. Set the dish, completely covered, in your desk. After 6 hours or longer separate the crystals from the remaining liquid by pouring the contents of the dish into a funnel in the bottom of which is placed the perforated porcelain filter plate without any paper. It may be possible to get additional crystals from the mother liquor by cooling it still more. After the crystals have drained dry them on paper towels. See Note 9 (*b*), page 15. The crystals should not be left more than over night wrapped in the paper towels. When they are dry place the crystals in an 8-ounce, cork-stoppered bottle.

QUESTIONS

1. What reasons have you for believing that the water in crystal hydrates is in chemical combination with the salt?
2. How could anhydrous sodium carbonate be prepared from the hydrate?
3. How could the monohydrate, $Na_2CO_3 \cdot H_2O$, be prepared?

PREPARATION 3

PREPARATION OF A HYDRATED DOUBLE SALT

AMMONIUM-COPPER SULPHATE, $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$

Besides forming molecular compounds with water (hydrates) certain salts have the property of combining with a second salt either with or without water. In these combinations the character of the individual salts is somewhat modified but not completely changed. Hence the name, "double salts". In physical properties such as crystalline form, solubility, and, in some cases, color, the crystals of the double salt differ from those of the simple salts. These compounds follow the law of definite proportions.

Ammonium sulphate crystallizes from solution as the anhydrous salt, $(NH_4)_2SO_4$; copper sulphate as the hydrate, $CuSO_4 \cdot 5H_2O$; but when equivalent amounts of the two salts are in solution together the double salt, $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, separates first because it is less soluble than either of the single salts.

Materials: copper sulphate, $CuSO_4 \cdot 5H_2O$, 50 grams = 0.2 F.W.
ammonium sulphate, $(NH_4)_2SO_4$, 27 grams = 0.2 F.W.

Apparatus: 8-inch porcelain dish.
8-inch crystallizing dish.
5-inch funnel and filter paper.
iron ring and ring stand.
Bunsen burner.

Procedure: Pulverize the copper sulphate, and dissolve it with the ammonium sulphate in 250 cc. of warm water, to which 10 drops of 6 N H_2SO_4 have been added. The solution should not be boiled. Filter the warm solution into an 8-inch crystallizing dish covered with a glass plate except where the stem of the funnel enters, and allow it to stand over night with the cover on. Remove the cover and allow water to evaporate slowly until a satisfactory yield has been obtained. This usually requires about 4 days. Seed crystals are available at the store room, but crystallization usually starts as soon as the solution cools to room temperature. If a crystal meal is desired follow the procedure suggested in Note 8 (*a*), page 14. Decant the mother liquor from the crystals, wash them with a little distilled water, and dry them thoroughly, at room temperature, on paper towels. The double salt tends to effloresce, and the crystals should be transferred to a stoppered bottle as soon as they are dry.

QUESTIONS

1. Determine whether double salts can be prepared containing sodium sulphate and copper sulphate; potassium sulphate and copper sulphate.

(*a*) Dissolve 1 gram of potassium sulphate and 2 grams of copper sulphate in 10 cc. of hot water. Pour the clear solution on a watch glass. When crystals have formed, see if they are all of the same kind (i.e., the double salt), or of two distinct kinds (the two simple salts).

(*b*) Repeat the experiment using 1 gram of anhydrous sodium sulphate and 2 grams of copper sulphate. Account for your results.

PREPARATION 4

POTASSIUM-COPPER SULPHATE, $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$

Read the preliminary discussion which precedes the preparation of ammonium-copper sulphate, page 61.

Materials: potassium sulphate, K_2SO_4, 35 grams = 0.2 F.W.
copper sulphate, $CuSO_4 \cdot 5H_2O$, 50 grams = 0.2 F.W.

Apparatus: 8-inch porcelain evaporating dish.
5-inch funnel and filter paper.
8-inch crystallizing dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Prepare potassium-copper sulphate from potassium sulphate and copper sulphate. Follow the procedure outlined in the previous preparation. Determine the volume of water to be used to give a saturated solution at 25°.

Solubility of the anhydrous salts in 100 grams water at 25°:

$CuSO_4$	23 grams
K_2SO_4	12 "
$K_2SO_4 \cdot CuSO_4$	11 "

Experiments

HYDRATES

1. Water of Hydration. Heat a crystal of blue vitriol $CuSO_4 \cdot 5H_2O$ rather cautiously in a dry test tube holding the tube in a nearly horizontal position. Observe that the crystal gradually loses its blue color and becomes white and powdery, also that drops of water condense on the cooler part of the tube. Let the tube cool to room temperature and add a few drops of water to the white copper sulphate. Observe that the material regains at once its original blue color and that it grows so hot that the hand cannot be held on that end of the tube.

Water combined as water of hydration in crystals is in a true state of chemical combination, for the hydrated crystal shows the following characteristics of a chemical compound.

First: Its crystalline form is different from that of the anhydrous compound. In some cases (as in this instance) there is a difference in color.

Second: It follows the law of definite proportions, for example, every sample of blue vitriol which has been crystallized from water at room temperature has exactly the composition expressed by the formula $CuSO_4 \cdot 5H_2O$. (The next experiment is a quantitative one designed to prove that a crystal hydrate has a definite composition.)

Third: There is a marked heat effect produced by the combination of the anhydrous salt and water.

2. Composition of a Crystal Hydrate. The mineral gypsum contains, besides calcium sulphate, also a certain proportion of water. The latter may be completely driven off by heat, leaving *anhydrous* calcium sulphate.

Weigh accurately a clean, dry, 15-cc. porcelain crucible. Place approximately 2 grams of gypsum in it and weigh again. Cover the crucible, support it on a nichrome triangle, and heat (to avoid breaking the cover warm this first uniformly by playing the flame over it carefully from above) to redness for 20 minutes in the Bunsen flame. Rest the triangle and crucible on top of a good-sized beaker and allow to cool. Again weigh the crucible and contents. Repeat the heating, and if a further loss of weight occurs repeat until two successive weighings are the same. This is to ensure that all the water is driven off. The cover is used for a double purpose: to prevent fragments of the crystals snapping out of the crucible from sudden expansion of the steam, and to keep the heat in.

Calculate the percentage by weight of water in gypsum. From this result calculate the number of molecules of water of crystallization in gypsum, assuming the formula to be $CaSO_4 \cdot nH_2O$ (atomic weights on front cover page).

If the experimental work is carefully done it will be found that n is an even whole number. Thus the substances calcium sulphate and water combine chemically in amounts proportional to simple integral multiples of their molecular weights just as elements combine in amounts proportional to simple integral multiples of their atomic weights. Although the crystal hydrate is just as truly a chemical compound as is calcium sulphate or water, nevertheless the force holding the substances together in this compound is secondary to that holding the elements together in the simpler compounds.

3. Efflorescence. Place on a watch glass some crystals of sodium carbonate $Na_2CO_3 \cdot 10H_2O$, zinc sulphate $ZnSO_4 \cdot 7H_2O$, or disodium phosphate $Na_2HPO_4 \cdot 12H_2O$, and leave them exposed to the air for some time.

Observe that the surface of the crystals soon becomes white and powdery and finally the whole crystal changes to a white powder.

This change which is known as *efflorescence* is caused by loss of water of hydration from the crystal, leaving either the anhydrous salt or a less hydrated salt (of definite composition, however). Every crystal hydrate has a definite vapor pressure at a given temperature. If this vapor pressure is greater than the partial pressure of the water vapor in the air the crystal hydrate will lose water to the air. This will continue until all the water is lost or equilibrium between the water vapor in the air and in the hydrate is reached.

	Vapor pressure in millimeters of mercury at 20°
$Na_2SO_4 \cdot 10H_2O$	13.25
$Na_2HPO_4 \cdot 12H_2O$	13.1
$Na_2CO_3 \cdot 10H_2O$	12.6
$ZnSO_4 \cdot 7H_2O$	10.07
$SrCl_2 \cdot 6H_2O$	5.8
$CuSO_4 \cdot 5H_2O$	4.8
$BaCl_2 \cdot 2H_2O$	4.04

The partial pressure of the water vapor in the air varies from day to day, but the average is about 8–10 mm. Hydrates like $Na_2CO_3 \cdot 10H_2O$ will lose water on exposure to such air, while salts like $BaCl_2 \cdot 2\ H_2O$ will not lose water unless the water vapor in the air is unusually low.

Heating blue vitriol increases its aqueous tension, and thus the dehydration by heating is in fact an artificially induced efflorescence.

4. Deliquescence. Place on a watch glass small lumps of any of the following compounds: calcium chloride, zinc chloride, potassium hydroxide, sodium hydroxide, ferric chloride. Note that in a few minutes the surface becomes covered with moisture, and that after a longer time the solids have completely changed to liquid. This liquefaction is due to condensation of the water vapor of the air at the surface of the solid and the dissolving of the solid material. All deliquescent substances are very soluble in water. The tension of the vapor escaping from water is always lessened by substances dissolved in it, and when this tension is lowered to below that of the water vapor existing in the atmosphere, water is absorbed by the solution from the air. In general, substances will deliquesce when the *aqueous tension of their saturated solutions* is less than the tension of water vapor in the air.

ELEMENTS AND WATER

When substances like salts and water form compounds the force of attraction is of a subordinate character, and the formula of a hydrate is usually written with a period between the formula of the salt and that of the water, for example, $CuSO_4 \cdot 5H_2O$. This indicates that the "primary" valence of the element is satisfied in the simple compounds, and that it is only some sort of "secondary" valence which holds the substances in combination.

When elements react with water, however, a change in the primary valence is usually involved.

A rather unusual instance of a hydrate of an element is chlorine hydrate, $Cl_2 \cdot 8H_2O$, which crystallizes from ice-cold water which is saturated with chlorine. This substance is clearly a molecular compound, for if these crystals are placed in a watch glass and allowed to come to room temperature, chlorine gas escapes and water containing only the amount of chlorine corresponding to an ordinary saturated solution is left.

> **5. Sodium and Water. Danger.** Pour about 50 cc. of water into a 4-inch porcelain dish. Select a piece of metallic sodium half the size of a pea and press it in a folded filter paper to remove the adhering kerosene. Drop the metal on the surface of the water. Stand at least 3 feet from the dish. Note that the sodium floats; that it almost immediately melts to a globule with a bright metallic surface; that a gas is given off freely under the impulse of which the globule races about over the surface of the water; that finally the globule entirely disappears, and then that the remaining solution is strongly alkaline, turning litmus blue and making the fingers slippery when wet with it. Often, after the sodium has melted and become hot, there is a violent explosion which throws the caustic solution and the burning metal about, hence the danger.

The gas evolved is hydrogen; the alkaline character of the solution is due to sodium hydroxide which is left dissolved in the water

$$2Na + 2HOH \rightarrow 2NaOH + H_2$$

Sodium is a much more active element than hydrogen and has displaced an equivalent amount of it from water. Sodium hydroxide then may be regarded as water in which sodium has taken the place of one-half of the hydrogen. A gram atom of sodium can replace a gram atom of hydrogen; in other words, the valence of sodium is 1.

> **6. Calcium and Water.** Drop a few pieces of metallic calcium (in the form of turnings) into a test tube of clear

water. Note that a gas is evolved; collect a little of it, and note that it burns like hydrogen. Note that the water remains clear for a little time but that soon it becomes cloudy owing to the separation of a finely divided white solid substance. The solution colors litmus blue but produces hardly a noticeable slippery feeling between the fingers.

This experiment is similar to the preceding one. Calcium displaces hydrogen from water

$$Ca + 2HOH \rightarrow Ca(OH)_2 + H_2$$

but the reaction is less violent; calcium is thus shown to be a less active metal than sodium. Furthermore, the product obtained by substituting calcium for hydrogen in water, calcium hydroxide, is sparingly soluble and appears as a solid substance as soon as more than enough of it has been formed to saturate the solution. The formula $Ca(OH)_2$ shows that one gram atomic weight of calcium can take the place of two gram atomic weights of hydrogen; therefore, the valence of calcium is 2.

It is only the most active metals that displace hydrogen freely from cold water; nevertheless, many of the metals do react with water but for one reason or another the reaction does not progress far. We just saw that calcium hydroxide was only sparingly soluble. The hydroxides of magnesium, zinc, aluminum, lead, iron are even less soluble. Thus, although a freshly cleaned piece of metal may react with water, the hydroxide which is produced adheres to the surface as a coating which separates the metal and the water. This is the main reason why most of the fairly active metals seem to be without action on water.

The following few experiments illustrate the action of such metals with water. In every case it is a question of removing or breaking through the film of insoluble material coating the surface.

7. Magnesium and Water. (*a*) Note the appearance of the surface of some magnesium ribbon. Scrape the surface with a knife and note the bright metallic luster. Note also that this luster quickly grows dim. Put the magnesium into a test tube half filled with water and note that no reaction takes place. Heat the water to boiling and note that hydrogen is not evolved.

(*b*) To try the effect of dry steam on hot magnesium, clamp a piece of Pyrex glass tubing 1 cm. in diameter and 18 inches long in position at an angle of about 5° with the horizontal. Connect the lower end of the tube with a flask in such a manner that steam generated from the water in the flask may be conducted through the tube. Connect the upper end of the tube with a delivery tube, arranged so that the gases produced in the reaction may be collected over water in a trough. Place some pieces of magnesium ribbon in the middle of the tube. Pass steam through the tube and heat it cautiously at the lower end until the condensed water is evaporated and the steam is "dry." Get the whole length of the tube well warmed with the burner, so that it appears perfectly dry inside, and then heat the section containing the magnesium as strongly as possible. It is rather difficult to get the magnesium to catch fire, and it may be necessary to stop the water boiling in the flask for a moment, because the steam cools the magnesium below its kindling temperature. As soon as the magnesium catches fire pass steam rapidly through the tube. Slip a test tube full of water over the end of the delivery tube. Notice that the magnesium appears to burn in the dry steam with much the same brilliancy as in air; that a white smoke and ash (magnesium oxide) is produced as in air. The blackening of the parts of the glass that were in contact with the melted magnesium or its vapor may be disregarded as far as the purpose of this experiment goes; it is due to a reduction of the silicon dioxide of the glass to silicon. The gas collected in the test tube is found to burn with a colorless flame and is thus shown to be hydrogen.

(*c*) Magnesium amalgam is an alloy (much like a solution) of mercury and magnesium. It is made by rubbing powdered magnesium and mercury together in a mortar. Considerable rubbing is necessary, because the oxide film on the surface of the metal has to be rubbed off before the mercury can begin to dissolve the metal. When the amalgamation once begins, a good deal of heat is produced and the process is soon finished. A semi liquid or a stiff amalgam is obtained, according to the proportions used.

Drop a small lump of magnesium amalgam into a test tube of cold water. A violent reaction takes place. A gas is evolved freely which burns with a colorless flame characteristic of hydrogen. The contents of this tube grow very hot, and the amalgam disintegrates to yield a finely divided gray powder which stays suspended in the water.

In experiment (*b*) the action was extremely slow until the magnesium reached its melting point. From then on no coherent film would stick to the liquid surface, and without this mechanical hindrance to the reacting substances coming in contact with each other, the natural activity of the magnesium came into play.

In experiment (*c*) the amalgam is liquid or at least semi liquid so that no coherent film of magnesium hydroxide can adhere to the surface.

That magnesium must be a much more active element than hydrogen is shown by the vigor with which it displaces it; in experiment (*b*), for example, the fact that the oxygen with which the magnesium was combining had to be withdrawn from its combination with hydrogen did not appear to diminish the vigor of the reaction sensibly, for the incandescence seemed as bright as if the magnesium ribbon had been burning in oxygen.

8. Iron and Water. Iron filings do not produce any measurable quantity of hydrogen either in cold or hot water. Set up the apparatus described in Experiment 7 (*b*). Put a layer of fine iron filings in the middle of the combustion tube in place of the magnesium. Heat cautiously to vaporize the liquid water condensed in the tube, and then heat the iron filings strongly. As the steam from the delivery tube condenses in the water in the trough it is seen that an occasional bubble of gas rises in the test tube. After a short time enough has collected to test and it is found to burn like hydrogen.

Apparently in this case the coating of oxide on the surface of the iron is not entirely impervious to gases. At the high temperature the steam diffuses more rapidly through the layer and thus the production of hydrogen becomes measurably rapid.

9. Removal of Protective Coating by Chemical Action. Note that aluminum metal resembles magnesium in that it displays a brilliant metallic luster when its surface has just been scraped but it quickly loses the brightness of its luster.

Drop some aluminum turnings into some sodium hydroxide solution. Note that gas is immediately given off and that the aluminum in time dissolves completely. The gas is found to burn like hydrogen.

Insoluble aluminum hydroxide is known to react readily with sodium hydroxide producing the soluble sodium aluminate

$$Al(OH)_3 + 3NaOH \rightarrow Na_3AlO_3 + 3H_2O$$

With the aluminum hydroxide coating thus continually removed by the sodium hydroxide there is nothing to prevent the progress of the primary reaction between aluminum and water.

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

10. Chlorine and Water. The "chlorine water" in the reagent bottle is prepared by dissolving chlorine gas in water. Take a few cubic centimeters of this solution and (to make sure that it has been acted upon by light) expose it a few minutes to direct sunlight or for a longer time to strong diffused daylight. Boil the solution under the hood to drive off any chlorine which is left, and then test the liquid with litmus. The litmus is turned red. Fill a test tube with chlorine water and invert it in a small beaker containing chlorine water. Leave the whole in the bright sunlight for several hours. A few cubic centimeters of a colorless gas collect in the top of the inverted test tube, and the yellow color of the chlorine water gradually fades out. The gas causes a glowing splinter to burst into flame, which identifies it as oxygen.

Metals more active than hydrogen displaced that element from water. Non-metals, on the other hand, if active enough, would displace the oxygen. It is obvious that this is what has happened and that the acid remaining in solution is hydrochloric acid, HCl.

The total effect of the change is given by the equation

$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$$

That chlorine is not greatly more active than oxygen is shown by the fact that this reaction does not take place in the dark, and only slowly under the action of sunlight.

OXIDES AND WATER

Nearly all the elements are capable of combining with oxygen to form oxides. All the oxides have a greater or less tendency to combine with water or with other oxides. In general the oxides of metals combine with water to form bases, and the oxides of non-metals combine with water to form acids.

11. Sodium Oxide and Water. Support a porcelain crucible cover on a triangle and heat it to redness; while it is thus hot, place upon it, by means of iron pincers, a piece of sodium the size of a small pea. Remove the burner and let the sodium burn. When cold dissolve the white oxide in a few cubic centimeters of water and test the solution with litmus. Notice some effervescence when the oxide is dissolving. Note that the solution turns litmus blue and feels very slippery when rubbed between the fingers.

When sodium burns in an abundance of air an oxide of the formula Na_2O_2 and called sodium peroxide is formed. When sodium peroxide is treated with water it reacts according to the equation

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

thus losing one-half of its oxygen and yielding soluble sodium hydroxide. If the peroxide is heated with sodium out of contact with the air sodium oxide, Na_2O, is formed. This compound has half as much oxygen to a given weight of sodium as the peroxide. Sodium oxide reacts with water to form sodium hydroxide without the liberation of oxygen.

$$Na_2O + H_2O \rightarrow 2NaOH$$

Sodium hydroxide, NaOH, is very soluble in water; it is one of the strongest *bases*.

12. Calcium Oxide and Water. The well-known substance "quicklime" is calcium oxide. Calcium oxide could be made by burning bits of calcium, but the oxide quickly coats over the surface of the metal, and it is difficult to make the interior portions of the lump react. For this experiment take a lump of quicklime out of a recently opened container. Cover it with water in a porcelain dish and then pour off the excess of water that did not soak into the porous lump. Note that the lump soon grows very hot, giving off clouds of steam, and swells up and tumbles apart to form a fluffy white powder. Stir a little of this powder with water. It makes a milky suspension. If some of this suspension is placed in a test tube the white solid settles and a clear liquid remains above. This liquid colors litmus blue.

It is obvious from the large amount of heat developed that the affinity between calcium oxide and hydrogen oxide is very great.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The same substance, calcium hydroxide, is formed here as in the action of calcium metal on water, only in this case no hydrogen is displaced. Calcium hydroxide is not very soluble in water, and mainly on that account it is not as strong a base as sodium hydroxide. The saturated solution is called "lime water."

13. Magnesium Oxide and Water. Burn a piece of magnesium ribbon held in pincers so that the ash falls into a clean dish. Stir half of the ash into a small beaker full of water and test the solution with litmus. Wet the other half of the ash with a single drop of water and place the moistened mass on one side of a strip of red litmus paper. Look on the other side of the paper and note that in a little while the center of the wet spot turns blue.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Magnesium oxide does not combine as energetically with water as calcium oxide, and the magnesium hydroxide formed is very much more insoluble than calcium hydroxide. Thus the saturated solution of the hydroxide is barely alkaline enough to color litmus blue.

The hydroxides of aluminum and of the heavy metals are much more insoluble even than magnesium hydroxide, and for the most part their suspensions do not affect litmus. The hydroxides of the metals are, however, considered basic although very weakly so.

14. Non-Metal Oxides and Water. Burn small pieces of (*a*) phosphorus (use red phosphorus), (*b*) sulphur, and (*c*) carbon (charcoal) successively in large, clean bottles of air. The phosphorus and sulphur may be introduced in a deflagrating spoon made by winding a piece of wire around a piece of chalk one end of which has been scooped out. A large piece of charcoal should be attached to a wire and held in the flame until it glows brightly before it is put in the jar. Quickly add 3 to 5 cc. of water to each bottle, close it with a glass plate (or the palm of the hand), and shake vigorously a few moments. Test the solutions with litmus. In each case the litmus turns red.

This experiment shows that non-metals form oxides which react with water to produce acids.

$$4P + 5O_2 \rightarrow 2P_2O_5 \qquad P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$
$$S + O_2 \rightarrow SO_2 \qquad SO_2 + H_2O \rightleftharpoons H_2SO_3$$
$$C + O_2 \rightarrow CO_2 \qquad CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The oxides of phosphorus and sulphur are quite readily soluble but carbon dioxide is very much less soluble.

WATER CONTAINS TWO SEPARATELY REPLACEABLE PORTIONS OF HYDROGEN

When sodium or calcium reacts with water hydrogen is liberated and sodium or calcium hydroxide is formed. The formula $NaOH$ or $Ca(OH)_2$ shows that the compound still contains one-half of the hydrogen of the original water, but let us imagine for a moment that we are in the place of the early chemists who were finding out things for the first time. They carefully dried these hydroxides and then tried experiments to see if any more hydrogen was obtained from the hydroxides. When they found that they could obtain an amount of hydrogen just equal to that displaced from the water by the metal when the hydroxide was prepared, they drew the conclusion that water contained two parts of hydrogen in combination with one part of oxygen. This experiment was one of the strong arguments which led to the adoption of the formula H_2O for water rather than HO.

15. Mix 2 grams of dry powdered sodium hydroxide and 3 grams of zinc dust in a mortar. Place the mixture in a hard glass test tube fitted with a delivery tube. Heat the mixture in the tube; collect a little of the evolved gas and show by a test that it is hydrogen.

Water as a Solvent: Concentration of Solutions

The importance of water depends in very large measure on its ability to dissolve other substances. Oftentimes substances which, in the dry state, will not react, do react when they are dissolved and their solutions mixed. If a reaction is to be brought about between two substances in solution it is a matter of importance to know how much of each solution to take, and to do this it is necessary to know the *concentration* of the solutions.

Concentration is the ratio of the amount of dissolved substance either to the volume of the solution or to the weight of the solvent. In the problems in this chapter, and generally in analytical and synthetic chemistry, the concentration is based on the volume of the solution, usually 1 liter. In Chapter III, on the other hand, concentrations are based on weight of solvent, usually 1,000 grams. The amount of dissolved substance may be expressed in weight — grams — but it is usual in chemical work to express it in moles, formula weights, or equivalent weights.

Mole. A mole is one gram molecular weight of a substance, *e.g.* 36.5 grams of HCl.

Molal Solution. A molal solution contains one mole of dissolved substance in 1 liter of solution, *e.g.*, 40 grams of NaOH or 98 grams of H_2SO_4. One liter of the solution contains less than 1,000 grams of water, but the weight of the whole solution is usually more than 1,000 grams.

Formula Weight. A formula weight of a substance means exactly the same as a mole if the formula is the molecular formula. Sometimes, however, the molecular weight of a substance is not known although its composition is known and an empirical formula is given. In such a case the meaning of the term mole is not certain, but the meaning of formula weight is perfectly definite: it is the number of grams obtained by adding up the total of the atomic weights in the formula as it is written.

Formal Solution. A formal solution contains one formula weight of the dissolved substance in 1 liter of solution.

Equivalent Weight. The gram equivalent weight of a substance is that amount which is equivalent in a reaction to 1.008 grams of hydrogen. The gram equivalent weight of an acid is found by dividing the molecular weight by the number of hydrogens available for a reaction such as neutralization. The gram equivalent weight of HCl is $\frac{36.5}{1}$ grams, and of H_2SO_4 $\frac{98}{2}$ grams.

The gram equivalent weight of a base is the weight in grams required to neutralize one gram atomic weight of hydrogen in an acid. In the reaction $HCl + NaOH \rightarrow H_2O + NaCl$ one mole of NaOH exactly neutralizes one mole of HCl. Therefore, 40 grams of NaOH are equivalent to 36.5 grams of HCl. If calcium hydroxide is used, the equation $Ca(OH)_2 + 2HCl \rightarrow 2H_2O + CaCl_2$ shows that the gram equivalent weight is $\frac{74}{2}$, or 37 grams.

The gram equivalent weight of salts is obtained in the same way. In the two neutralization reactions mentioned above, one mole of NaCl and one-half mole of $CaCl_2$ are each equivalent to one mole of HCl. The equivalent weights are $\frac{58.5}{1}$ grams of NaCl and $\frac{111}{2}$ grams of $CaCl_2$.

Normal Solution. A normal solution contains one equivalent weight of the dissolved substance in 1 liter of solution. In a liter of normal hydrochloric acid (written $1\,N$ HCl) there are $\frac{36.5}{1}$ grams of hydrogen chloride and enough water to make 1 liter of solution. A liter of $6\,N$ HCl contains 6 times as much acid, $\frac{6 \times 36.5}{1}$ grams of hydrogen chloride in a liter of solution. Since it is not convenient to measure or weigh hydrogen chloride gas in making solutions, a concentrated solution of known composition is diluted to the desired normality. The concentrated acid of commerce is approximately $12\,N$, and, to make a $1\,N$ solution from it, $\frac{1,000}{12}$ cc. are diluted to 1 liter. A liter of normal sulphuric acid contains $\frac{98}{2}$ grams of the pure acid. In practice, concentrated sulphuric acid, which is approximately $36\,N$, is diluted to give the desired normality. A normal solution of sodium hydroxide contains 40 grams of base in a liter of solution; one of $Ba(OH)_2$ contains $\frac{171.4}{2}$ grams of base in 1 liter of solution.

From this discussion it is obvious that 1 liter or $1\,N$ acid will neutralize exactly 1 liter of $1\,N$ base. It follows that a given volume of a $1\,N$ solution of any acid will exactly neutralize an equal volume of a $1\,N$ solution of any base.

Experiment 6

STANDARDIZATION OF SOLUTIONS

If we have a solution of an acid of known normality we can determine the concentration of an unknown basic solution by finding what volumes of the two solutions are required to produce neutrality. For example, it is found that 60 cc. of a $0.5\,N$ hydrochloric acid solution are required to neutralize 25 cc. of a sodium hydroxide solution of unknown concentration. The normality of the base is 1.2, or the solution contains 48 grams of solid NaOH per liter. In general

$$N_A : N_B = V_B : V_A$$

V_A = volume of acid and N_A = normality of acid.

V_B = volume of base and N_B = normality of base.

Instead of a hydroxide a carbonate may be used to neutralize an acid

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

A $1\,N$ solution of sodium carbonate (molecular weight = 106) contains $\frac{106}{2}$ grams of solid in a liter of solution. Since sodium carbonate can be obtained in a high state of purity and can be accurately weighed it is frequently used to determine the exact concentration of an acid solution. Any solution, the concentration of which has been accurately determined, is known as a "standard solution."

In this experiment hydrochloric acid will be standardized against a known weight of pure sodium carbonate. A solution of methyl orange will be used as an indicator to tell when the solution is neutral. This indicator is pink in acid solution and yellow in alkaline solution (see page 135).

The process of comparing the concentration of solutions is known as titration. The apparatus used is a burette, a glass tube accurately graduated in cubic centimeters.

Apparatus: two 50-cc. burettes.
2 burette clamps.
500-cc. graduated cylinder.
bottle with glass stopper.
bottle with rubber stopper.
300-cc. Erlenmeyer flask.
large vial.

Materials: 12 N hydrochloric acid.
sodium hydroxide, pellet form.
sodium carbonate, anhydrous.
solution of methyl orange.

Procedure: (*a*) Prepare an approximately 0.5 N HCl solution by diluting 21 cc. of 12 N HCl with 479 cc. of distilled water. After thoroughly mixing, store it in the glass-stoppered bottle.

(*b*) Prepare an approximately 0.5 N NaOH solution by weighing out 10.5 grams of the solid fused NaOH (0.25 F.W., allowing 5 per cent for impurities). After thoroughly mixing with 500 cc. of distilled water, store it in the rubber-stoppered bottle.

(*c*) Pour about 10 cc. of the hydrochloric acid solution into one of the burettes. Rinse it back and forth, and let the acid drain out of the tip. Repeat the rinsing with two more 10-cc. portions of acid. Fill the burette with the acid solution and clamp it to a ring stand. In the same manner rinse and fill the other burette with the sodium hydroxide solution. Clamp this burette to the same ring stand. Make sure that there are no bubbles of air in the tip of the burettes. If any are found, they must be removed. This can be done by opening the stop cock and allowing the solution to run out rapidly. Drain enough of the solution from the burette to bring the meniscus on the graduated scale. Allow the solution to stand a minute until the film of liquid on the wall of the tube has time to drain. Read the position of the *lower* curve of the meniscus. This should be done by putting a strip of white paper around the burette with the upper straight edge two small divisions below the bottom of the meniscus and bringing the eye to a position exactly horizontal with upper edge of the paper (Fig. 16). Record this reading as the initial volume. Do not try to set the meniscus on any particular line, but read it exactly wherever it comes to rest. Run approximately 40 cc. of the HCl into the 300-cc. Erlenmeyer flask; add 100 cc. of water and 2 drops of methyl orange. Then run in NaOH until the color changes from pink to yellow. Rotate the flask to insure thorough mixing, and rinse down the wall of the flask with distilled water from the wash bottle. Since the "end point" is probably overstepped a little,

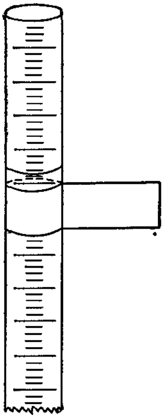

FIG. 16

add HCl, drop by drop, until the color changes to pink, and then make sure that a single drop, or less, of NaOH turns the color yellow after thorough mixing. Record the final reading of both burettes. Calculate the number of cubic centimeters of HCl equivalent to 1 cc. of NaOH. Confirm your result by running a duplicate, and for the final value use the average of your two determinations. Enter your data in your note book according to the following plan:

HCl AGAINST NaOH

	First trial	Second trial
HCl end reading	41.23 cc.	41.20 cc.
Initial reading	1.33	0.05
	39.90 cc.	41.15 cc.
NaOH end reading	40.70 cc.	42.43 cc.
Initial reading	0.25	0.65
	40.45 cc.	41.78 cc.
1 cc. NaOH = cc. HCl	0.9864	0.9849
	Average 0.9857	

(*d*) Standardize the HCl solution against pure anhydrous sodium carbonate. Put some dry sodium carbonate (balance room) into a large vial, and weigh it accurately. Transfer approximately 1 gram of the solid to a dry 300-cc. Erlenmeyer flask. Weigh the vial again to find the exact weight of the sodium carbonate. Add 100 cc. of distilled water to the flask, and 2 drops of methyl orange. When the carbonate has dissolved completely, run in the HCl from the burette, about 2 cc. at a time, with shaking after each addition, until the pink color disappears more slowly on shaking; and then proceed more cautiously until a single drop of the acid turns the color from yellow to red. If the "end point" is overstepped, add NaOH to bring the yellow color back, and again add HCl, a drop at a time, until the exact end point is reached. Immediately perform a duplicate standardization with a second sample of pure Na_2CO_3. On the left-hand page of the note book should be recorded the weight of the Na_2CO_3, and the initial and final reading of both the HCl and NaOH burettes.

From the total HCl subtract the volume equivalent to the NaOH that may have been used in titrating back. Find the number of equivalent weights of Na_2CO_3 equal to 1,000 cc. of the HCl. Take the average of the duplicate determinations as the normality of the HCl. Calculate also the exact normality of the NaOH.

Preserve these standardized solutions for the later determination of the yield of NaOH in the electrolysis of brine (page 185) and in the preparation of NaOH (page 183).

Specific Gravity. The specific gravity of a liquid is the ratio of its weight to the weight of an equal volume of pure water at the temperature of its maximum density (4°C.). This applies alike to pure liquids such as acetic acid and to solutions.

Substances dissolved in water change the specific gravity, and since specific gravity is one of the properties of a liquid most easily measured with great precision, it is much used by chemists for determining the concentration of solutions which are known to contain only a single dissolved substance.

Tabulations have been prepared for many common substances such as hydrochloric acid, sodium hydroxide, ammonia, and alcohol, in which the specific gravity and the corresponding percentage by weight of the solution have been placed in parallel columns covering the whole range from pure water to saturated solution. For example, if we wish to find the concentration of a given solution of NaOH, we measure its specific gravity which proves to be 1.390. Opposite this specific gravity in the table we find (interpolating if necessary) the percentage composition by weight, and we derive the concentration as follows:

SOLUTION OF NaOH

Specific gravity 1.390 Percentage by weight 36.00

Weight of 1 liter $= 1{,}000 \times 1.390 = 1{,}390$ grams

Grams NaOH per liter $= 1{,}390 \times 0.3600 = 500.4$

F.W. of NaOH per liter $= 500.4/40 = 12.5$

Normality of NaOH solution $= 12.5$

The Use of the Formula Weight Method in Chemical Arithmetic. A chemical equation tells not only what substances, but also how much of these substances, are involved in a chemical reaction. For example, the equation

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$

reads: 1 F.W., or 106 grams, of sodium carbonate reacts with 1 F.W., or 74 grams, of calcium hydroxide to give 1 F.W., or 100 grams, of calcium carbonate and 2 F.W., or 80 grams, of sodium hydroxide.

If now we want to find the weight of materials necessary to provide 400 grams of NaOH we translate this into F.W. From inspection of the equation we find the number of F.W. of each material and then translate into grams:

400 grams NaOH = 400/40 = 10 F.W.
Na_2CO_3 required = $\frac{1}{2} \times 10 = 5$ F.W. = $5 \times 106 = 530$ grams
$Ca(OH)_2$ required = $\frac{1}{2} \times 10 = 5$ F.W. = $5 \times 74 = 370$ grams

PROBLEMS

1. How many times normal is each of the following solutions?

(*a*) molal H_2SO_4.
(*b*) formal $Al_2(SO_4)_3$.
(*c*) molal $AlCl_3$.
(*d*) 0.1 molal Na_3PO_4.
(*e*) 3 molal H_2SO_4.
(*f*) 6 molal HNO_3.
(*g*) 2.5 formal $MgSO_4$.

2. How many times formal are the following solutions?

(*a*) 6*N* HCl.
(*b*) normal Na_3PO_4.
(*c*) 0.5*N* K_2SO_4.
(*d*) 0.1*N* $K_4(FeC_6N_6)$.
(*e*) 0.4*N* $Ba(OH)_2$.
(*f*) normal $CuSO_4$.

3. (*a*) What is the normality of a solution of HCl containing 39 per cent by weight of HCl and of specific gravity 1.19?

(*b*) of a solution of HCl containing 20 per cent by weight and of specific gravity 1.12?

(*c*) of a solution of HNO_3 containing 68.6 per cent by weight and of specific gravity 1.41?

(*d*) of sulphuric acid containing 96 per cent H_2SO_4 and of specific gravity 1.84?

4. What is the percentage by weight of the following solutions?

(*a*) 6*N* HNO_3, specific gravity 1.195.
(*b*) 6*N* HCl specific gravity 1.100.
(*c*) 6*N* H_2SO_4, specific gravity 1.181.
(*d*) 0.5*N* $H(C_2H_3O_2)$, specific gravity 1.00.

5. How many cubic centimeters of the concentrated sulphuric acid of 3 (*d*) should be taken to make 1 liter of normal solution?

6. How many liters of HCl (gas, figured at standard conditions) are required to make 1 liter of 12 *N* acid?

7. (*a*) How many cubic centimeters of 6 *N* HCl are needed to dissolve 1 gram of zinc? $Zn + 2HCl \rightarrow ZnCl_2 + H_2$.

(*b*) How many cubic centimeters of hydrogen are evolved?

8. (*a*) What weight of calcium carbonate will react with 1 liter of 6 *N* HCl? $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$.

(*b*) What volume of carbon dioxide will be evolved?

9. It is desired to find the concentration of a solution of calcium hydroxide. Five hundred cubic centimeters of this solution are carefully measured into a beaker, litmus is added, and a 0.5 *N* solution of HCl is run in until the color just changes from blue to red. The volume of the HCl solution thus used is 40 cc.

(*a*) What is the normal concentration of the calcium hydroxide solution?

(*b*) the molal concentration?

(*c*) the percentage by weight (specific gravity = 1.00)?

General Questions II

1. Define solution.

2. Water is essential to the maintenance of plant and animal life. Discuss the properties of water that make it so.

3. Discuss the nature of the compounds of salts and water.

4. Describe two different classes of compounds formed from oxides and water.

5. What is the meaning of the term hydrate? Why is the compound of an oxide and water not regarded as a hydrate?

6. Explain the use of the term hydroxide in naming the compound of a metal oxide and water.

7. Contrast the action of a metal with that of a metal oxide on water in the formation of a hydroxide.

8. Contrast the formation of chlorine hydrate with the action of chlorine and water in sunlight.

CHAPTER III

THE THEORY OF IONIZATION

A substance dissolved in a liquid is in a state that resembles the gaseous state in many respects. It is thoroughly dispersed, and just as a gas expands into any available space, so a dissolved substance or *solute* expands or diffuses until its concentration is uniform throughout the solution. It is its tendency to expand which makes a gas exert pressure. The similar tendency of a solute to expand throughout the liquid causes *osmotic pressure,* which is very similar to gas pressure and has approximately the same magnitude as the pressure of an equal number of moles of a gas in the same volume at the same temperature. The molecular weights of gaseous substances can be determined when the weight, volume, temperature, and pressure are known. Similarly the molecular weight of a solute can be determined when its weight, volume of the solution, temperature, and osmotic pressure are known. Although osmotic pressure is difficult to measure there are other properties of solutions, related to osmotic pressure, which are readily measured and serve to determine the molecular weight of the solute.

Soluble substances fall into two classes: those that give solutions which do not conduct electricity, called non-electrolytes; and those that give solutions that do conduct electricity, called electrolytes. In solution non-electrolytes behave normally, or in other words, molecular weight methods show the same number of moles that one would expect to find in the gaseous state of that substance if it were volatile. Electrolytes, on the other hand, show a greater number of moles than one would normally expect to find.

These facts are accounted for in the theory of ionization, according to which electrolytes in solution are dissociated into ions. These ions are the positively and negatively charged parts into which the electrolytes dissociate. The individual ion has the same effect as a complete unionized molecule in causing osmotic pressure and related effects. Under electrical attraction the ions can move through the solution towards the respective electrodes and thus they can conduct a current.

A careful study of the laboratory experiments and a working out of the problems in the following sections should give one an understanding of the theory of ionization, a theory which is of the greatest service in interpreting the chemistry of solutions. Although the experiments are printed consecutively in one section and the problems in the next, the two sections should be studied together.

Experiments

1. Osmotic Pressure. The formation of osmotic membranes, as well as the existence of osmotic pressure, may be qualitatively shown by what may be called the *mineral garden*, prepared as follows: small lumps or crystals of certain very soluble salts, such as ferric chloride, copper chloride, nickel nitrate, cobalt chloride, and manganese sulphate, are dropped into 50 cc. of a solution of sodium silicate, or water glass (sp. gr. 1.1), in a small beaker. The success of the experiment depends on using *small, distinct fragments* of the salts. Their behavior resembles that of growing seeds, as they appear to sprout immediately and to send up shoots toward the surface of the liquid, which grow with a visible rapidity.

Record this experiment in the note book, giving a description and an explanation in your own words. Wash the beaker immediately after the experiment, as the sodium silicate solution will etch the glass.

ELECTRICAL CONDUCTIVITY OF SUBSTANCES IN SOLUTION

Use the conductivity apparatus found on the ends of the desks, a diagram of which is given in Fig. 17.

Electrodes *A* consist of copper rods set so that they will pass into the two arms of a U-tube when it is raised from underneath. A lamp of high wattage should be used with these electrodes, which are designed to show differences in conductivity among good conductors.

Electrodes *B* consist of fine platinum wires supported upon glass rods, and are to be used with a lamp of about 15 watts. They are to be used in testing the conductivity of solutions of weak electrolytes in a 3-inch vial. This vial may be raised until the electrodes are immersed in the liquid. Before testing the conductivity of any given solution rinse the platinum electrodes with distilled water until, when they are immersed for 10 seconds or more, no sign of a *glow* is seen in the lamp filament. To illustrate the necessity for this precaution, first immerse the electrodes in hydrochloric acid solution, then, without rinsing, immerse them in a vial of pure water; the lamp will glow very distinctly.

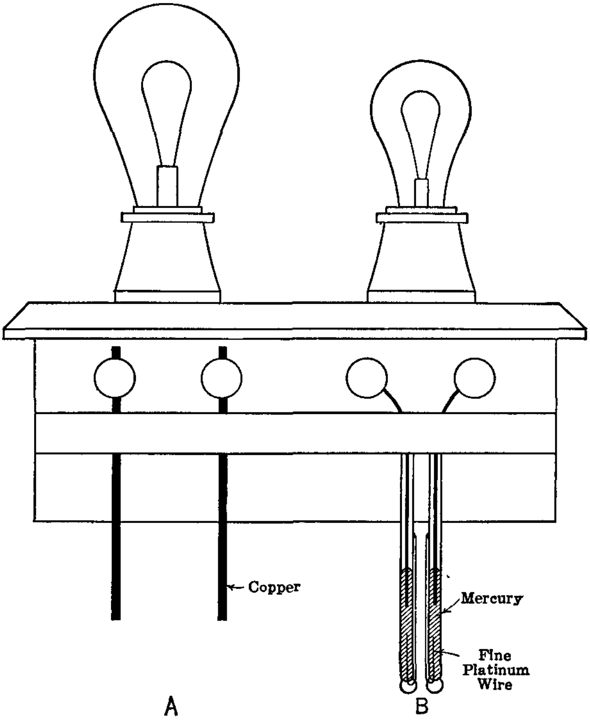

Fig. 17

2. Electrical Conductivity. (*a*) **Pure Substances.** Note that the lamp does not glow when air fills the space between the electrodes. Then raise successively between electrodes *B* distilled water, alcohol, pure acetic acid (labeled "glacial acetic acid"), and place in contact with electrodes *A* lumps of any two dry salts found in the laboratory, for example, common salt, NaCl, and blue vitriol, $CuSO_4 \cdot 5H_2O$.

What general statement can be made about the conductivity of pure non-metallic substances, gaseous, liquid, or solid?

(*b*) **Solutions of Electrolytes.** Test for conductivity each of the following solutions: Crush about 0.3 gram of each of the solid salts tested in (*a*) to a powder and dissolve each in 10 cc. of water. Add 10 drops of glacial acetic acid to 10 cc. of water. Dilute 2 cc. of each of the laboratory acids (which are already in solution in water) with 10 cc. of water. Dissolve about 0.3 gram each of sodium hydroxide and potassium hydroxide in 10 cc. of water. Dilute 2 cc. of ammonium hydroxide solution with 10 cc. of water.

List the above solutions in the order of their conductivity. What classes of substances conduct when in solution? What explanation can you give of electrolytic conductance, and how can you account for the fact that some solutions conduct much better than others?

(*c*) **Solutions of Non-Electrolytes.** Dissolve 0.5 gram of cane sugar, 0.5 gram of urea, 0.5 cc. of alcohol, 0.5 cc. of glycerine each in 10 cc. of water, and test the conductivity of the solutions.

ACIDS

3. Test the conductivity of pure tartaric acid (a solid) and of pure acetic acid (glacial acetic acid).

Then test the conductivity of these same acids dissolved in 10 to 20 parts of water, and also of other common laboratory acids diluted with water.

Look up the percentage of ionization in $0.1\,N$ solution (table on page 100) of each of the acids. What component is common to all acids and is responsible for the characteristic properties of acids? Name the other components (*i.e.*, species of ions or molecules) in any acid solution.

4. Strong and Weak Acids. In order to compare the strength of acids it is necessary to have solutions of the same concentration. Prepare 50 cc. each of $0.1\,N$ hydrochloric and acetic acids by diluting 5 cc. of $1\,N$ acid with 45 cc. water. Carefully compare the conductivity of these $0.1\,N$ acids, using electrodes *B*. Carefully compare the intensity of the sour or acid taste,* but do not swallow any of the acid. Rinse out the mouth with water. Quite a bit of experimenting is necessary to find just the amount of acid

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* Since a chemist should be familiar with the taste of hydrogen and hydroxyl ions, we have set the very bad precedent here of giving directions to taste the dilute solutions of acids and bases. In no other case should any laboratory chemical be taken in the mouth.

to take and how long to hold it on the tongue in order to get a fair estimate of the comparative acidity. It must be borne in mind that the strong acid may partly paralyze the nerves of the tongue for a short time; therefore, after tasting one acid, wait a short time before tasting another. Compare the effect of the two $0.1\,N$ acids on blue litmus.

The conductivity of the two acids ought to be proportional to the degree of ionization; likewise the sour taste, which is the property of the hydrogen ion, ought to be proportional to the degree of ionization; even the weaker acid contains enough hydrogen ions completely to turn the color of the very sensitive litmus, so no difference is shown by this indicator.

Make a tabulation for each acid of the number of grams of the four components present in 1 liter of $0.1\,N$ solution: (1) water, (2) un-ionized acid, (3) hydrogen ion, (4) acid radical ion. (Consult table of ionization values on page 100.) Arrange the tabulation for each acid somewhat on the following plan.

COMPONENTS IN 1 LITER OF $0.1\,N$ ACETIC ACID

Total acetic acid	0.1×60	= 6.0	grams
Water	$1000 - 6$	= 994	“
Ionized acetic acid	....	=	“
Un-ionized acid	....	=	“
H^+ ion	....	=	“
$C_2H_3O_2^-$ ion	....	=	“

BASES

5. Test the electrical conductivity of a dry lump of sodium or potassium hydroxide (do not handle it with the fingers) before its surface has become wet by taking moisture from the atmosphere. Then test the conductivity of dilute solutions of sodium, potassium, and ammonium hydroxides. Rub a single drop of $1\,N$ NaOH lightly between the thumb and forefinger and note the slippery feeling. Immediately rinse the alkali from the fingers since it would very soon take off the skin. Repeat the experiment with a drop of $1\,N$ NH_4OH.

Look up the percentage of ionization in $0.1\,N$ solution of each of the bases. What component is common to all bases and is responsible for the characteristic properties of bases? Name the other components in any base solution.

6. Strong and Weak Bases. Repeat in every detail Experiment 4, using sodium hydroxide and ammonium hydroxide as typical of a strong and a weak base. Make similar tabulations of the weight of each of the components, (1) water, (2) un-ionized base, (3) metal radical ion, and (4) hydroxyl ion, in 1 liter of 0.1 *N* solution.

NEUTRALIZATION

7. Neutralization of a Strong Acid and a Strong Base. Fill a narrow U-tube with 1 *N* hydrochloric acid and insert electrodes *A* until the lamp glows dimly but distinctly. Note carefully the depth to which the electrodes are inserted. Then refill the tube with 1 *N* sodium hydroxide, again insert the electrodes to the same depth, and notice how strongly the lamp glows.

Run 10 cc. of 1 *N* hydrochloric acid into a beaker, add 1 drop of litmus solution, and then add 1 *N* sodium hydroxide until the color changes to blue. Add a drop or two more acid until the color again changes, and finally bring the solution to the exact neutral point when 1 drop of acid will turn the litmus red and a single drop of base will bring back the blue.

Fill the same U-tube with this neutralized solution, insert the electrodes to the same depth as before, and compare the conductivity of the neutral solution with that of the acid and the base.

Explain the process of neutralization according to the ionic theory, and account for any differences noted in the conductivity. Write the ionic equation.

Write ionic equations from now on whenever it is possible. Use the intersecting method as described in Rules 1–8 on page 104. Do not, however, neglect to give the explanation in words in addition to the equation.

8. Neutralization of a Weak Acid and a Weak Base. Test separately the conductivity of 1 *N* acetic acid and of 1 *N* ammonium hydroxide, this time using electrodes *B*. Neutralize 10 cc. of the 1 *N* acid by adding the 1 *N* base in the same manner as in Experiment 7; and compare the conductivity of the neutralized solution with that of the acid and base separately.

Explain the neutralization of a weak acid and a weak base according to the ionic theory, and account for the change observed in the conductivity. Explain why the neutral solution contains no undissociated molecules of the acid and base.

9. High Ionization of All Salt Solutions. The object of Experiments 7 and 8 was to show the relative number of ions in equivalent acid and base solutions and in the neutral solution resulting from adding the two together. In Experiment 7 the same electrodes held the same distance apart with the same volume of liquid between them were used on all three solutions tested. Hence the brightness of the lamp was proportional to the number of ions in the solution. But in Experiment 8 a different kind of electrode was used, and, although a valid comparison of the concentration of ions in the three solutions of that experiment was obtained, the brightness of the lamp shown for the neutral solutions of the two experiments gives no comparison of the number of ions. Remember that the neutral solution in each experiment is 0.5 *N* with respect to the salt.

Prepare again a neutral solution of sodium chloride by neutralizing normal sodium hydroxide with normal hydrochloric acid, and a neutral solution of ammonium acetate by neutralizing normal ammonium hydroxide with normal acetic acid. Test the conductivity of both solutions with electrodes *A* and again test both with electrodes *B*.

What general statement can be made about the ionization of salts? Explain again (although the write-up of Experiment 8 should already contain the explanation) why the salt of a weak acid and a weak base can be as highly ionized as the salt of a strong acid and a strong base.

DISPLACEMENT OF WEAK ACIDS AND BASES

10. Displacement of a Weak Acid from its Neutral Salt by Means of a Stronger Acid. (*a*) To 2 cc. of 1 *N* sodium benzoate solution, $NaC_7H_5O_2$, add a few drops of 6 *N* H_2SO_4. At 30 drops to the cubic centimeter how many drops of the 6 *N* acid would be equivalent to the 2 cc. of 1 *N* salt? How does this experiment illustrate the displacement of a weak acid from its salt?

(*b*) Observe cautiously the odor of 6 *N* acetic acid. Dilute 1 cc. with 5 cc. of water to make the solution 1 *N* and see whether the odor is still detectable in the cold. Warm the solution and see if the odor is noticeable.

Warm 2 cc. of 1 *N* sodium acetate solution, $NaC_2H_3O_2$, barely to the boiling point. Remove it from the flame and observe whether it has an odor. Add a few drops of 6 N H_2SO_4 to the warm sodium acetate solution and observe whether there is an odor of acetic acid. Suppose that exactly equal volumes of 0.2 N $NaC_2H_3O_2 + 0.2\,N$ HCl had been used; what percentage of the way to completion would the reaction have gone? Compare the completeness of this reaction with that of neutralization.

(*c*) To 5 cc. of sodium carbonate solution add acetic acid, a few drops at a time, till action ceases. What is the gas formed? What acid is displaced in this case? How is the completeness of its displacement affected by the escape of the gas?

(*d*) Treat a small quantity of calcium carbonate with an excess of dilute hydrochloric acid, and see whether it will all dissolve. Calcium carbonate is usually considered as an insoluble substance, nevertheless it is slightly soluble in pure water. Look up its exact solubility (solubility table on page 364). How would the acid react with the small amount of calcium carbonate in solution? How would the equilibrium between the solid calcium carbonate and its saturated solution be affected by this reaction? To sum up, explain how the calcium carbonate dissolves in acids.

11. Displacement of a Weak Base from Its Neutral Salt by Means of a Stronger Base. (*a*) Note whether a solution of ammonium chloride has the odor of ammonia. Warm 2 cc. of this solution to about 50°, note again whether there is an odor; add a little sodium hydroxide solution and again note if there is an odor.

At 50°, ammonia, NH_3, from the non-electrolytic dissociation of NH_4OH (see page 111), escapes as a gas from the solution to a sufficient extent to give a powerful odor. Thus the odor of ammonia indicates the presence of NH_4OH in solution. On the other hand, the amount of gas which escapes during this experiment is too small to cause a significant change of concentration of the components of the solution. If equal volumes of cold 0.2 N NH_4Cl and 0.2 N NaOH are mixed, to what degree of completion does the formation of un-ionized NH_4OH proceed?

(*b*) To 1 cc. of a magnesium sulphate solution add 5 cc. of water and then a few drops of sodium hydroxide solution. Look up the solubility and the degree of ionization of magnesium hydroxide (page 101). Calculate the hydroxyl-ion concentration in a saturated solution of $Mg(OH)_2$.

(*c*) To 1 cc. of magnesium sulphate solution add 5 cc. of water and then a few drops of ammonium hydroxide solution. Then add some ammonium chloride solution. Explain the effect on the hydroxyl-ion concentration of adding an ammonium salt to an ammonium hydroxide solution.

(*d*) To 1 cc. of a ferric chloride solution add 5 cc. of water and then a few drops of ammonium hydroxide solution. Then add some ammonium chloride solution.

CHARACTERISTIC REACTIONS OF CERTAIN IONS

If two ionized substances are brought together in a solution, and one of the possible new combinations of a positive and a negative ion is an insoluble solid substance, that substance will form as a precipitate. Characteristic precipitates serve as a means of identifying specific ions.

Some ions possess characteristic colors which they impart to a clear solution. Thus the cupric ion, Cu^{++}, is blue and all dilute solutions of cupric salts are clear blue unless the color is modified by another colored component. Thus the appearance of a color or a change of color in a clear solution when a reagent is added helps to identify the ions present.

In the following experiments an inexperienced student always is impelled to make the mistake of using too concentrated solutions and adding too much reagent. This not only wastes expensive chemicals, but it also obscures the effects to be observed. The procedure that should be followed is to take about 1 cc. of the solution to be tested, dilute this with 5 cc. of water, and add the reagent a single drop at a time, shaking thoroughly after each drop. In this way keep adding reagent until no further change is brought about. It often happens that a limited amount of reagent will produce an effect, say a precipitate, and a larger amount will produce another effect, say redissolve the precipitate. If the reagent is "dumped in" carelessly these effects may be missed.

12. Chloride Ions. To solutions of various chlorides, such as hydrochloric acid, sodium chloride, and calcium chloride, add a few drops of a solution of a silver salt — silver nitrate or silver sulphate. To the resulting suspension add $6N$ HNO_3. Does the precipitate dissolve?

To a solution of potassium chlorate (free from chloride) add a few drops of silver nitrate.

How may the presence of chloride ions be recognized? Why is not the same test given by the chlorine in potassium chlorate?

13. Sulphate Ions. To solutions of soluble sulphates, such as sodium sulphate, copper sulphate, sulphuric acid, add barium chloride solution. After the effect of this reagent is noted add hydrochloric acid to see whether the precipitate is redissolved by acid.

14. Copper Ions. (*a*) To 5 cc. of copper sulphate solution, add NH_4OH in small amount and then in excess.

In writing ionic equations consider the light blue precipitate as $Cu(OH)_2$, for the sake of simplicity, instead of the rather indefinite basic salt. To explain the deep blue color consult page 118.

(*b*) To another sample of cupric salt solution add ammonium sulphide. Divide the black suspension in two parts; add HCl to one part, and NH_4OH to the other, to see whether the precipitate is soluble in either of these reagents.

15. Zinc Ions. Repeat every step of the preceding experiment using a zinc salt instead of a copper salt.

Using the information gained in these two experiments, devise a method by which you could detect the presence of a small amount of zinc salt in a solution containing copper salt.

16. Ferrous Ions. Repeat (*a*) and (*b*) of Experiment 14 upon a ferrous salt instead of a cupric salt.

(*c*) To a solution of ferrous sulphate add a freshly prepared solution of potassium ferricyanide, $K_3(Fe(CN)_6)$.

17. Ferric Ions. (*a*) To a solution of ferric chloride add NH_4OH.

(*b*) To other samples of the ferric salt solution add potassium ferrocyanide $K_4(Fe(CN)_6)$, and potassium thiocyanate, KCNS, respectively.

18. Silver Ions. (*a*) Recalling Experiment 12, state how chloride ions may be used as a reagent for silver ions.

(*b*) To 2 cc. of $0.1\,N$ $AgNO_3$ add NH_4OH very cautiously as follows so as to avoid an excess at the beginning. Dilute 1 cc. of the $6\,N$ NH_4OH with 10 cc. of water, and transfer 1 drop of the dilute solution, hanging to the end of a stirring rod, to the $AgNO_3$ solution. Continuing to add the reagent in these very small portions, observe whether a precipitate is formed at any time, and whether it redissolves with an excess of the reagent.

(*c*) To 2 cc. of $0.1\,N$ $AgNO_3$ add 0.5 cc. of $1\,N$ NaCl, which gives an excess of chloride ions.

Add $6\,N$ NH_4OH cautiously so as to avoid a large excess until the precipitate has redissolved. The object of the rest of this experiment is to show that a very appreciable excess of NH_4OH is necessary to keep AgCl from reprecipitating. Add 6 *N* HNO_3 1 drop at a time by means of a stirring rod until a precipitate which fails to redissolve with shaking just appears. With the thumb over the mouth of the test tube, shake so that any drops of reagent clinging to the sides of the tube are completely mixed into the suspension. Remove the thumb and note whether the odor of ammonia can be detected.

Ionic Displacements

19. Electromotive Series of the Metals. (*a*) Place a few pieces of zinc in 5 cc. of 0.2 *N* solution of copper sulphate, shake the mixture frequently, and after about 15 minutes withdraw 1 cc. of the solution and test it for copper and for zinc ions, applying the information obtained from the preceding experiments. If any copper ions are still present let the remainder of the mixture stand for 15 minutes more with frequent shaking, and repeat the test. Continue until you have reached a conclusion as to whether copper ions can be completely displaced from solution by zinc.

(*b*) Repeat (*a*) using 5 cc. of about 0.5 *N* $CuSO_4$ solution and some clean pieces of iron wire.

(*c*) Again repeat (*a*) using 5 cc. of 0.1 *N* $AgNO_3$ solution and some clean pieces of copper wire.

(*d*) Recall (or find out by experiment, if preferred) the behavior of silver, copper, iron, and zinc with hydrochloric acid or dilute sulphuric acid. Make a list of these metals, including hydrogen, in the order of their ionizing potential.

Hydrolysis

20. Dissolve about 0.5 gram each of ferric chloride, sodium chloride, and sodium carbonate in a little water, and test each solution with red and blue litmus.

Explain the relation of hydrolysis to the observed results.

Are the reactions of hydrolysis complete? If not, explain why.

21. Hydrolysis a Reversible Reaction. (*a*) To a solution made by dissolving 0.5 gram of solid ferric chloride in 10 cc. of water add powdered calcium carbonate. How is the extent of the hydrolysis of ferric chloride affected by the calcium carbonate?

(*b*) To about 0.2 gram of powdered bismuth oxide, Bi_2O_3, in a dry test tube add 6 *N* HCl a drop at a time with shaking until the powder is dissolved. About 12 drops should be necessary. Instead of bismuth oxide one may start with basic bismuth nitrate ($Bi(OH)_2NO_3$ or $BiONO_3$). Then add 20 cc. of water to the tube and mix the contents, observing the white precipitate. Again add 6 *N* HCl drop by drop with shaking until the precipitate just redissolves. Then add the solution to 200 cc. of water in a beaker. The hydrolysis product of the chloride may be a mixture of $BiOHCl_2$, $Bi(OH)_2Cl$, $Bi(OH)_3$. For simplicity consider it all as $Bi(OH)_2Cl$. Write ionic equation for the hydrolysis, and explain its reversibility.

SOLUBILITY PRODUCT

22. Prepare a nearly saturated solution of potassium chlorate by shaking vigorously about 5 grams of the finely powdered salt with 15 cc. of water for 5 minutes. Let the undissolved salt settle and pour off the clear solution, dividing it equally among three test tubes.

(*a*) To one portion add about 0.5 gram of solid potassium chloride.

(*b*) To a second portion add about 0.5 gram of solid sodium chlorate.

(*c*) To a third portion add about 1.5 grams of solid sodium nitrate. In each tube agitate the mixture until the added crystals have dissolved. These crystals can be distinguished from any finely crystalline precipitate that falls out of the solution.

Tabulate the solubility in formula weights per liter at room temperature of $KClO_3$, KCl, $NaClO_3$, and $NaNO_3$.

What is the numerical value of the solubility product of $KClO_3$?

How many formula weights of $KClO_3$ could dissolve in a liter of 1.5 formal $NaClO_3$? How many grams?

HYDROGEN ION CONCENTRATION

23. Effect of Its Neutral Salt on the Strength of a Weak Acid. (*a*) Methyl orange is an indicator which is used much in the same way as litmus to show the presence of hydrogen ions. In the presence of a considerable hydrogen-ion concentration it is pink. As the hydrogen-ion concentration grows less the color passes through transition shades to a clear yellow, the latter color being reached before the neutral point is reached. The yellow color remains the same in neutral solution and in the presence of hydroxyl ions.

In five test tubes place respectively 10 cc. of 1 *N* HCl, 10 cc. of 1 *N* HAc, 10 cc. of 1 *N* HAc, 10 cc. of pure water, 10 cc. of 1 *N* NaOH, and to each add 2 drops of methyl orange solution. The first tube shows the pink color imparted by strong acids, and the fourth and fifth the yellow color. The second and third tubes should, of course, show exactly the same color tone. Now drop into the third tube about a gram and a half of crystallized sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, and dissolve the salt by shaking. Now compare the colors of the second and third tubes, still keeping the other tubes for reference colors.

(*b*) The acid strength may be compared by the rapidity of the reaction with calcium carbonate. In each of two small beakers place 1 gram of powdered calcium carbonate and 10 cc. of water, and stir until the powder is entirely wet. Have ready two solutions as follows: one consists of 30 cc. of 1 *N* acetic acid, the other of 30 cc. of 1 *N* acetic acid in which an equivalent amount, about 4 grams of sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, has been dissolved. At the same instant add the two solutions to the respective beakers containing calcium carbonate. The rapidity of effervescence should be compared, also the time it takes for the solid to dissolve entirely.

Notes and Problems

MEASUREMENT OF IONIZATION

Molal Lowering of the Freezing Point. The temperature at which pure water is in equilibrium with ice is the standard fixed point of thermometry and is designated as 0° on the centigrade scale. This point, which is called the freezing point, is reproducible to the greatest precision of thermometric measurements. This point is reproducible, however, only when the water is pure. Substances in solution in the water always lower the freezing point, and not only that, the extent of the lowering of the freezing point follows some very simple rules with a precision great enough to make those rules apparent: For non-electrolytes, that is, substances whose solutions do not conduct electricity, the first rule is that, with the same substance, the extent of the freezing point depression is proportional to the quantity of substance dissolved in a given weight of water. The second rule is that, for different substances, equimolal amounts produce the same freezing point lowering with the same amount of water. A statement combining these two rules is as follows: The lowering of the freezing point is proportional to the number of moles of dissolved substance in a given amount of water. The proportionality factor is given by the *molal lowering of the freezing point,* which is 1.86°C. and is the effect produced by one mole of dissolved substance in 1,000 grams of water. This rule holds only when the solid separating from the solution is pure ice, but this is almost invariably the case when the solution is fairly dilute.

It should be clear that the above statements show a method of determining the molecular weight of a substance dissolved in water provided that the substance is a non-electrolyte.

The same regularities hold for solutions in solvents other than water except that there is a different proportionality factor; *i.e.*, the molal lowering of the freezing point is different for each different solvent.

The following set of problems will allow the student to find whether he has grasped the significance of the statements in the foregoing paragraphs. For the present we will consider the behavior of electrolytes as irregular. In a later section we will try to discover any regularity that may appear in the " irregularities " and see if that too can be reduced to any significant rule.

1. At what temperature will a solution freeze that is made by dissolving 1 gram of sugar, $C_{12}H_{22}O_{11}$, in 10 grams of water?

2. — one mole of urea, $CO(NH_2)_2$, in 10 liters of water?

3. How many grams of methyl alcohol, CH_3OH, should be added to 1,000 grams of water to give a solution that will freeze at $-10°$?

4. What is the molecular weight of a substance, 3 grams of which dissolved in 50 grams of water gives a solution freezing at $-0.93°$? The solution does not conduct electricity.

5. Pure benzene freezes at 5.48°. What is the molecular lowering of the freezing point for benzene if a solution of 6.4 grams of naphthalene, $C_{10}H_8$, in 100 grams of benzene freezes at 3.03°?

6. When 4.88 grams of a certain other substance are dissolved in 50 grams of benzene the solution freezes at 2.85°. What is the molecular weight of the substance?

Osmotic Pressure. From a consideration of the nature of osmotic pressure (page 83) one would wonder how it could ever be measured. The pressure of a pure gas against a mercury surface or a piston is readily determined. The total pressure of a gas mixture is also just as readily determined, but the partial pressures of the individual gases in the mixture cannot be separately measured. Although osmotic pressure resembles the partial pressure of one gas in a mixture, the problem is much more complicated than with gases because of the enormous cohesion of liquids. If water, for example, did not possess cohesion the expansive force of liquid water at room temperature would be about 1,000 atmospheres. Thus the cohesive force of water, or of a solution, is more than 1,000 atmospheres, and this force would apply to the molecules of solute as well as of solvent to prevent them from escaping from the bounding surface. Osmotic pressure does not exert its force against a bounding surface such as a beaker or the air. Within the solution the cohesive force acting upon the molecules of solute is the same in every direction, and hence the net effect is zero. Thus the solute resembles a gas, the cohesion between its own molecules is negligible, and it expands until it has filled the whole solution at a uniform concentration.

If a solution of sugar is placed in the bottom of a tall cylindrical jar and pure water is carefully run in on top of it, so as to avoid mixing the layers, and the whole is left undisturbed, the sugar by virtue of its osmotic pressure diffuses upward until it has filled the whole solution. The diffusion is of course slow because of the friction between the sugar molecules and the water. If now we could imagine a movable membrane impermeable to sugar, the pores of which were filled with water, and if this membrane were placed above the layer of sugar solution, and the cylinder above the membrane were filled with pure water, then if the sugar diffused upward it would have to push the membrane before it and water would pass through the membrane as the latter moved upward. Such a membrane is called a *semipermeable membrane.* The pressure which would have to be applied to the membrane to prevent its being pushed upward would be equal to the osmotic pressure of the sugar.

Such membranes do actually exist. Many animal membranes and the cell walls of plants serve as more or less perfect semi-permeable membranes. Many films of inorganic substance also can be prepared which are permeable to water but not to dissolved substances.

Experiment 1 in the first part of this chapter illustrates qualitatively the effect of osmotic pressure. The very soluble salts dropped into the sodium silicate solution at once begin to dissolve, forming a layer of solution about the lumps. At the junction between this layer and the sodium silicate solution a coherent film of insoluble silicate of the metal is formed:

$$\begin{array}{cc} 2Fe^{+++} & 6Cl^{-} \\ 3SiO_3^{--} & 6Na^{+} \\ \downarrow & \\ Fe_2(SiO_3)_3\downarrow & \end{array}$$

This film is impermeable to salt molecules and ions and permeable to water. The concentration of the nearly saturated salt within is higher than that of the sodium silicate outside, and hence the osmotic pressure from within is greater than that from without and the film is forced to expand, allowing water to enter and dissolve more of the salt. The actual result is the same as if the water were sucked in through the film. This creates an hydrostatic pressure which is, of course, uniform inside the sac and consequently the film is expanded at the point where it is thinnest which is at the top. Thus the osmotic pressure accounts for the effect which we observed — the little colored sprouts shooting up from the lumps of the salt towards the top of the solution.

7. Find the osmotic pressure of 1 gram of sugar dissolved in 10 grams of water at 0°.

8. — of 1 gram of urea, $CO(NH_2)_2$, in 10 grams of water at 0°.

9. How many grams of sugar should be dissolved in 1000 grams of water to give an osmotic pressure of 1 atmosphere at 0°?

10. — to give the same pressure at 38°?

11. What is the molecular weight of a substance, 5 grams of which at 0° in 250 cc. of water has an osmotic pressure of 2.24 atmospheres?

Ionization. The electrical conductance of electrolytes is explained in terms of the ionic theory by the presence of independent charged radicals — the ions — which move through the solution and carry the current to the electrodes. The question arises as to how these charged particles affect the freezing point. Ions of opposite charge exert an enormous attraction for each other, and this attraction would be expected to impede their freedom of motion. On the other hand, each ion in the interior of the solution is surrounded by ions of opposite charge, and the resultant force of strong ionic attraction from all directions is zero. Hence at the other extreme we might expect the motion of each ion to be as unrestricted as the motion of an uncharged molecule.

The actual measurement of the freezing-point lowering caused by electrolytes has led us to choose the second postulate, that is, of the freedom of motion of the charged ions, as the nearer approximation to the true condition within the solution.

If we proceed, then, in the assumption that charged ions have the same effect on the freezing point as uncharged molecules, we can again regard the freezing-point lowering as proportional to the total number of moles in a given solution, only we must revise our definition of mole so as to include moles of ions as well as moles of non-electrolytes. For example, if 1 formula weight of AB is 50 per cent ionized into A^+ B^- we have 0.5 mole of AB, 0.5 mole of A^+ and 0.5 mole of B^-, or in all 1.5 moles, and the effect of AB on the freezing point would be 1.5 times what we would expect if AB were a non-electrolyte.

The following set of problems will test our grasp of the principle discussed in this section.

12. Assuming complete ionization of the electrolyte, what would be the freezing point of 10 grams of NaCl in 500 grams of water?

13. — of 10 grams of $CaCl_2$ in 500 grams of water?

14. — of 10 grams of $FeCl_3$ in 500 grams of water?

15. — of 10 grams of $K_4Fe(CN)_6$ in 500 grams of water?

$$K_4Fe(CN)_6 \rightarrow 4K^+ + Fe(CN)_6^{----}$$

16–19. What is the osmotic pressure at 0° of the salt in Questions 12–15, inclusive?

20. What is the osmotic pressure of 0.1 mole of NaCl in 1,000 grams of water if the salt is 86 per cent ionized?

21. — of 0.1 mole of $BaCl_2$ in 1,000 grams of water if the salt is 72 per cent ionized?

The degree of ionization of a salt may be calculated from the freezing point of its solution. For example, if 0.1 mole of K_2SO_4 (17.4 grams) dissolved in 1,000 grams of water freezes at $-0.454°$, we know that 0.1 mole of un-ionized substance will lower the freezing point $0.1 \times 1.86 = 0.186°$, and that 0.1 mole of a completely ionized substance giving 3 ions will lower the freezing point $3 \times 0.186 = 0.558°$. The actual freezing-point lowering, 0.454°, lies between these values and thus indicates incomplete ionization. The proportion of the salt ionized is found by dividing the difference caused by the actual ionization, $0.454 - 0.186 = 0.268°$, by that which would be caused by 100 per cent ionization, $0.558 - 0.186 = 0.372°$, thus giving $0.268/0.372 = 0.72$. Thus the salt is 72 per cent ionized.

22. If 9.45 grams of chloracetic acid, $H(C_2H_2O_2Cl)$, dissolved in 1,000 grams of water show an osmotic pressure of 2.51 atmospheres, find the per cent ionization of the acid, assuming that only one hydrogen is ionizable and that the negative ion has the composition of the radical shown in the parenthesis.

23. A solution of 101 grams of potassium nitrate in 1,000 grams of water freezes at -3.05. Calculate what percentage of the salt is ionized.

EXTENT OF IONIZATION

In the last section the method was illustrated by which per cent ionization could be calculated from freezing point on the assumption that ions and un-ionized molecules are of equal effect. In the following tables are given the values calculated for the ionization of various electrolytes in 0.1 equivalent solution on the basis of this assumption. These values we shall designate as the apparent ionizations. They come out approximately the same whether they are calculated from electrical-conductivity measurements or from freezing points.

Since the solvent is undeniably the agent that facilitates ionization, it is obvious that the more solvent, or in other words the more dilute the solution, the greater the percentage of ionization. In very dilute solutions (1 mole of solute in 10,000 liters of solvent) strong electrolytes are practically completely ionized. In solutions more than 0.1 equivalent the apparent ionization is less than

SALTS

Neutral salts, with very few exceptions, are highly ionized If they are classified, as in the table below, according to the valence of their ions, it is found that all belonging to any one class have practically the same degree of ionization The six classes which are indicated may be typified by KNO_3, $Ba(NO_3)_2$, K_2SO_4, $FeCl_3$, Na_3PO_4, and $ZnSO_4$, respectively.

Type of salt	Percentage ionization in 0 1 equivalent solution
$M^{+}R^{-}$	86
$M^{++}R^{-}R^{-}$	72
$M^{+}M^{+}R^{--}$	72
$M^{+++}R^{-}R^{-}R^{-}$	65
$M^{+}M^{+}M^{+}R^{---}$	65
$M^{++}R^{--}$	45

ACIDS

Substance	Percentage ionization in 0 1 equivalent solution
HCl, HBr, HI, HNO_3 $HClO_3$, $HClO_4$, $HMnO_4$	90
$H_2SO_4 \rightleftarrows H^{+} + HSO_4^{-}$	90
$HSO_4^{-} \rightleftarrows H^{+} + SO_4^{--}$	30
$H_2C_2O_4 \rightleftarrows H^{+} + HC_2O_4^{-}$	50
$H_2SO_3 \rightleftarrows H^{+} + HSO_3^{-}$	20
$HSO_3^{-} \rightleftarrows H^{+} + SO_3^{--}$	1 0
$H_3PO_4 \rightleftarrows H^{+} + H_2PO_4^{-}$	27
$H_2PO_4^{-} \rightleftarrows H^{+} + HPO_4^{--}$	0 2
$HPO_4^{--} \rightleftarrows H^{+} + PO_4^{---}$	0 0002
$H_3AsO_4 \rightleftarrows H^{+} + H_2AsO_4^{-}$	20
HF	9 0
$H_2C_4H_4O_6 \rightleftarrows H^{+} + HC_4H_4O_6^{-}$	8 0
HNO_2	7 0
$HC_2H_3O_2 \rightleftarrows H^{+} + C_2H_3O_2^{-}$	1 4
$H_2CO_3 \rightleftarrows H^{+} + HCO_3^{-}$	0 12
$HCO_3^{-} \rightleftarrows H^{+} + CO_3^{--}$	0 002
$H_2S \rightleftarrows H^{+} + HS^{-}$	0 05
$HS^{-} \rightleftarrows H^{+} + S^{--}$	0 0002
$HCN \rightleftarrows H^{+} + CN^{-}$	0 01
$H_3BO_3 \rightleftarrows H^{+} + H_2BO_3^{-}$.	0 01

BASES

Substance	Percentage ionization in 0.1 equivalent solution
KOH, NaOH	86
$Ba(OH)_2 \rightleftarrows Ba^{++} + 2OH^-$	75
NH_4OH	1.4

$Ca(OH)_2$, $Mg(OH)_2$ are but slightly soluble, but so far as they do dissolve they are dissociated to about the same extent as $Ba(OH)_2$ in a solution of the same concentration.

The hydroxides of the heavy metals are very insoluble and, as a rule, very weakly basic.

AgOH is soluble to the extent of 1 part in 15,000 of water, in which solution about 33 per cent of its molecules are ionized. It is thus a moderately strong base.

Hydroxides of the type $Zn(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$ are less basic than AgOH, and hydroxides of the type $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ are still much less basic.

Pure water contains 0.000,000,1 mole of H^+ ions and 0.000,000,1 mole of OH^- ions per liter.

that given in the table, for example hydrochloric acid in $12N$ solution is only 13 per cent ionized.

The data above have been calculated from measurements of electrical conductivity and freezing-point lowering. Although both methods give concordant results for the degree of ionization, it has for a long time been felt that these results are subject to considerable uncertainty. The proximity of other ions retards or dampens the effect of ions in causing electrical conductivity or lowering of freezing point in such a way that the calculated percentage of ionization is almost certainly too low for strong electrolytes. For weak electrolytes the data in the above table are reliable. The practice generally followed in the succeeding pages of ignoring any un-ionized fraction of salts, strong acids, and strong bases has a good deal of justification beyond that of mere convenience.

IONIC REACTIONS

It is very probably true that all chemical reactions are due to a rearrangement of the electrical forces residing in the atoms and molecules concerned. Reactions taking place in water solution among substances that are ionized are clearly electrical in nature. On the other hand, a very large number of organic substances (that is, compounds of carbon) are not perceptibly ionized even in water solution. At ordinary temperature such substances do not enter into rapid chemical reaction as electrolytes do.

Non-Ionic Reactions. This term is applied to all slow reactions in which none of the substances involved show any measurable degree of ionization; there seems to be no great advantage in trying to deal with them from the electrical viewpoint.

Ionic Reactions. All reactions among ionized substances clearly involve electrical forces, and it is the purpose of this outline to deal with various types of ionic reactions.

Ionization as a Reversible Reaction. The ionization of a substance is itself a chemical reaction. Pure *anhydrous* acetic acid does not possess the properties of an acid: it does not react with zinc or calcium carbonate, nor does it turn blue litmus red. Yet if a little acetic acid is dissolved in water it acquires the properties of an acid: it dissolves zinc with evolution of hydrogen, it dissolves calcium carbonate with evolution of carbon dioxide, and it turns blue litmus red. These new properties betoken the presence of new substances, the ions, and that the reaction $HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-$ has taken place. From the preceding table it will be seen that if 0.1 mole, or 6 grams, of acetic acid is dissolved in 1 liter of water 1.4 per cent of the acetic acid molecules are ionized.

To show that this reaction may take place in the opposite direction let us take 1 liter of a 0.2 molal sodium acetate solution. This solution has no odor of acetic acid. Sodium acetate is a *strong* electrolyte, and we may regard it as 100 per cent ionized in this fairly dilute solution. Let us now mix with this solution 1 liter of 0.2 molal hydrochloric acid, another strong electrolyte which we may regard as 100 per cent ionized. We will now have brought together into 2 liters the ions of 0.2 mole of sodium chloride, which remains ionized, and 0.2 mole of acetic acid. The latter, however, does not remain fully ionized but immediately comes to the *equilibrium* point at which 1.4 per cent only of the total acetic acid is ionized (the solution is 0.1 molal in acetic acid). That acetic acid has actually been formed, $H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2$, can be perceived by the odor of acetic acid which is now apparent.

Equilibrium. When 0.1 mole of $HC_2H_3O_2$ is dissolved in 1 liter of water and the two opposing reactions have adjusted themselves so that 1.4 per cent of the acid is in the ionized condition and 98.6 per cent is in the un-ionized condition, a state of equilibrium is said to exist. Such a point of equilibrium exists for every ionic reaction and, as in the example just cited, it is independent of the direction from which it is approached.

Ionization is a very rapid reaction, as is, indeed, the reverse reaction, or association; and the point of equilibrium is reached with great rapidity. In fact, in the time taken to dissolve an electrolyte in water, and uniformly mix the solution by stirring, complete equilibrium is attained.

For the sake of comparison a non-ionic reaction may be cited. If 2 volumes of hydrogen (uncombined hydrogen, not hydrogen ions) are mixed with 1 volume of oxygen in a glass jar at ordinary temperature, nothing appears to happen. Yet we know this mixture is not in equilibrium. By the careful use of certain catalyzers, the two gases will combine slowly but completely to form water, even if the temperature is kept from rising. As we well know, if a spark is applied to the mixture a violent reaction takes place. Equilibrium for this reaction exists only when it has gone practically to completion in the direction $2H_2 + O_2 \rightarrow 2H_2O$, and yet at ordinary temperature and without catalyzers the reaction is so slow that it will not have reached an equilibrium condition in many years.

Equations for Ionic Reactions. Reactions involving ionized substances cannot be adequately represented by single equations, because such equations cannot show all the species of ions and molecules that take part in the changes. In fact, each species of undissociated molecule concerned requires a separate equation to show its passage into, or out of, the ionized condition; but these equations may be written together so as to intersect and give a complete picture of the whole change.

In the next section eight rules to be observed in writing ionic equations are given, and by following these rules one is able to give, by means of the equations alone, both a fairly complete description, and a remarkably good explanation, of the reaction.

Until the student has thoroughly mastered the ionic theory, he should write equations in the fully ionized intersecting form for every reaction which he studies. Later, with the practice thus acquired, he will be able to interpret ordinary single equations in terms of the ionic theory.

Rules for Writing Equations in Ionic Form:

1. Solid substances are underlined: *e.g.*, $\underline{NaCl}$.
2. The un-ionized part of substances in solution is shown by the molecular formula without ionic charges: *e.g.*, $HC_2H_3O_2$.
3. Ionized substances in solution are shown by the formulas of the ions: *e.g.*, $Na^+ \; Cl^-$.
4. All salts, strong acids and strong bases (that is, those which are as much as 45 per cent ionized in 0.1 equivalent solution) are to be treated, as far as equation writing is concerned, as if they were completely ionized: *e.g.*, $Na^+ \; Cl^-$; $H^+ \; Cl^-$; $Na^+ \; OH^-$; $2H^+ \; SO_4^{--}$.
5. In equations showing the reactions of weak acids and bases, the un-ionized parts cannot be neglected. Both the un-ionized and ionized parts must be shown, *e.g.*:

$$\begin{array}{ll} HC_2H_3O_2 & \rightleftharpoons H^+ + C_2H_3O_2^- \\ NH_4OH & \rightleftharpoons NH_4^+ + OH^- \end{array}$$

6. Solid substances formed in a reaction and thus precipitated are indicated by an arrow pointing downward: *e.g.*, $AgCl\downarrow$
7. Gaseous substances formed in a reaction and thus escaping from the solution are indicated by an arrow pointing upward: *e.g.*, $CO_2\uparrow$
8. Intersecting equations. To represent a reaction which takes place between two ionized substances, the formulas of the ions should be arranged so that positive will always be adjacent to negative in either the horizontal or vertical direction. An arrow then should be inserted to point toward the formula of the new combination.

$$\begin{array}{ll} Ag^+ & NO_3^- \\ Cl^- & Na^+ \\ \downarrow & \\ AgCl\downarrow & \end{array}$$

When weak electrolytes are brought together a series of reactions ensues. First the ionization of these electrolytes is shown in horizontal equations as in Rule 5, but the ionic products must be placed with positive ion above negative so that, if either new pair of ions combines, the reaction may be shown by an intersecting vertical equation.

$$\begin{array}{lcl} \mathrm{HC_2H_3O_2} \rightleftharpoons & \mathrm{H^+} & + \mathrm{C_2H_3O_2^-} \\ \mathrm{NH_4OH} \rightleftharpoons & \mathrm{OH^-} & + \mathrm{NH_4^+} \\ & \downarrow & \\ & \mathrm{H_2O} & \end{array}$$

Types of Reactions. A student who tries simply to remember each chemical reaction which comes to his attention very soon becomes bewildered, then discouraged so far as chemistry is concerned, and finally he may acquire a dislike for the subject.

The remedy for this condition is to compare each new reaction with those previously considered and to group together all those which show such similarities as to warrant their being classified as of the same type.

In the following pages several types of ionic reactions are discussed and illustrated with specific examples.

The most important distinction among the types is whether or not a change of valence is involved. Valence, as we shall use the term, is the algebraic number of unit electric charges on an ion or radical.

TYPES OF IONIC REACTIONS

Metathesis — interchange of radicals — no change of valence.
(*a*) Precipitation.
(*b*) Neutralization.
(*c*) Displacement of a weak acid from its salt.
(*d*) Displacement of a weak base from its salt.
(*e*) Hydrolysis.
Formation of Complex ions — no change of valence.
Oxidation and Reduction — valence changes.

METATHESIS

Metathesis, or double decomposition, is one of the main types of chemical reaction, and it takes place between two compounds, consisting merely in an interchange of radicals, the positive radical of the first compound pairing off with the negative radical of the second, and the negative radical of the first pairing off with the positive of the second. Such a reaction involves no change in the valence of any radical concerned.

When solutions of two ionized substances are mixed, the opportunity is thereby furnished for the formation of two new substances. What will actually take place depends on the properties of these two substances, as well as upon the properties of the original substances. The various types of metathetical reactions are classified on this basis.

Precipitation. When a solution of silver nitrate is added to a solution of sodium chloride a voluminous, curdy, white precipitate instantly appears and analysis of the precipitate shows it to be silver chloride.

The mixing together of the solutions brings together the four ions, Ag^+, NO_3^-, Na^+, and Cl^-, from which four different pairs, or complete substances, are possible, $AgNO_3$, $NaCl$, $NaNO_3$, $AgCl$. Reference to a solubility table shows that the first three of these are very soluble, and reference to the table of ionization values shows that each of the three is highly ionized; on the other hand, AgCl is very insoluble. The latter salt, therefore, precipitates until there are left in solution only the extremely few of its ions corresponding to its solubility.

$$\begin{array}{cc} \mathrm{Ag^+} & \mathrm{NO_3^-} \\ \mathrm{Cl^-} & \mathrm{Na^+} \\ \downarrow & \\ \mathrm{AgCl}\downarrow & \end{array}$$

For writing the equations of ionic reactions the set of rules given on page 104 has been devised. Silver nitrate and sodium chloride are each about 86 per cent ionized, according to the table. In the equation these substances both appear as completely ionized, the 14 per cent un-ionized portion of each which exists before mixing the solutions being disregarded (Rule 4). As a matter of fact, as soon as AgCl is precipitated and Ag^+ and Cl^- ions are thus removed, the original 14 per cent of un-ionized $AgNO_3$ and NaCl are no longer in equilibrium with the ions; further ionization ensues, and the salts enter as completely into reaction as if they had been 100 per cent ionized at the start.

Sodium nitrate, according to the table, is 86 per cent ionized. Hence 14 per cent of the total amount of this salt must have passed into the un-ionized condition. It will be noticed that this fact is neglected in the equation. For all practical purposes the major part of the Na^+ and NO_3^- ions are left in exactly the same condition after the reaction as they were in the beginning, and it is exactly this fact which is emphasized by this manner of writing the equation, for these ions simply appear beside the oppositely charged ions with which they were originally paired and nothing happens to them. They are placed adjacent to each other, showing that after the changes have taken place they are capable of balancing each other electrically.

The arrow is indicative of the real reaction, and the formulas of the components which do change are placed in the line of the arrow and constitute the equation $Ag^+ + Cl^- \rightarrow AgCl$, which, for convenience, was arranged in a vertical line.

Experiments have shown that any ionized silver salt, *e.g.*, Ag_2SO_4, $AgC_2H_3O_2$, $AgClO_3$, may be substituted for $AgNO_3$, and any ionized chloride may be substituted for the NaCl, and the same results will be obtained. The union of Ag^+ and Cl^- ions to form insoluble AgCl is in no wise affected by the other ions with which these ions are at the outset in electrical balance. These other ions will simply remain in the solution unless they, too, are the ions of some insoluble salt, for example, $BaSO_4$ or an undissociated molecule like H_2O.

The above principles do not apply solely to silver salts and chlorides, but to all solutions. Reference to the table of solubilities on page 364 will inform one whether or not a precipitate will be formed when any two solutions of electrolytes are mixed together.

PROBLEMS

Divide a good-sized sheet of paper into two columns; in the left-hand column describe the observable effects of bringing together the substances noted in the cases below; in the right-hand column write the equation in the fully ionized intersecting form, following Rules 1 to 8, inclusive, on page 104. In the following, unless otherwise specified, the formula stands for the substance in a fairly dilute solution. The table of solubilities in the Appendix should be consulted.

24. $AgNO_3 + NaCl$.
25. AgCl (solid) + NaI.
26. $BaCl_2 + Na_2CO_3$.
27. $Pb(NO_3)_2 + H_2SO_4$.
28. $PbSO_4$ (solid) + Na_2S.

29. $Cd(NO_3)_2 + Na_2S$.
30. $CaCl_2 + Na_2SO_4$.
31. $CaSO_4$ (solid) $+ Na_2CO_3$.

Neutralization. Acids and bases have the ability to mutually neutralize the distinctive properties of each other.

An acid tastes sour, it turns blue litmus red, and it imparts distinctive colors to a number of other organic substances which may be used in the same way as litmus; it reacts with active metals, hydrogen being evolved and salts of the metal being left; it reacts with calcium carbonate with an effervescence due to the escape of carbon dioxide. These properties of an acid are all lost when the acid has reacted with an equivalent quantity of a base.

A base tastes alkaline, that is, like lime water; it turns red litmus blue, as well as imparting distinctive colors to the other organic substances which may be used in a similar manner; it causes a slippery feeling if a drop of its solution is rubbed between the finger tips. These properties of a base are all lost when the base has reacted with an equivalent quantity of an acid.

When the neutralization has been very carefully carried out, so that exactly equivalent quantities of acid and base have been used, the resulting solution shows none of the characteristic properties or either acid or base. It still conducts electricity strongly, showing that it contains ions; if it is evaporated a solid salt is left.

Since we know that all acids yield hydrogen ions when dissolved, although the negative ions may be of most divergent kinds, it is obvious that the distinctive properties of acid solutions must be the properties of hydrogen ions. Likewise it is obvious that the distinctive properties of solutions of bases must be the properties of hydroxyl ions.

Since we may see in the table of ionization values that pure water contains but 0.000,000,1 mole of H^+ ions and 0.000,000,1 mole of OH^- ions per liter, we may know in advance that when an acid and a base are mixed the H^+ and OH^- ions cannot remain in the presence of each other, but must unite according to the reaction

$$H^+ + OH^- \rightarrow H_2O$$

until only a number corresponding to the exceedingly small concentration just stated is left.

A salt may be defined as a compound consisting of the positive radical of a base and the negative radical of an acid. Hence the products of neutralization are always un-ionized water and a salt. But the table of ionization values tells us that all salts are highly ionized, although acids and bases may or may not be.

Neutralization of a Strong Acid and a Strong Base. When a strong, that is, a highly ionized acid (for example, HCl), is neutralized with a strong base (for example, NaOH), and the resulting salt, in this case NaCl, is soluble, the essential reaction is the formation of water from its ions.

$$\begin{array}{ll} H^+ & Cl^- \\ OH^- & Na^+ \\ \downarrow & \\ H_2O & \end{array}$$

In this connection a most interesting fact comes to our attention, namely, that the heat produced by the neutralization of one equivalent of any strong base with one equivalent of any strong acid is always the same, namely, 13,700 calories. That the heat effect is the same is in itself a strong indication that the reaction is in each case the same, and this fact, then, is in entire accord with our conception of the reaction of neutralization. In the following table are given some of the measured values of the heat of neutralization of acids and bases, both weak and strong.

Heat evolved by the neutralization of one equivalent of acid with one equivalent of base (in calories)

	HCl	HNO_3	$HC_2H_3O_2$	H_2S
NaOH	13,700	13,700	13,300	3,800
KOH	13,700	13,800	13,300	3,800
NH_4OH	12,400	12,500	12,000	3,100

Neutralization of a Weak Acid or a Weak Base. Weak acids and weak bases are but sparingly ionized. Acetic acid is typical of a rather weak acid, being 1.4 per cent ionized in 0.1 N solution. Ammonium hydroxide is typical of a rather weak base, it having the same degree of ionization as acetic acid, namely, 1.4 per cent in a 0.1 N solution. Neither acetic acid nor ammonium hydroxide solution conducts the current strongly, but if the two solutions are mixed, we observe what is a rather startling fact if we have not thought out in advance what to expect, namely, that the resulting solution is a strong conductor.

Neither the acid nor the base alone furnishes many ions, but when they are mixed, the H^+ and OH^- ions present unite at once. This leaves the un-ionized parts of the acid and base out of equilibrium, and further ionization occurs in consequence. This process continues until both the acid and the base have become fully ionized because there can be no accumulation of H^+ and OH^- ions in presence of each other.

The neutralization of a weak acid and a weak base then consists of three simultaneous but distinct ionic reactions: the ionization of the acid, the ionization of the base, and the formation of water from its ions. These reactions may be arranged in an intersecting form in order to show which of the components take part simultaneously in two reactions:

$$\begin{array}{lcccl} HC_2H_3O_2 & \rightleftharpoons & H^+ & + & C_2H_3O_2^- \\ NH_4OH & \rightleftharpoons & OH^- & + & NH_4^+ \\ & & \downarrow & & \\ & & H_2O & & \end{array}$$

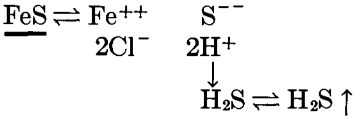
As this train of reactions proceeds it is obvious that NH_4^+ and $C_2H_3O_2^-$ ions, that is, the ions of the salt ammonium acetate, accumulate in the solution, and that their presence accounts for the high conductivity of the neutral solution.

The total heat effect, 12,000 calories, produced by the action of one equivalent of acetic acid and one equivalent of ammonium hydroxide, is the sum of the heat effects of the three separate reactions, and we should expect the value to be different from the value of the neutralization of a strong acid and a strong base. Since 13,700 calories must be generated by the formation of 1 mole of water, the difference between this value and 12,000, or 1,700 calories, must have been absorbed in the ionizing of the acid and the base.

Displacement of a Weak Acid from Its Salt. When a salt of a weak acid is treated with the solution of a strong acid the ions of the weak acid unite to form un-ionized molecules and the salt of the strong acid remains. One example of such a displacement has been seen (p. 88, Exp. 10 (*b*)) in the action of sulphuric acid with sodium acetate

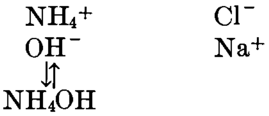
$$\begin{array}{ll} 2H^+ & SO_4^{--} \\ 2C_2H_3O_2^- & 2Na^+ \\ \downarrow\uparrow & \\ 2HC_2H_3O_2 & \end{array}$$

This type of reaction is particularly interesting when the salt of the weak acid is sparingly soluble. Ferrous sulphide is a salt of the weak acid H_2S. It is very insoluble in water, but it passes completely into solution in dilute HCl. The formation of the un-ionized H_2S removes S^{--} ions and thus allows the ionization of the ferrous sulphide to continue unchecked



$$\begin{array}{lll} \underline{FeS} \rightleftharpoons & Fe^{++} & S^{--} \\ & 2Cl^- & 2H^+ \\ & & \downarrow \\ & & H_2S \rightleftharpoons H_2S\uparrow \end{array}$$

Displacement of a Weak Base from Its Salt. An example of this kind of process is given by the action of the strong base, sodium hydroxide, upon a solution of the salt, ammonium chloride. The salt solution is odorless, but the odor of ammonia is observed as soon as the strong base is added.



$$\begin{array}{ll} NH_4^+ & Cl^- \\ OH^- & Na^+ \\ \downarrow\uparrow & \\ NH_4OH & \end{array}$$

In this case, as in the case of the weak acid, the major part of the ions of the weak base combine to form un-ionized molecules.

The strong odor is due to the escape of small amounts of ammonia, NH_3, from the solution. Ammonium hydroxide is capable of undergoing two kinds of dissociation: the electrolytic dissociation, or ionization, which we have already discussed, and a non-electrolytic dissociation,

$$NH_4OH \rightleftharpoons H_2O + NH_3$$

The latter sort of dissociation is subject to the same rules of equilibrium as is ionization, and we can have un-ionized ammonium hydroxide at the same time in equilibrium with two sets of dissociation products,

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O$$

Therefore, whenever NH_4^+ and OH^- ions are brought together, they must come to equilibrium with a large proportion of NH_4OH and the latter must come to equilibrium with NH_3 and H_2O and, through the NH_4OH, the NH_3 and H_2O must be in equilibrium with the ions. In dilute solutions, where the proportion of H_2O

is large, the amount of NH_3 necessary to produce equilibrium is small. Such a substance as pure ammonium hydroxide of the composition shown by the formula is unknown, because, if it existed for a moment, it would at once undergo non-electrolytic dissociation until it came to a state of equilibrium with the products H_2O and NH_3, the first product remaining as a part of the NH_4OH solution, and the larger part of the NH_3 escaping as gas. The more water present, however, obviously the less NH_3 is necessary to maintain equilibrium with the NH_4OH.

Basic Properties of the Metal Oxides. The oxides of the metals are characterized as a class in that they are basic. The term "basic" implies the presence of OH^- ions when these oxides are dissolved in or suspended in water. The most strongly basic oxides, such as Na_2O, K_2O, CaO, BaO, react violently with water and produce well-defined hydroxides $NaOH$, KOH, $Ca(OH)_2$, $Ba(OH)_2$ which can be isolated as well-defined solid substances of the exact composition shown by the formulas. These hydroxides are soluble ($Ca(OH)_2$ sparingly so) in water, and the dissolved hydroxides are highly ionized into simple metal ions and OH^- ions.

The oxides of the heavy metals are likewise basic, but they are only feebly basic. These heavy metal oxides are as a class almost insoluble, yet when they are suspended in water a certain low concentration of metal ions and OH^- ions is built up in the solution. Let us discuss two heavy-metal oxides, ferric oxide, Fe_2O_3, and cupric oxide, CuO, as typical of this class.

Powdered black copper oxide when stirred into water gives a black suspension and does not visibly dissolve. If the suspension is allowed to stand the black powder settles to the bottom and the clear liquid above contains so few ions of Cu^{++} and OH^- that they cannot be detected by the reagents commonly used for detecting these ions, NH_4OH, Na_2S. Yet we are confronted with the fact that, when acid is added to the suspension of copper oxide, the black powder dissolves completely and we obtain a clear blue solution of the cupric salt. The initial and final substances in this reaction are given in the equation

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O$$

which shows that 1 F.W. of CuO neutralizes 2 F.W. of HCl.

In a similar manner red powdered ferric oxide stirred into water gives a red suspension. Upon adding HCl this red powder very slowly dissolves (much more slowly than copper oxide), and finally a clear yellow solution of ferric salt is obtained

$$\mathrm{Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O}$$

Although we are very uncertain about the intermediate formation of definite hydroxides we are certain that the water in which the metal oxides is suspended contains metal ions and hydroxide ions, and we can represent the equilibrium condition by the reversible reactions:

$$\begin{array}{l} \underline{\mathrm{CuO}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cu(OH)_2} \rightleftharpoons \mathrm{Cu^{++}\ 2OH^-} \\ \underline{\mathrm{Fe_2O_3}} + \mathrm{3H_2O} \rightleftharpoons \mathrm{2Fe(OH)_3} \rightleftharpoons \mathrm{2Fe^{+++}\ 6OH^-} \end{array}$$

The removal of OH^- by acids allows the reactions to run completely to the right and the metal oxides to dissolve completely.

Precipitation of Metal Hydroxides. In general the addition of a soluble base to the solution of a metal salt produces a precipitate. This precipitate is of rather variable composition, but its nature is best understood if it is regarded as the hydroxide of the metal. Thus, sodium hydroxide added to copper sulphate solution gives a light blue voluminous precipitate and sodium hydroxide added to ferric chloride gives a voluminous reddish brown precipitate. These precipitates which we have designated as the hydroxides, $Cu(OH)_2$ and $Fe(OH)_3$, certainly consist of the metal oxides in combination with water, although whether it is the definite amount to form these definite hydroxides* is rather doubtful. These fresh precipitates will dissolve instantly in dilute acids instead of slowly as do the anhydrous oxides. Furthermore these precipitates if separated on a filter and dried will lose all their water content and revert to the oxides. The light blue copper hydroxide even when suspended in water will turn black at the boiling temperature, indicating at least a partial loss of water.

$$\begin{array}{llcll} \mathrm{Cu^{++}} & \mathrm{SO_4^{--}} & \qquad & \mathrm{Fe^{+++}} & \mathrm{3Cl^-} \\ \mathrm{2OH^-} & \mathrm{2Na^+} & & \mathrm{3OH^-} & \mathrm{3Na^+} \\ \quad\downarrow & & & \quad\downarrow & \\ \mathrm{Cu(OH)_2}\downarrow & & & \mathrm{Fe(OH)_3}\downarrow & \end{array}$$

---

* These precipitates also contain variable amounts of the metal salts, that is, they are basic salts in reality. It is better, however, to ignore this fact at present as it tends to confuse the argument.

Formation of Volatile Products. When a product of a reaction is volatile it has a tendency to escape from the sphere of action, and the progress of the reaction towards the formation of this product is favored.

When all the products of a reaction taking place in solution are soluble, their concentration will increase as the reaction progresses, until a point of equilibrium is reached, at which point the products react with each other to form the original substances again, and the backward reaction takes place with sufficient rapidity just to offset the effect of the forward reaction.

But with the escape of one of the products as a gas, and thereby the removal of this product from the sphere of action, the reverse reaction is eliminated, and the forward reaction is thus enabled to run to completion.

PROBLEMS

Describe the observable effects and write the fully ionized equations for the following cases:

32. $HNO_3 + NaOH$.
33. $HC_2H_3O_2 + NH_4OH$.
34. $Mg(OH)_2$ (solid) + HNO_3.
35. CuO (solid) + H_2SO_4.
36. H_2S (gas) + $NaOH$.
37. NH_3 (gas) + HCl.
38. $H(C_7H_5O_2)$ (solid) + $NaOH$.

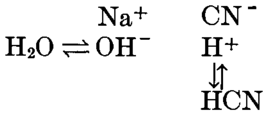
Benzoic acid $H(C_7H_5O_2)$ is a sparingly soluble solid, and a little stronger than acetic acid.

39. $K(C_7H_5O_2) + HCl$.
40. $Ca(C_2H_3O_2)_2 + HNO_3$. Note odor.
41. $(NH_4)_2SO_4 + NaOH$. Note odor.
42. NH_4Cl (in excess) + $Ca(OH)_2$ (solid). Note odor.
43. $CaCO_3$ (solid) + HNO_3.
44. $CaCO_3$ (solid) + $HC_2H_3O_2$.
45. FeS (solid) + HCl.
46. $MgCl_2 + NaOH$.
47. $MgCl_2 + NH_4OH$.
48. $MgCl_2 + NH_4Cl + NH_4OH$.
49. $Ca(OH)_2$ (solid) + $FeCl_3$.
50. $Ca(OH)_2$ (saturated solution) + CO_2 (gas, in moderate amount and then in excess).

HYDROLYSIS

The ionization of water is so slight that often it can be totally disregarded. It cannot be neglected, however, in solutions of salts when either the acid or the base — or both, from which the salt is derived, is extremely weak.

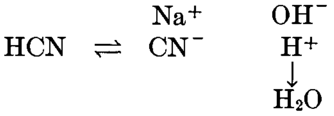
Sodium cyanide is the salt of the weak hydrocyanic acid, HCN (ionization = 0.01 per cent in 0.1 equivalent solution), and the strong base, sodium hydroxide. A solution of this salt shows an alkaline reaction to litmus, thus demonstrating that the solution contains an appreciable quantity of OH^- ions. This is the result of hydrolysis, and the process may be explained as follows:



$$\begin{array}{lll} & \mathrm{Na^+} & \mathrm{CN^-} \\ \mathrm{H_2O} \rightleftharpoons & \mathrm{OH^-} & \mathrm{H^+} \\ & & \downarrow\uparrow \\ & & \mathrm{HCN} \end{array}$$

The salt, in accordance with the general rule for salts, will exist in solution in the ionized condition. Water is in equilibrium with a very small number of its own ions. But even the small number of H^+ ions thus furnished to the solution is more than can exist in presence of the large concentration of CN^- ions of the salt. Undissociated hydrocyanic acid, HCN, must form; but since this removes some of the H^+ ions, the equilibrium between water and its ions is temporarily destroyed. The equilibrium must be reëstablished through the ionization of more water. This cycle of reactions repeats itself a great many times until complete equilibrium among all the components is established. When this condition is reached, as really happens in a very short time, there has been a considerable accumulation of OH^- ions and of an equivalent amount of un-ionized HCN.

In order to fully comprehend the extent and the limitation of this hydrolysis, we should consider the reverse reaction which occurs when solutions of hydrocyanic acid and sodium hydroxide are mixed:



$$\begin{array}{lll} & \mathrm{Na^+} & \mathrm{OH^-} \\ \mathrm{HCN} \rightleftharpoons & \mathrm{CN^-} & \mathrm{H^+} \\ & & \downarrow \\ & & \mathrm{H_2O} \end{array}$$

The few ions furnished by the acid combine at once with OH^- ions of the base to form water, and this removal of H^+ ions allows more of the acid to ionize. This cycle of operations repeats itself until we have the same state of equilibrium as existed in the solution obtained by dissolving pure sodium cyanide in pure water.

The reaction of neutralization in this case goes about 99 per cent of the way to completion when equivalent amounts of the acid and base are mixed. The reverse reaction, that is, the hydrolysis of sodium cyanide, progresses only about 1 per cent of the way to completion before the state of equilibrium is reached.

If we consider the case of a salt of a much weaker acid than hydrocyanic acid, or of a salt of both a very weak acid and a very weak base, it is fairly obvious that hydrolysis will be much more extensive.

Aluminum sulphide furnishes a good example of this, for when it is treated with water its hydrolysis is complete:

$$\begin{array}{lcl}
\underline{Al_2S_3} \rightleftharpoons 2Al^{+++} & & 3S^{--} \\
6H_2O \rightleftharpoons 6OH^{-} & & 6H^{+} \\
\qquad\quad \downarrow & & \ \downarrow \\
\qquad 2Al(OH)_3 & & 3H_2S \\
\qquad\quad \downarrow & & \ \downarrow \\
\qquad 2Al(OH)_3 \downarrow & & 3H_2S \uparrow
\end{array}$$

Note in this reaction that solid $\underline{Al_2S_3}$ disappears, and solid $Al(OH)_3\downarrow$ and gaseous $H_2S \uparrow$ appear.

IONIZATION OF POLYBASIC ACIDS

It is usually true with polybasic acids that one hydrogen radical ionizes with greater facility than the remaining ones. Thus phosphoric acid ionizes primarily as a monobasic acid

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

to the extent of 27 per cent in 0.1 equivalent solution. The fairly high concentration of H^+ ions thus established prevents appreciable ionization of the $H_2PO_4^-$ ion, but if one equivalent of NaOH is added for each mole of H_3PO_4, the H^+ ions from the first H radical are entirely removed and the $H_2PO_4^-$ ion itself ionizes

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$$

to the extent of 0.2 per cent. If a second equivalent of NaOH is now added, the HPO_4^{--} ion is enabled to ionize to the extent of 0.0002 per cent.

$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$$

When the hydrolysis of the salt of a polybasic acid is considered, the different H radicals must be treated separately. Thus when 1 mole of tertiary sodium phosphate, Na_3PO_4, is dissolved in water, hydrolysis takes place very extensively as follows:

$$\begin{array}{lcccc} & Na^+ & Na^+ & Na^+ & PO_4^{---} \\ H_2O \rightleftharpoons & OH^- & & & H^+ \\ & & & & \downarrow\uparrow \\ & & & & HPO_4^{--} \end{array}$$

The solution will have a very strong alkaline reaction, since it contains a large fraction of 1 mole each of ionized NaOH and of ionized secondary sodium phosphate, Na_2HPO_4. The OH^- ions thus formed check the hydrolysis of the secondary sodium phosphate; but if solid secondary sodium phosphate is dissolved in water, hydrolysis of this salt ensues to a sufficient extent to make the solution alkaline to litmus.

$$\begin{array}{lccc} & Na^+ & Na^+ & HPO_4^{--} \\ H_2O \rightleftharpoons & OH^- & & H^+ \\ & & & \downarrow\uparrow \\ & & & H_2PO_4^{-} \end{array}$$

When primary sodium phosphate, NaH_2PO_4, is dissolved, a weakly acid solution is obtained, this effect being due to the tendency of the second hydrogen radical of the acid to ionize.

$$\begin{array}{cc} Na^+ & H_2PO_4^{-} \\ & \downarrow\uparrow \\ & H^+ \\ & HPO_4^{--} \end{array}$$

PROBLEMS

When the following salts are dissolved in water, decide from a consideration of the degree of ionization of the base and acid concerned in each case whether the solution will be neutral, weakly acidic, strongly acidic, weakly basic, or strongly basic, and give the explanation and an intersecting ionized equation.

51. KNO_3.
52. $Ca(CN)_2$.
53. $NH_4C_2H_3O_2$.
54. $AlCl_3$.
55. $Al(C_2H_3O_2)_3$.
56. Na_3AsO_4.
57. Na_2CO_3.
58. $NaHCO_3$.
59. $NaHSO_4$.
60. NaH_2PO_4.
61. Na_2HPO_4.
62. Na_3PO_4.
63. $AgNO_3$.

COMPLEX IONS

Ammoniates. Review what was said in Chapter II about water of crystallization and hydrates (pp 62–65). Two definite crystalline compounds of sodium carbonate and water are the monohydrate and the decahydrate. Both of these will dissolve in water, but both solutions are absolutely identical. Furthermore, either one or the other of these hydrates can be caused to crystallize from the solution by adjusting the temperature.

In solution, undoubtedly some water is in combination with the salt, but it is impossible to say how much, because there is no physical means of distinguishing the water thus held in combination from the solvent water.

There are other substances than water, notably ammonia, which form compounds similar to hydrates, in this case ammoniates. Numerous solid compounds containing ammonia of crystallization are known, for example ammonio-copper sulphate $CuSO_4 \cdot 4NH_3 \cdot H_2O$, which is the subject of one of our later preparations (page 227). This substance is easily soluble in water containing a little excess of ammonia, and it is possible to measure how much ammonia is held to the salt, or rather to the positive ion, in the solution. This may be done, for example, by passing an electric current through the solution and measuring the proportionate amounts of copper and ammonia which travel with the positive current. Results show that 4 moles of NH_3 travel with each mole of Cu^{++} ions. The formula of the deep blue ammonio-copper ion is therefore $Cu \cdot 4NH_3^{++}$.

When a moderate amount of ammonia is added to a copper salt solution, a light blue precipitate is formed which is really a basic salt but which for simplicity we shall treat as the simple hydroxide.

$$\begin{array}{rcl} & Cu^{++} & \quad SO_4^{--} \\ 2NH_4OH \rightleftharpoons & 2OH^- & \quad 2NH_4^+ \\ & \downarrow\uparrow & \\ & Cu(OH)_2 \downarrow & \end{array}$$

Addition of more ammonia quickly causes this precipitate to redissolve, giving an intensely deep blue solution

$$\begin{array}{lcll} \underline{Cu(OH)_2} & \rightleftharpoons & Cu^{++} + 2OH^- & \\ 4NH_4OH & \rightleftharpoons & 4NH_3 & \quad + 4H_2O \\ & & \downarrow\uparrow & \\ & & Cu \cdot 4NH_3^{++} & \end{array}$$

If the two sets of ionic equations are now put together it is seen that $2NH_4^+$ and $2OH^-$ have been left and these will combine to form $2NH_4OH$, which will cancel. Thus the net result becomes:

$$\begin{array}{lcl} & \mathrm{Cu^{++}} \qquad \mathrm{SO_4^{--}} & \\ 4\mathrm{NH_4OH} \rightleftharpoons & 4\mathrm{NH_3} \qquad\qquad & + \; 4\mathrm{H_2O} \\ & \downarrow \qquad\qquad & \\ & \mathrm{Cu{\cdot}4NH_3^{++}} & \end{array}$$

the resulting solution containing ionized $(Cu{\cdot}4NH_3)SO_4$ and only enough excess of ammonia to prevent the dissociation of this ammoniate.

It is interesting to note that, if freshly precipitated and thoroughly washed $Cu(OH)_2$ is treated with ammonia, a similar deep blue solution is obtained, but in this case the negative ions are hydroxyl instead of sulphate. Ammonio-copper hydroxide is very soluble and very highly ionized, and the solution compares in basic strength with one of sodium hydroxide.

It is most interesting that the addition of ammonia to the simple ions of several of the heavy metals produces similar effects. The base-forming character of the metals seems thereby to be greatly strengthened. The following list gives the metals which possess this property to a marked degree and also the formulas of their ammonio ions:

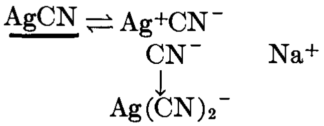
copper	(ous)	$Cu{\cdot}2NH_3^+$	colorless
	(ic)	$Cu{\cdot}4NH_3^{++}$	deep blue
silver		$Ag{\cdot}2NH_3^+$	colorless
zinc		$Zn{\cdot}4NH_3^{++}$	colorless
cadmium		$Cd{\cdot}4NH_3^{++}$	colorless
nickel		$Ni{\cdot}4NH_3^{++}$	blue
cobalt	(ous)	$Co{\cdot}4NH_3^{++}$	red
	(ic)	$Co{\cdot}6NH_3^{+++}$	brownish yellow

Aluminum, iron, tin, lead, and some other metals do not have the power of forming such ammonio compounds.

Complex Negative Ions. When an equivalent amount of sodium cyanide is added to a solution of silver nitrate, quantitative precipitation of silver cyanide takes place

$$\begin{array}{ll} \mathrm{Ag^+} & \mathrm{NO_3^-} \\ \mathrm{CN^-} & \mathrm{Na^+} \\ \downarrow & \\ \mathrm{AgCN}\downarrow & \end{array}$$

When another equivalent of sodium cyanide is added the precipitate entirely redissolves. In this solution the silver is found to be in the negative ion, and to be associated with 2 cyanide radicals.



$$\begin{array}{lll} \underline{AgCN} \rightleftharpoons Ag^{+}CN^{-} & & \\ \qquad\qquad\quad CN^{-} & & Na^{+} \\ \qquad\qquad\quad \downarrow & & \\ \qquad\quad Ag(CN)_2^{-} & & \end{array}$$

There are thus two possible reactions between Ag^{+} and CN^{-} ions

$$Ag^{+} + CN^{-} \rightleftharpoons AgCN \downarrow \quad \text{and} \quad Ag^{+} + 2CN^{-} \rightleftharpoons Ag(CN)_2^{-}$$

The effect of increasing CN^{-} ion concentration upon the second reaction is far greater than on the first. Thus when an excess of CN^{-} ion is employed the removal of Ag^{+} ions in the second reaction is so complete as to cause the first reaction to go backward.

This example is typical of complex ion formation. The formulas of a few complex ions in the decreasing order of their stability are:

$Co(CN)_6^{---}$	yellow
$Fe(CN)_6^{----}$	yellow
$Fe(CN)_6^{---}$	red
$Ag(CN)_2^{-}$	colorless
$Cu(CN)_2^{-}$	colorless
$Ni(CN)_4^{--}$	colorless
$CuCl_2^{-}$	colorless
AgI_2^{-}	colorless
$AgCl_2^{-}$	colorless

The last in the list is so little stable that it can exist only in a concentrated chloride solution. Dilution of such a solution causes precipitation of all the silver as simple silver chloride.

In solution complex ions are in equilibrium with their constituents, for example, $Cu{\cdot}4NH_3^{++} \rightleftharpoons Cu^{++} + 4NH_3$. In fact, an excess of ammonia is necessary to stabilize the complex in solution. The ions NO_3^{-}, SO_4^{--}, CO_3^{--}, PO_4^{---} are so very stable that we do not think of them as other than simple ions. Nevertheless they may be similar in nature to the complex ions just considered except for the fact that no simple constituents, of which they might be supposed to be built, have ever been identified.

PROBLEMS

Describe observable effects and write the fully ionized equation for the following cases, when the reagent (second formula) is added (*a*) in limited amount, and (*b*) in excess.

64. $ZnSO_4 + NH_4OH$.
65. $CuCl$ solid $+ NH_4OH$.
66. $Ag_2SO_4 + NH_4OH$.
67. $(Cu{\cdot}4NH_3)SO_4 + HNO_3$.
68. $(Ag{\cdot}2NH_3)Cl + HNO_3$.
69. $AgNO_3 + KI$.
70. $AgCl$ (solid) $+ NaCl$ (saturated solution, in very large excess).
71. $AgNO_3 + KCN$.
72. $CuCl$ solid $+ KCN$.

Reactions of Oxidation and Reduction

Ionic Displacement. Electromotive Series. When a strip of zinc is placed in a solution of copper sulphate, it is noticed that a spongy deposit of copper metal soon appears on the surface of the zinc, and that the solution loses its blue color. Then if the solution is tested for the presence of copper and zinc ions by adding ammonium sulphide, it is found that this reagent gives a white precipitate. This test shows that copper ions are now absent and that zinc ions are present because we know ammonium sulphide will precipitate black copper sulphide from a solution of copper ions, and white zinc sulphide from a solution of zinc ions. Since ordinary pieces of metal are not charged, it is obvious that the reaction consists in a transfer of the positive charges of the copper ions to the zinc atoms, or, more strictly, of negative electrons from the zinc atoms to the copper ions:

$$\begin{array}{lll} \mathrm{Zn}^0 \rightarrow & \mathrm{Zn}^{++} + & 2\ominus \\ & \mathrm{SO_4}^{--} & \mathrm{Cu}^{++} \\ & & \downarrow \\ & & \mathrm{Cu}^0 \end{array}$$

The small zero mark ^{0} is not essential; it may be used when it is desired to attract particular attention to the fact that the atom to which it is attached is not electrically charged. Since the SO_4^{--} ions take no part in the above reaction beyond balancing by their charges the positive charges of the metal ions, we can eliminate them from the equation, which then becomes simplified to:

$$\mathrm{Cu}^{++} + \underline{\mathrm{Zn}^0} \rightarrow \mathrm{Cu}^0 \downarrow + \mathrm{Zn}^{++}$$

The metals, including hydrogen, may be arranged in the order in which they tend to pass into the ionic condition, as, in this case, zinc does at the expense of copper. Such a series is known as the electromotive series, because the electromotive force of such reactions, if properly disposed in a cell, may be made to send a current through an external wire connector. (See Electromotive Series, Appendix, page 353.)

A characteristic of metallic elements is that they can form simple positive ions, but never simple negative ions. In other words, a metal atom may lose one or more negative electrons, but it can never attach to itself electrons in excess of those forming the make-up of the unelectrified atom.

On the other hand, a characteristic of some of the most pronouncedly non-metallic elements, fluorine, chlorine, bromine, iodine, and sulphur, is that they can form simple negative ions. No non-metal ever forms simple positive ions. The non-metals may be arranged in a negative electromotive series.

The broadest, as well as the simplest, definition of oxidation is the increasing of the positive valence of an element. This can be accomplished only through the simultaneous and equivalent decrease of the valence of another element involved in the reaction. The other element is said to be reduced. Thus oxidation and reduction always occur together; one cannot occur alone. In the above definition, positive valence is considered from an algebraic standpoint. Thus iodine in an iodide is said to be oxidized when its valence is changed from -1 to 0; as, for example, in the reaction

$$\begin{array}{ll} & \mathrm{Cl}_2^0 \\ 2\mathrm{I}^- \rightarrow & 2\ominus + \mathrm{I}_2^0 \\ & \downarrow \\ 2\mathrm{K}^+ & 2\mathrm{Cl}^- \end{array}$$

If we take the viewpoint that valence is due to the attraction of electrical charges on the atoms, the difference between reactions of oxidation and reduction and of metathesis resolves itself into this: *oxidation and reduction involve a transfer of charges from one atom* *to another; metathesis involves no transfer of charges, but simply a regrouping of the charged radicals.*

The simplest type of oxidation and reduction reaction is that which involves merely the charging and discharging of simple ions. The course of such a reaction can be predicted from a knowledge of where the elements concerned stand in the electromotive series.

PROBLEMS

In the left-hand column state the observable effect and in the right-hand column write the fully ionized equations.

73. Fe (metal) + $CuSO_4$.
74. Zn (metal) + HCl.
75. Cu (metal) + HCl.
76. Ag (metal) + $AuCl_3$.
77. Cu (metal) + $PtCl_4$.
78. AgCl (finely divided solid) + Zn (zinc dust) suspended in water.
79. Ag (in a photographic print) + $PtCl_4$.
80. $FeCl_2 + Cl_2$.
81. CuCl (solid) + Cl_2.
82. Na (metal) + H_2O.

FARADAY'S LAW

Let us consider an electric circuit consisting of a dynamo and metallic conductors connecting the poles of the dynamo to the two poles of an electrolytic cell. The same amount of electricity flows through every section of the circuit, but the mechanism by which the current passes in the different parts of the circuit is of three different kinds:

(1) Through the metallic conductor the current passes without any alteration of the conductor. The electrons, which may be regarded as atoms of negative electricity, simply pass through the metallic mass without dislocating the atoms of the metal. (2) Through the electrolytic conductor the current passes solely by the movement of positive and negative ions in opposite directions. (3) At the surface of the electrode electrons are transferred to or from the atoms or ions at that surface. This involves a change of valence, and at the *cathode,* which is the electrode at which elec-

trons flow into the cell from the metallic conductor, reduction occurs. At the *anode*, which is the electrode at which electrons flow out through the metallic conductor, oxidation occurs.

The sum of the changes at the anode and cathode makes a complete reaction of oxidation and reduction, but the location of the oxidation is remote from the location of the reduction.

Michael Faraday studied quantitatively the extent of the chemical change at the electrodes when electric currents pass through solutions, and in 1834 he stated a law which has since borne his name:

Faraday's Law: When the same amount of electric current is passed through several electrochemical cells the quantities of the new substances produced at the several electrodes are chemically equivalent to each other.

The amount of electricity which must pass to effect the change of one chemical equivalent (for example, to liberate 1.008 gram of hydrogen) has been found to be 96,500 coulombs. This quantity has been named the faraday, and it is designated by the symbol F.

The explanation of the mechanism of the electrolytic conductance in specific cases will make the application of Faraday's law clearer.

A current is passed through a solution of copper sulphate in a U-tube with copper electrodes in the opposite arms. At the cathode copper ions are reduced

$$2\ominus + Cu^{++} \rightarrow Cu^0$$

thus impoverishing the solution of Cu^{++} ions. At the anode copper atoms at the surface have electrons withdrawn, thus producing Cu^{++} ions

$$Cu^0 \rightarrow Cu^{++} + 2\ominus$$

and enriching the solution in Cu^{++} ions. It is fundamental that every portion of the solution shall at all times remain electrically neutral, and this condition is preserved through the movement of the ions through the solution, the SO_4^{--} ions moving towards the anode and the Cu^{++} ions towards the cathode.

It is to be remarked that in the cell just described the SO_4^{--} ions are not discharged. They simply *migrate* through the solution to preserve the electric balance with the copper ions which are entering the solution at the anode and leaving in equal numbers at the cathode. If the anode were of an unattackable material, such as platinum, the current would have to pass the anode surface by some different mechanism. As a matter of fact, oxygen gas escapes at a platinum anode in a $CuSO_4$ solution, the mechanism being indicated in the equation

$$SO_4^{--} + H_2O \rightarrow 2H^+ SO_4^{--} + \frac{1}{2}O_2 + 2\ominus$$

It should be remarked that just as the symbol Cu stands for 63.6 grams of copper or 6.06×10^{23} actual atoms, the symbol $\ominus$ stands for 96,500 coulombs of electricity or 6.06×10^{23} actual electrons.

It should also be stated, to make the relation of positive and negative electricity clearer, that neutral atoms of elements apparently contain both positive and negative electricity in equal amounts. The positive electricity is confined within the structure of the atom. In chemical changes atoms may alter their net charge by the loss or gain of a small number of electrons without destroying their identity.

Electric currents forced through chemical cells from an outside source of energy such as a dynamo can force chemical reactions of oxidation and reduction to take place. Reactions of oxidation and reduction which will take place spontaneously under their own power may on the other hand cause a current to flow through an external metallic conductor if the solutions and electrodes are properly arranged. For example, if zinc is placed in a copper sulphate solution, zinc passes into solution and copper is deposited. No useful electric current is thereby generated. To dispose the materials of this reaction so that an external current will flow let us place a porous clay jar in a beaker; in the porous jar let us place a copper sulphate solution in which dips a copper electrode; outside the porous jar in the beaker let us place zinc sulphate solution in which dips a zinc electrode. The pores of the clay jar become filled with solution so that ions can pass through, but the jar prevents the copper sulphate solution mixing with the solution in contact with the zinc. The oxidizing agent, Cu^{++} ions, and the reducing agent, Zn, are remote from each other. Now if the zinc and copper electrodes are connected by a wire, a current flows, and zinc dissolves from the zinc electrode and copper deposits on the copper electrode: $Zn \rightarrow Zn^{++} + 2\ominus$; $2\ominus + Cu^{++} \rightarrow Cu$. The electrons passing through the wire constitute the current in that part of the circuit. The passage of Zn^{++} ions through the porous wall in one direction and of SO_4^{--} ions in the other direction comprise the current in that part of the circuit.

PROBLEMS

If an electric current is passed through each of the following cells, state observations and write electrochemical reactions for both the anode and the cathode.

83. Dilute silver nitrate with silver electrodes.

84. Dilute sulphuric acid with copper electrodes.

85. Dilute sulphuric acid with platinum (unattackable) electrodes.

86. A current of 0.5 ampere passes between silver electrodes in a silver nitrate solution for 2 hours. What is the change of weight of the anode and of the cathode? (1 ampere = 1 coulomb per second.)

LAW OF MOLECULAR CONCENTRATION

The treatment of equilibrium in the preceding pages has been qualitative, having been based on the obvious principle that the tendency of a reversible reaction, say

$$A + B \rightleftharpoons C + D$$

to proceed to the right is determined by the concentrations of A and B, whereas the tendency to proceed to the left is determined by the concentrations of C and D and that equilibrium is reached when the effects of these two opposing changes exactly nullify each other.

A fairly exact quantitative relationship exists among the concentrations of all the components of a reversible reaction when this reaction is at equilibrium; this is known as the *law of molecular concentrations,* and may be stated as follows: when a reversible reaction has reached a state of equilibrium, the product of the molecular concentrations of all the components on one side of the reaction bears a definite numerical ratio to the product of the molecular concentrations of all the components on the other side of the reaction. This ratio is known as the *equilibrium constant* of the reaction, and it is always the same at the same temperature although it may have different values at other temperatures. The word *molecule* here signifies any individual component whether electrically charged or not. Thus, a solution of acetic acid would contain the components H^+, $C_2H_3O_2^-$, and $HC_2H_3O_2$. *Concentration* signifies the amount of the component divided by the volume and is usually expressed in gram molecular weights per liter. For example, take 100 cc. of a solution containing 0.6 gram (0.01 mole) of $HC_2H_3O_2$. Dividing the amount (0.01 mole) by the volume, 0.1 liter, gives the ratio 0.1, and thus the concentration of the total acetic acid is 0.1 F.W. (formula weight) per liter. Since the fraction ionized is 0.014 the concentration of hydrogen ion, $[H^+]$,* is 0.0014; the concentration of the acetate ions $[C_2H_3O_2^-]$ is also 0.0014, and the concentration of un-ionized acetic acid $[HC_2H_3O_2]$ is $0.1 - 0.0014 = 0.0986$.

Derivation of the Law of Molecular Concentration from a Consideration of the Speed of Reaction. Let us consider again the general reaction

$$A + B \rightleftharpoons C + D$$

It is obvious that for a molecule of A to react with a molecule of B the two must come into contact or collide. The chance for collision of any single molecule of A with molecules of B is proportional to the number of B in a given volume, that is, to the concentration of B, but there are a great many molecules of A each of which has the same chance to collide with molecules of B. Therefore, the total number of collisions is proportional to the product of the concentrations of A and B. However, the velocity of the reaction towards the right, that is, the amount changed in unit time in unit volume, is proportional to the number of collisions. Thus

$$\text{Velocity } (\rightarrow) = k_1\,[A]\,[B]$$

The factor k_1 is a definite numerical value known as the proportionality constant.

As the reaction progresses and C and D accumulate it is obvious that collisions between C and D will ensue, and an exactly similar consideration will show that the velocity in the opposite direction is given by the expression

$$\text{Velocity } (\leftarrow) = k_2\,[C]\,[D]$$

---

* In mathematical equations the formula enclosed in brackets signifies the concentration of the substance.

in which k_2 is likewise a constant which depends on the chemical affinities of C and D and naturally has a different numerical value from k_1.

Now a reversible reaction is at a point of equilibrium when no further apparent change is taking place. The two opposing reactions are without doubt taking place just the same, but they exactly undo the effect of each other, making the total change zero. Therefore

$$\text{vel}\ (\rightarrow) = \text{vel}\ (\leftarrow)$$
$$k_1\,[\mathrm{A}]\,[\mathrm{B}] = k_2\,[\mathrm{C}]\,[\mathrm{D}]$$

or

$$\frac{[\mathrm{C}]\,[\mathrm{D}]}{[\mathrm{A}]\,[\mathrm{B}]} = \frac{k_1}{k_2} = K$$

K is known as the equilibrium constant of the reaction. It is the ratio of the two velocity constants k_1 and k_2.

The number of components taking part in a reversible reaction is not always four as in the equation involving ABCD. Thus in the ionization of acetic acid, (HAc),

$$\mathrm{HAc} \rightleftharpoons \mathrm{H}^+ + \mathrm{Ac}^-$$

there is but one component on the left. Each molecule of HAc has a definite tendency to ionize which is not dependent on any other dissolved molecules or ion. Therefore the amount of acetic acid which will ionize in unit time depends solely on the amount present or

$$\text{vel}\ (\rightarrow) = k_1\,[\mathrm{HAc}]$$

The speed of the opposing reaction is given by

$$\text{vel}\ (\leftarrow) = k_2\,[\mathrm{H}^+]\,[\mathrm{Ac}^-]$$

and the condition of equilibrium is given in the expression

$$\frac{[\mathrm{H}^+] \times [\mathrm{Ac}^-]}{[\mathrm{HAc}]} = K$$

K is the ionization constant of acetic acid and has a numerical value of 0.000018 when concentrations are given in moles per liter.

Another example of equilibrium is that between sulphur trioxide and its dissociation products at a temperature above 500°.

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

The velocity towards the right is dependent on the number of collisions of SO_3 molecules with each other or

$$\text{vel } (\rightarrow) = k_1 [SO_3] [SO_3] = k_1 [SO_3]^2$$

The velocity toward the left is determined by the number of collisions of three different molecules or one oxygen molecule with two SO_2 molecules

$$\begin{aligned} \text{vel } (\leftarrow) &= k_2 [O_2] [SO_2] [SO_2] \\ &= k_2 [O_2] [SO_2]^2 \end{aligned}$$

and the equilibrium condition is determined by the expression

$$\frac{[SO_2]^2 \cdot [O_2]}{[SO_3]^2} = K$$

Interesting as the foregoing line of reasoning is, and logical as the deductions seem to be, the scientists who thought this out would at once have discarded it if they had not found that it agreed to a considerable degree of accuracy with the actual conditions found to exist in systems in equilibrium.

Thus actual measurements of the three components in solutions containing acetic acid, hydrogen ions, and acetate ions show that, whatever the actual concentrations, the ratio always has the same value, namely that of the equilibrium constant.

The importance of the manufacture of sulphuric acid has caused a great amount of study to be made of the equilibrium between sulphur dioxide, oxygen, and sulphur trioxide, and the validity of the law of molecular concentrations, as applied to this reaction, has been put to a rigid test.

The law is in fact of very wide application; it holds for non-ionic as well as ionic reactions. The degree of ionization of weakly ionized substances can be calculated with high precision according to the law. But the behavior of strong electrolytes does not conform as closely to this law, and the law is of value only in a qualitative fashion to predict the extent of the ionization of these substances. In this connection we may recall Rule 4 for writing ionized equations, which directed to treat all strong electrolytes as if they were completely ionized.

PROBLEMS

87. Acetic acid in 0.1 molal solution is 1.4 per cent ionized. Find the value of the ionization constant K.

$$\mathrm{HAc} \rightleftharpoons \mathrm{H}^+ + \mathrm{Ac}^-$$

$$\frac{[\mathrm{H}^+] \times [\mathrm{Ac}^-]}{[\mathrm{HAc}]} = K$$

88. Find the percentage ionization of acetic acid in molal solution. Take the value of the ionization constant as 0.000018 and solve the quadratic equation by the method of approximation.

89. What is the concentration of hydrogen ions in a 0.1 molal solution of acetic acid?

90. What is the concentration of hydrogen ions in a solution containing in a liter 0.1 mole of acetic acid and 0.1 mole of NaAc? Assume as an approximation that the salt is 100 per cent ionized.

91. For the sake of showing the different effects of a neutral salt of a strong acid upon the ionization of the acid, find first the ionization constant of nitric acid if it is 90 per cent ionized in 0.1 molal solution. Then using the constant thus found calculate the hydrogen-ion concentration in a solution containing, in 1 liter, 0.1 mole of HNO_3 and 0.1 mole of KNO_3. Assume in this calculation that the law of molecular concentration holds accurately. The result shows that the effect of a neutral salt of a strong acid upon the ionization of the acid is not marked as it is in the similar case of a weak acid. As a matter of fact, the actual effect is even less than that calculated according to the law.

92. The ionization constant of ammonium hydroxide is 0.000018. (*a*) Find the concentration of OH^- ions in a molal solution of NH_4OH. (*b*) Find the concentration of OH^- ions in a molal solution of NH_4OH which contains also 0.5 mole of NH_4Cl per liter, assuming the latter to be completely ionized.

93. What is the ionization constant of hydrocyanic acid if the ionization in 0.1 N solution is 0.01 per cent?

94. What is the hydrogen-ion concentration in a solution containing, in 1 liter, 0.1 mole of HCN and 0.1 mole of KCN, assuming the latter to be 100 per cent ionized?

SOLUBILITY AND SOLUBILITY PRODUCT

The solubility of a substance is defined as the concentration of the solution when it is in equilibrium with some of the undissolved substance. Such a solution in equilibrium is known as a saturated solution. Supersaturated solutions of many substances are possible when there is none of the undissolved substance in contact with the solution. At the surface of contact two processes are going on: (1) Molecules or ions are passing into solution at a constant rate per unit of surface. (2) Molecules or ions are depositing on the surface and thus building up the crystal structure of the solid, but the rate is dependent on the concentration of the dissolved substance. When these opposing rates are equal the solution is saturated. If the dissolved substance is a non-electrolyte there is a definite concentration which gives this equilibrium condition. If the substance is a salt and ionized in the solution there is also a definite concentration which gives the equilibrium provided the ions of the salt are present in equivalent amounts. We frequently have to consider cases in which we have two salts in solution which have an ion in common, for example, silver acetate and sodium acetate. The tendency to build up the silver acetate crystals is proportional to the concentration of the Ag^+ ions and of the Ac^- ions. The latter includes all the Ac^- ions, whichever salt they originally came from. Equilibrium is reached when the product of the concentration $[Ag^+] \times [Ac^-]$ has a definite value which is called the *solubility product.*

The solubility of AgAc at room temperature is 0.06 F.W. per liter. Therefore, in a saturated solution the concentration of each ion is 0.06 and the solubility product $= 0.06 \times 0.06 = 0.0036$. If we stir crystals of AgAc into a 0.1 formal NaAc solution the crystals will dissolve until equilibrium is reached and the product of $[Ag^+] [Ac^-] = 0.0036$. Let the solubility of AgAc per liter $= x$. Then $x = [Ag^+]$ and $x + 0.1 = [Ac^-]$ and

$$[Ag^+] [Ac^-] = x (x + 0.1) = 0.0036$$

Solving, $x = 0.028$, and therefore the solubility of AgAc in 0.1 N NaAc = 0.028 F.W. per liter.

When we consider the solubility of a salt in which the ions are of different valence, as for example lead iodide $PbI_2 \rightleftharpoons Pb^{++} + I^- + I^-$, the product must include as many concentrations as there are ions to make the neutral molecule. Thus the solubility of lead iodide is 0.002 F.W. per liter, the concentration of Pb^{++} ions is 0.002, and the concentration of I^- ions is 0.004 in the saturated solution. The solubility product of

$$PbI_2 = [Pb^{++}]\,[I^-]^2 = 0.002 \times 0.004^2 = 0.000{,}000{,}032$$

To determine the solubility of PbI_2 in a 0.1 formal solution of KI let $x =$ F.W. of PbI_2 per liter. Then $x = [Pb^{++}]$ and $2x + 0.1 = [I^-]$

$$[Pb^{++}]\,[I^-]^2 = x\,(2x + 0.1)^2 = 0.000{,}000{,}032$$

Solving, $x = 0.000{,}003$, and therefore the solubility of PbI_2 in 0.1 formal KI is 0.000,003 F.W. per liter.

PROBLEMS

95. The molal solubility of $AgBrO_3$ at 24.5° is 0.0081. How many grams of $AgBrO_3$ could dissolve in a liter of 0.1 molal $AgNO_3$? Assume complete ionization of the salts.

96. The solubility of $PbSO_4$ is 0.04 gram per liter at 25°. How many grams of sodium sulphate should be added to 1 liter to reduce the solubility of the lead sulphate to 0.0001 gram per liter?

Hydrogen Ion Concentration; The *p*H Scale

The properties common to all acids are due to hydrogen ions, but there are two ways in which the extent of the effect of hydrogen ions must be gauged. In the first place the normality of an acid solution is a measure of the amount of base it will neutralize. One liter of 1 *N* strong acid, such as HCl, will neutralize the same amount of base as 1 liter of 1 *N* weak acid, such as $HC_2H_3O_2$. The normality of an acid thus measures the total amount of available hydrogen ions. Yet the concentration of the active or ionized hydrogen in the HCl is about one hundred times as great as in the $HC_2H_3O_2$. Vinegar is about 3 per cent or 0.5 *N* acetic acid. Its taste is sour, but it is possible to hold it in the mouth and even swallow some of it. On the other hand, 0.5 *N* HCl is so extremely sour that it cannot be held in the mouth. The sour taste is proportional to the active H^+ ion concentration. Many other physiological effects, as well as effects in promoting industrial chemical reactions, are likewise proportional to the active H^+ ion concentration rather than to the total available H^+ ion, and it becomes important to have a convenient scale by which to measure this activity.

In 1 N strong acid, assuming complete ionization, the concentration of the H^+ ion is 1 mole per liter ($[H^+] = 1$). In pure water $[H^+] = 0.000,000,1 = 10^{-7}$, $[OH^-] = 0.000,000,1 = 10^{-7}$. Since the law of molecular concentration gives for the ionization of water

$$\frac{[H^+]\,[OH^-]}{[H_2O]} = K$$

and since $[H_2O]$ is constant for all dilute solutions it follows that

$$[H^+] \times [OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

and 10^{-14} is the ion product of water which is constant. In a 1 N solution of a strong base since $[OH^-] = 1$ the value of $[H^+]$ must be 10^{-14}.

With a range of hydrogen ion concentrations from 1 to 10^{-14} in solutions commonly used it has been found advantageous to adopt a logarithmic notation for expressing the concentration of the hydrogen ions. This is the so-called pH scale. The pH value is the logarithm to the base 10 of the number of liters of the solution in question which would contain 1 mole of active H^+ ions. When the concentration is expressed by the exponential method, the pH value is simply the exponent to the base 10 with the negative sign omitted.

THE pH SCALE

pH	$[H^+]$	*Normality of strong acid or base*	
0	10^0	1 N acid	
1	10^{-1}	0.1 N acid	
2	10^{-2}	0.01 N acid	
3	10^{-3}	0.001 N acid	
4	10^{-4}		Buffer Range
5	10^{-5}		
6	10^{-6}		
7	10^{-7}	exact neutrality	
8	10^{-8}		
9	10^{-9}		
10	10^{-10}		
11	10^{-11}	0.001 N base	
12	10^{-12}	0.01 N base	
13	10^{-13}	0.1 N base	
14	10^{-14}	1 N base	

Control of pH. Values of pH near the top and near the bottom of the scale may be definitely controlled by adjusting the normality of a strong acid or base. For values of 4 through 10 the amount of the strong acid or strong base which would be added to water is so small that its effect is commonly exceeded by that of uncontrollable impurities. However, by the use of *buffers* the pH value can be established precisely at any desired point and held there with extremely little change against large accidental additions of either acid or base.

Buffers. A mixture of a weak acid and a salt of that acid or a mixture of a weak base and a salt of that weak base serves as a buffer. Let us consider a liter of solution containing 0.1 F.W. of HAc and 0.1 F.W. of NaAc. The ionization constant of acetic acid is given in the expression

$$\frac{[\mathrm{H}^+]\,[\mathrm{Ac}^-]}{[\mathrm{HAc}]} = 0.000{,}018$$

which may be transposed:

$$[\mathrm{H}^+] = 0.000{,}018 \times \frac{[\mathrm{HAc}]}{[\mathrm{Ac}^-]} \tag{1}$$

Since [HAc] = 0.1 (the ionization of HAc is repressed to almost zero by the Ac^- ions of the salt) and $[\mathrm{Ac}^-] = 0.1$ (the 0.1 mole of salt is completely ionized)

$$[\mathrm{H}^+] = 0.000{,}018 \times \frac{0.1}{0.1} = 0.000{,}018 = \frac{18}{1{,}000{,}000} = \frac{10^{1.26}}{10^6} = 10^{-4.74}$$

The pH value of this buffered solution is therefore 4.74.

To appreciate the effectiveness of this buffer solution let us compare the effect upon the pH value of adding small amounts of strong acid or base to pure water and then to the buffered solution. If we add 1 cc. of 1 N HCl to 1 liter of pure water we obtain a solution 0.001 N in H^+ ions with a pH of 3. If, on the other hand, we add 1 cc. of normal HCl to 1 liter of the buffered solution, the reaction

$$\mathrm{H}^+ + \mathrm{Ac}^- \rightarrow \mathrm{HAc}$$

increases [HAc] by 0.001 and decreases $[\mathrm{Ac}^-]$ by 0.001 so that

$$[\mathrm{H}^+] = 0.000018 \times \frac{0.1 + 0.001}{0.1 - 0.001} = 0.0000184 = 10^{-4.735}$$

and the new *p*H value is 4.735, which is thus not materially changed from its original value.

If we add 1cc. of 1 *N* NaOH to 1 liter of pure water we obtain a solution 0.001 *N* in OH^- ions with a *p*H of 11. If on the other hand we add 1 cc. of 1 *N* NaOH to 1 liter of the buffered solution the reaction

$$OH^- + HAc \rightarrow H_2O + Ac^-$$

decreases [HAc] by 0.001 and increases $[Ac^-]$ by 0.001 so that

$$[H^+] = 0.000018 \times \frac{0.1 - 0.001}{0.1 + 0.001} = 0.0000176 = 10^{-4.755}$$

and the new *p*H value is 4.755, which again is not materially changed.

From the above equation (1) it is apparent that the maximum buffering action is obtained when the ratio of $\frac{\text{added weak acid}}{\text{added salt of that acid}}$ is unity, also that a numerically greater *p*H (lower $[H^+]$) can be obtained by lowering this ratio and a lower *p*H by increasing this ratio. However, to obtain an essentially greater *p*H value than 5 it would be more advantageous to use a weaker acid and its salt for the buffer.

The above reasoning applies to weak bases and their salts which may be advantageously used as buffers to establish *p*H values between 7 and 11.

It goes without saying that, although absolutely pure water has a *p*H value of 7, the *p*H value is subject to a variation of 1 or 2 units through almost unavoidable contamination from glass or from NH_3, H_2S, or CO_2 from the air, and that to maintain an unfluctuating value of 7 a buffer must be used.

INDICATORS

Indicators are highly colored substances which change in color at certain *p*H values. The color is so intense that the amount of indicator needed is so small that it itself has practically no effect in altering the *p*H value. There are a great many such indicators, and it is possible to choose a list covering the whole range of *p*H values. Thus, if a solution is colorless it is possible to apply to different portions of it the successive indicators in this list, and when the one is found which shows its color change in this solution the *p*H value of the solution is determined. Three of the most commonly used indicators are included in the following table.

Indicator	*Acid color*	pH *range of color transition*	*Basic color*
methyl orange	red	3.2–4.4	yellow
litmus	red	4.5–8.3	blue
phenolphthalein	colorless	8.3–10	red

PROBLEMS

97. From the per cent of ionization of hydrocyanic acid in 0.1 *N* solution find the value of the ionization constant of that acid.

98. Calculate the H^+ ion concentration in a solution 0.1 *N* in HCN and 0.1*N* in KCN. What is the *p*H value of this solution?

99. Calculate the *p*H value of 0.01 *N* acetic acid. What color would this solution impart to methyl orange?

100. Calculate the *p*H value of 0.01 *N* $HC_2H_3O_2$ containing 0.1 F.W. of $NaC_2H_3O_2$ per liter. What color would this solution impart to methyl orange?

CHAPTER IV

THE NON-METALLIC ELEMENTS IN BINARY COMPOUNDS

One of the distinctive chemical properties of non-metallic elements is their ability to combine with metals forming simple binary compounds in which they are the negative constituent. It is the purpose of this chapter to deal with such simple compounds of the more pronounced non-metals: chlorine, bromine, iodine, oxygen, sulphur, and nitrogen.

PREPARATION 5

COPPER OXIDE, CuO

The most obvious method of making a metal oxide is to heat the metal in air or oxygen, but the difficulty with such a method is that the oxide is solid and adheres to the surface, preventing the action on the metal underneath. Better results are obtained if an oxy-salt of the metal is prepared and then heated to a sufficient temperature to drive off the non-metal oxide and thus leave the oxide of the metal as a residue. Carbonates, nitrates, and some sulfates can be decomposed in this way.

Dilute nitric acid attacks copper, forming copper nitrate, a soluble salt, so that the surface of the metal remains free until the copper has all reacted. Copper oxide may be obtained by heating the solution, first to expel the water, and then with a somewhat stronger heat to decompose the residue of copper nitrate; oxides of nitrogen escape as red fumes, and copper oxide remains as a black solid. This is the method by which zinc was converted quantitatively into zinc oxide, page 24.

Since copper carbonate decomposes at a lower temperature than copper nitrate and yields an impalpable powder instead of black crusts, it is advantageous in this preparation to first precipitate copper carbonate (actually a basic carbonate) from the copper nitrate solution and after drying it, to heat the carbonate.

Materials: copper metal (turnings or wire), 13 grams = 0.2 F.W.
6 *N* HNO_3, 88 cc.
anhydrous sodium carbonate, Na_2CO_3, 30 grams.

Apparatus: 2-liter common bottle.
5-inch funnel.
8-inch porcelain dish.
4-inch porcelain dish.
600-cc. beaker.
Bunsen burner.
iron ring and ring stand.

Procedure: Put the copper in a 600-cc. beaker and under the hood add the nitric acid in small portions until solution is complete; observe Note 7, page 13. The mixture may be heated toward the end of the reaction if necessary. When all the copper has dissolved add 200 cc. of water and filter the solution, if it is not clear, into an 8-inch porcelain evaporating dish.

Dissolve 30 grams of anhydrous sodium carbonate in 300 cc. of water. Filter the solution if it is not clear. Pour 250 cc. of this solution into the copper nitrate solution. Stir the mixture and heat to boiling. The solid should turn nearly black. If this does not happen add small portions of the sodium carbonate solution until it does. Boil and stir the mixture for about 3 minutes. Allow the solid to settle in the dish and pour off most of the liquid. Stir up the solid with the remainder of the liquid and pour it into approximately a liter of cold water in a 2-liter bottle. Wash the solid by decantation until the soluble salts are reduced to less than one one-thousandth of the original concentration. (Estimate the volume of liquid poured into the bottle with the solid the first time. Follow Note 5 (*b*), page 10.)

Pour the solid onto a filter and allow it to drain as completely as possible. Spread the paper and its contents on a watch glass and continue the drying on the hot plate. Separate the black basic copper carbonate from the paper and place it in a 4-inch porcelain evaporating dish. Heat with a small flame, and stir the solid with a glass rod. A low temperature suffices to decompose the basic carbonate. When the solid has changed to a uniform black powder test it for carbonate. Place about 0.1 gram in a test tube, cover it with 5 cc. of water, and heat to the boiling temperature. We now have a suspension of the copper oxide from which all air has been expelled. Add a few drops of $6N$ HCl and observe very closely for "effervescence," that is, for bubbles of escaping gas. Such gas would be carbon dioxide and would show that the copper carbonate had not been entirely decomposed. When the test shows the absence of carbonate, transfer the solid to a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Could hydrochloric acid take the place of nitric acid in this preparation? Explain.
2. Basic copper carbonate is a variable mixture of copper carbonate and copper hydroxide. Assuming that it has the composition $Cu(OH)_2 \cdot CuCO_3$, write intersecting ionic equations to show how it is formed. What type of ionic reaction does this illustrate?

PREPARATION 6

HYDROGEN PEROXIDE AND BARIUM PEROXIDE HYDRATE, H_2O_2 AND $BaO_2 \cdot 8H_2O$

The ordinary oxide of barium has the formula BaO, and it forms the corresponding base $Ba(OH)_2$ when it combines with water. Barium salts are formed when this base is neutralized with acids. In addition there is another oxide of barium containing twice as much oxygen, BaO_2, which is easily obtained when barium oxide is heated to a dull red heat in air free from carbon dioxide.

This oxide, however, does not behave like an ordinary oxide; for example, it does not react with water to give such a base as $Ba(OH)_4$ nor with acids to yield such a salt as $Ba(NO_3)_4$. Both oxygen atoms seem to be present as a single radical having the same valence, namely 2, as the simple oxygen radical in ordinary barium oxide, because, when barium peroxide is treated with acids, the ordinary barium salt and hydrogen peroxide are formed.

$$BaO_2 + 2HCl \rightarrow BaCl_2 + H_2O_2$$

The name *peroxide* has been given to oxides which contain the O_2^{--} radical and which yield hydrogen peroxide when acidified with acids.

The common heavy metals do not form peroxides; only the most strongly metallic elements such as the alkali and alkaline earth metals do so. For example, when sodium metal burns freely in air the peroxide, Na_2O_2, is formed. It is difficult to limit the access of oxygen to burning sodium so as to obtain the ordinary oxide, Na_2O.

In the following preparation crude barium peroxide is treated with hydrochloric acid to obtain a solution of hydrogen peroxide. Crude barium peroxide invariably contains a little iron which appears in the solution as $FeCl_3$. The iron, however, is completely precipitated as the insoluble hydroxide if an excess of barium peroxide is used. The peroxide hydrolyzes, making the solution basic.

$$BaO_2 + 2H_2O \rightleftharpoons Ba(OH)_2 + H_2O_2$$
$$2FeCl_3 + 3Ba(OH)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3BaCl_2$$

Pure barium peroxide hydrate $BaO_2{\cdot}8H_2O$ is precipitated when barium hydroxide is added to a hydrogen peroxide solution. Hydrogen peroxide is not a stable substance; its solution decomposes slowly in any event into oxygen and water. This decomposition is greatly hastened by suspended solid matter and by hydroxyl ions; in the following preparation one should work to minimize the amount of this decomposition.

After removal of impurities by filtration, a solution of barium hydroxide is added whereby pure, crystalline barium peroxide hydrate $BaO_2{\cdot}8H_2O$ is precipitated.

Hydrogen peroxide may be regarded as a weak acid. It is excessively weak, the extent of its ionization being comparable with that of water itself. Yet its acid character is manifest from the way it reacts with barium hydroxide:

$$Ba(OH)_2 + H_2O_2 \rightarrow BaO_2 \downarrow + 2H_2O$$

Were the barium peroxide soluble this reaction would shortly come to equilibrium, but since the barium peroxide is very insoluble, the reaction is fairly complete. Sodium peroxide is soluble, and it hydrolyzes very extensively, as would be expected of the salt of so weak an acid; this is equivalent to the statement that the neutralization of sodium hydroxide by hydrogen peroxide is very incomplete.

Materials: 6 *N* HCl, 67 cc.
barium hydroxide, $Ba(OH)_2{\cdot}8H_2O$, 63 grams = 0.2 F.W.
crude BaO_2 40 grams.
ice.

Apparatus: 8-inch porcelain dish.
5-inch funnel.
2-liter common bottle.
600-cc. beaker.
suction filter and trap bottle.
mortar and pestle.
Bunsen burner.
iron ring and ring stand.

Procedure: Dissolve the barium hydroxide in 500 cc. of warm water and pour through a filter, without suction, into a 2-liter bottle. Add 1 liter of cold water.

While the filter is draining place the HCl, 250 cc. ice water, and about 100 grams ice in an 8-inch porcelain dish. Grind the BaO_2 in a mortar with water until a smooth uniform paste is obtained and add enough water to make 100 cc. Add the BaO_2 suspension, a little at a time, with constant stirring, to the cold HCl solution until the BaO_2 ceases to dissolve. Then add the remainder of the BaO_2 suspension all at once and stir until the suspension has turned brown due to the precipitation of $Fe(OH)_3$. Then filter the solution without suction into a 600-cc. beaker.

Pour, in a thin stream, with constant stirring, the hydrogen peroxide solution into the barium hydroxide solution in the 2-liter bottle. Let the flaky barium peroxide hydrate settle and then collect it on a suction filter. As soon as the water is drawn out, shut off the suction, wash with 15 cc. cold water, press the solid into a compact cake, and again suck dry. Do not draw any quantity of air through the product. Wrap the crystals in paper towels and dry them according to Note 9 (*b*), page 15. Preserve the product in a 4-ounce cork-stoppered bottle.

QUESTIONS

1. Explain why barium chloride would not give a precipitate with hydrogen peroxide.

2. The hydrogen peroxide solution obtained as an intermediate product in this preparation contained barium chloride. Suggest with what reagent one might treat the purified barium peroxide hydrate to obtain a pure solution of hydrogen peroxide. Give explanation.

PREPARATION 7

HYDROCHLORIC ACID, HCl

Hydrogen chloride may be formed by direct synthesis from the elements. Although this method has been used on a commercial scale and yields a very pure product, it is not the one commonly used. It is far more convenient to treat sodium chloride with concentrated sulphuric acid. The volatile hydrogen chloride escapes from the reaction mixture and the reaction goes to completion.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$$

The gas is dissolved in water to give hydrochloric acid.

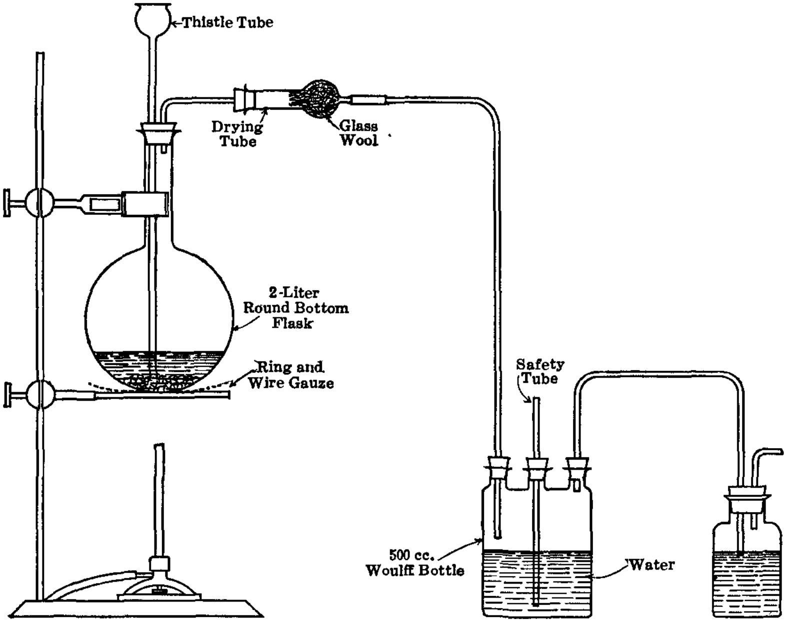


FIG. 18

Materials: sodium chloride, rock salt, NaCl, 117 grams = 2 F.W.
36 *N* sulphuric acid, 222 cc.

Apparatus: 2-liter round-bottom flask.
500-cc. Woulff bottle, 3-necked.
8-ounce wide-mouth bottle.

thistle tube.
2-hole rubber stopper to fit flask and bottles.
three 1-hole rubber stoppers to fit Woulff bottle.
one 1-hole rubber stopper to fit drying tube.
glass delivery tube fitted as in diagram.
drying tube packed with glass wool.
pan of cold water.
8-ounce glass-stoppered tincture bottle.
burette clamp. Bunsen burner.
iron ring and ring stand.

Procedure. Set up the apparatus as in Fig. 18 with the rock salt in the large flask and 150 cc. of water in each absorption bottle. Pour enough of the sulphuric acid through the thistle tube to seal the lower end of the tube. Watch the action carefully to see that the foam does not rise into the neck of the flask. As rapidly as seems safe add the rest of the sulphuric acid. When the action slackens apply heat very cautiously to the flask and finally heat it strongly until all the salt has dissolved and effervescence has ceased. When the reaction is finished remove the burner. Apply a gentle suction to the exit tube in the second absorption bottle and draw all the hydrogen chloride from the large flask into the absorption bottle.

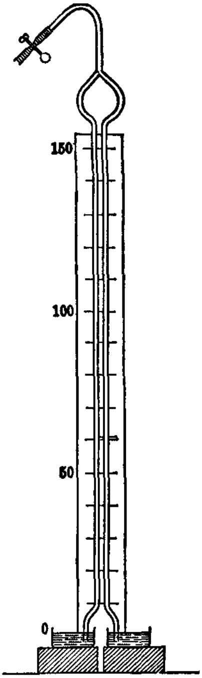


FIG. 19

FIGURE 19

The scale at the back is marked off in divisions of 0.1 inch. The acid is placed in the shallow dish at the left and water in the dish at the right, both being at the same temperature. The level is adjusted in both dishes so that the surface of each liquid is exactly at the zero point of the scale. Suction is applied at the top until the acid rises exactly to the 100 mark when the pinch cock is closed. The reading of the scale at the top of the water column divided by 100 gives the specific gravity of the acid.

Allow the contents of the flask to cool until crystals of $NaHSO_4$ begin to form. Wrap a towel around the neck of the flask. Cautiously pour the contents of the flask into running water under the hood. If allowed to cool completely the by-product of the reaction will form a solid cake and the flask may be broken in trying to remove it. It is important, however, to allow the contents of the flask to cool nearly to room temperature before the mixture of acid and acid sulphate are poured into water.

When the hydrochloric acid has cooled to room temperature determine the volume and the specific gravity of the solution in both absorption bottles. Use either a hydrometer or the apparatus shown in Fig. 19. Consult the table on page 371 and determine the percentage composition of the preparation. Calculate the weight of hydrogen chloride obtained, the normality of the solution, and the percentage yield.

Practically all the hydrochloric acid will be found in the first absorption bottle. Transfer this to a 250-cc. narrow-necked glass-stoppered bottle.

QUESTIONS

1. How much of an excess of sulphuric acid was used in this preparation? What is the advantage of using such an excess?
2. Why was air drawn through the apparatus after the reaction was complete?
3. What conditions are necessary for the formation of Na_2SO_4 in the preparation of HCl? Why is $NaHSO_4$ called an acid salt?

PREPARATION 8

HYDROBROMIC ACID, HBr

The obvious method for preparing hydrobromic acid would be to treat solid sodium bromide with concentrated sulphuric acid. This is not a successful method, however, owing to the fact that hydrogen bromide reacts to some extent with concentrated sulphuric acid according to the equation

$$H_2SO_4 + 2HBr \rightarrow 2H_2O + SO_2 + Br_2$$

and the gas passing over to the absorption bottles would be contaminated with sulphur dioxide and bromine. To prepare pure hydrobromic acid it is necessary to employ a different procedure.

The method we shall use starts with bromine and allows it to react with red phosphorus and water. Phosphorus and bromine combine very easily to form PBr_3, but the phosphorus bromide hydrolyzes completely and hydrogen bromide passes over to the absorption flask.

$$PBr_3 + 3H_2O \rightarrow P(OH)_3 + 3HBr$$

Materials: bromine, 40 grams = 12.5 cc. = 0.25 F.W.
red phosphorus, 7 grams.
sand.
broken glass.

Apparatus: 125-cc. separatory funnel.
300-cc. flask.
two 4-inch side arm U-tubes.
8-inch plain U-tube.
one 1-hole rubber stopper to fit flask.
4 solid rubber stoppers to fit small U-tubes.
one 1-hole rubber stopper to fit large U-tube.
glass delivery tubes as in diagram.
glass wool.
3 ring stands.
4-inch iron ring.
4 burette clamps.

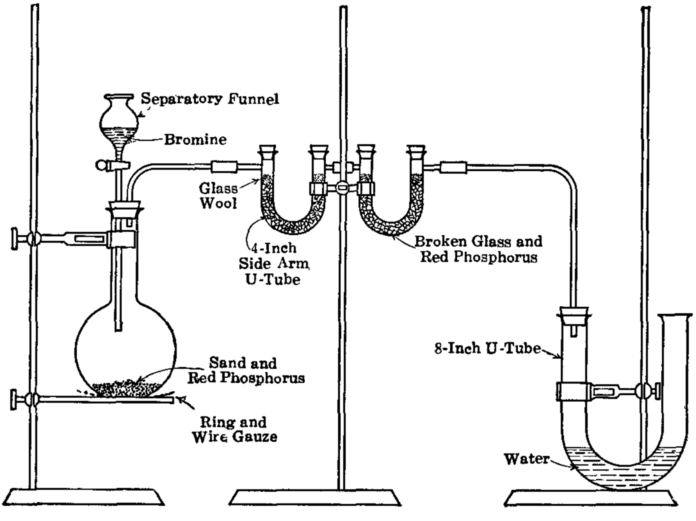


FIG. 20

Procedure: After carefully studying the diagram (Fig. 20) construct the apparatus. Place 6 grams of the red phosphorus, 12 grams of sand, and 6 cc. of water in the flask. The success of this preparation depends very largely on the care with which the phosphorus is spread out over the surface of the broken glass in the small U-tubes. To this end mix 2 grams of the phosphorus and 25 grams of the broken glass by shaking in a 300-cc. flask.

The phosphorus will not stick to the glass. Add water one drop at a time, shaking after each addition until the phosphorus adheres to the glass, but avoid using enough water to give any appearance of wetness. Place the uncoated broken glass in the bend of each small U-tube and fill the vertical arms nearly up to the side arm with the glass coated with phosphorus. Pack a little glass wool on top of the broken glass. Pour 25 cc. of distilled water, or enough to close the bend, into the large U-tube. *Caution: Use extreme care in handling bromine.* The liquid produces severe burns on the skin and the vapor is very irritating to the eyes and throat. Make sure that the stop cock of the separatory funnel is tight, properly lubricated, and turns easily. When manipulating it after the bromine has been added, hold the bulb with one hand, and exert a slight inward pressure on the stop cock while turning it with the other hand. Be very careful that the cock does not slip out of the socket letting the bromine leak out over the fingers.

After making sure that the apparatus is tight, measure the bromine and pour it into the funnel. Then let a single drop of bromine fall into the flask, watching its effect. Add the rest of the bromine a drop at a time as rapidly as proves safe. After the gas ceases to be absorbed in the large U-tube disconnect the apparatus. When the hydrobromic acid has cooled to room temperature determine its volume and specific gravity. Use either a hydrometer or the apparatus shown in Fig. 19. Consult the table on page 371 and determine the percentage composition of your solution. Calculate the weight of hydrogen bromide obtained, the normality of the solution, and the percentage yield. Preserve your preparation in a 2-ounce glass-stoppered bottle. Wash out the apparatus at the sink under the hood.

QUESTIONS

1. Why would not a metal like zinc, which will combine vigorously with bromine, serve instead of phosphorus?
2. Explain why phosphorus is placed in the small U-tubes.
3. Explain why at the outset of the process bubbles pass outward through the large U-tube, and later they pass in the opposite direction.
4. What are the products of the reaction of concentrated sulphuric acid with potassium bromide? (See Experiment 13, page 167.) Write the equations. What property possessed by hydrogen bromide, but not by hydrogen chloride, is shown?

PREPARATION 9

BARIUM CHLORIDE, $BaCl_2 \cdot 2H_2O$

A general method of preparing a salt is by neutralizing an acid with the appropriate base. It is almost as effective to use the carbonate of the metal as the base, because carbonic acid is so easily displaced. Barium carbonate is found naturally as the mineral witherite, which contains iron and silica as impurities. In this country barium carbonate (known as "precipitated" barium carbonate) is made commercially by reducing barium sulphate to sulphide, and converting the latter to the carbonate by means of carbon dioxide. The resulting product frequently contains silica, barium sulphate, barium sulphide, and iron as impurities. After the acid has been neutralized with barium carbonate a little barium peroxide is added to the mixture. The barium peroxide is nearly insoluble, but it does hydrolyze to a small extent forming barium hydroxide and hydrogen peroxide. Any iron present is oxidized and precipitated as ferric hydroxide.

$$4\ BaO_2 + 8\ H_2O + 4\ FeCl_2 = 4\ Fe(OH)_3 + 4\ BaCl_2 + 2\ H_2O_2$$
$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

After the solution has been filtered it is made acid with hydrochloric acid.

Materials: barium carbonate, $BaCO_3$.
barium peroxide, BaO_2, 3 grams.
hydrochloric acid.

Apparatus: 8-inch porcelain dish.
5-inch funnel.
8-inch crystallizing dish and cover.
two 5-inch watch glasses.
iron ring and ring stand.
Bunsen burner.

Procedure: The hydrochloric acid obtained in Preparation 7 may be used for this preparation or 166 cc. of 12*N* HCl (2 F.W.) may be used. Calculate the weight of barium carbonate required to convert your sample of hydrochloric acid into barium chloride.

Pour the acid into an 8-inch porcelain evaporating dish and add enough water to make 600 cc. of solution. Remove 10 cc. of this dilute acid and save it for use later in the preparation. Add the solid barium carbonate in small portions. Stir the mixture after each addition. (If the carbonate is added too rapidly the mixture will froth out of the dish.) After all the carbonate has been added heat the mixture to boiling. Add an additional 5 grams of barium carbonate and test the solution with litmus paper. If it is not neutral add barium carbonate in small portions until the acid is completely neutralized and an excess of carbonate is present. Add 3 grams of barium peroxide, stir the mixture, and boil it gently for 5 minutes. Enough water should be added to make the total volume 600 cc.

Filter without suction into a 600-cc. beaker, keeping both the funnel and the beaker covered with watch glasses to prevent the solution from cooling and crystallizing prematurely. Add the reserve 10 cc. of dilute HCl to the filtrate and make sure that a drop of the solution will turn litmus red. Pour the solution into the crystallizing dish and allow it to stand uncovered until a satisfactory crop of crystals is obtained. Barium chloride has a tendency to "creep." To prevent this it is advisable to grease the rim of the crystallizing dish. Decant the liquid from the crystals, and wash them with a little distilled water. Dry them thoroughly at room temperature on white paper towels.

QUESTIONS

1. How could you show that your preparation is a hydrate?
2. Barium carbonate dissolves in water to the extent of 0.0023 gram in 100 cc. of water. Explain how it was possible to dissolve the carbonate since it is so insoluble. Write an ionic equation.
3. Write equations to show how barium carbonate is prepared from barium sulphate. Indicate the conditions for each step.
4. Dissolve a small amount of your preparation in 10 cc. of water. Divide this solution into three portions. To one add a drop of sulphuric acid; to the second add a drop of potassium chromate; to the third add a drop of silver nitrate. Record your observations and write ionic equations for each reaction.
5. To a solution of barium hydroxide add a few drops of hydrogen peroxide. Record your observations and write an equation. What is the rôle of hydrogen peroxide in this reaction?
6. To a solution of $BaCl_2$ add H_2O_2 and explain why the same effect is not observed as in Experiment 5.

PREPARATION OF OTHER BARIUM SALTS

By suitable modification, the procedure used to prepare barium chloride may be adopted to prepare other barium salts such as the acetate, bromide, and nitrate. The final volume of the solution should be adjusted so as to give a nearly saturated solution at 25°. The solubility of these salts will be found on page 365.

PREPARATION 10

ALUMINUM SULPHIDE, Al_2S_3

Although the obvious method of preparing a binary compound would seem to be to bring the two elements together, such a procedure is not very often followed. Aluminum and sulphur can be made to combine directly, it is true, but when the finely divided substances are mixed and the mixture is heated, either the sulphur entirely distils off without any reaction taking place, or if a reaction starts it is too violent to control. We have, therefore, selected lead sulphide as a source of the sulphide radical because this substance is not volatile and cannot escape before it reacts, and the reaction is not too violent. A part of the energy furnished by the combination of aluminum and sulphur is expended in separating lead and sulphur.

Materials: granulated aluminum, Al, 27 grams = 1 F.W.
pulverized galena, lead sulphide, PbS, 359 grams (a fairly pure sample of the mineral must be used to obtain good results).

Apparatus: 30-gram clay crucible without cover.
6-inch sand bath pan.
gas furnace.

Procedure: Mix the powdered galena and granulated aluminum. Place the mixture in the clay crucible and put it in the gas furnace. Place the cover on the furnace and if possible slip it a little toward the front, so that, by standing on a stool, one can look down through the hole in the cover and see the charge in the crucible. Light the furnace and heat it as rapidly as possible. Make sure the iron pan is dry by holding it with the tongs over the furnace. *Caution:* If the pan should be wet, the heat of the molten material poured into it would cause an explosive formation of steam. Watch the furnace every moment of the time after it begins to get hot. A white puff of smoke indicates that the reaction is taking place. If one can see the charge one can see an incandescence rapidly spread through it. After this reaction, leave the crucible in the furnace for 30 seconds, then remove it with the tongs and pour the liquid contents into the iron pan. Leave the latter unmoved until the contents have solidified. Then, working in the furnace room, crack the brittle aluminum sulphide from the lead; place the latter in the box for scrap lead, and pack the aluminum sulphide in a 2-ounce common bottle fitted tightly with a cork stopper. *Caution:* Aluminum sulphide reacts with the moisture of the air producing hydrogen sulphide. Do not take any part of the preparation outside of the furnace room except the well-stoppered bottle of product. The crucible with adhering aluminum sulphide can best be disposed of by putting it in a pail of water as soon as it is cool, thus getting rid of the hydrogen sulphide all at once.

QUESTIONS

1. *Experiment.* Drop a small lump of aluminum sulphide (at the hood) into a test tube of water. What is the gas formed, and what is the insoluble residue left? This is a case of hydrolysis. Write the equation in ionized form, and name the acid and the base.

2. Lead sulphide does not hydrolyze. Compare the basic strength of $Pb(OH)_2$ and $Al(OH)_3$. Does this fully account for the difference? Perhaps the relative solubility of PbS and Al_2S_3 would account for some of the difference. Explain how. Would this explanation require the solubility of Al_2S_3 (as such) in water to be greater or less than that of PbS?

PREPARATION 11

CALCIUM SULPHIDE, CaS

In this preparation an oxy-salt of sulphur, calcium sulphate, is reduced at a high temperature by means of carbon. Calcium is too active to be reduced to the metal by this means, but sulphur is readily reduced from its valence of $+6$ to its minimum valence of -2.

The most abundant source of calcium sulphate is the mineral gypsum $CaSO_4 \cdot 2H_2O$. We desire anhydrous $CaSO_4$ as our starting material, but plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$, which is made in enormous quantities by gently heating gypsum, is so available that we shall choose it and let it become fully dehydrated in the furnace.

Materials: plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$, 145 grams = 1 F.W.
powdered charcoal, C, 48 grams.

Apparatus: 30-gram clay crucible and cover.
gas furnace.

Procedure: Unless the charcoal is already very finely powdered, grind it thoroughly in a large porcelain mortar. Add the plaster of Paris, mix the two materials, and pack the mixture in the clay crucible. Heat the crucible in a gas furnace to between a bright red and a yellow heat for 1½ hours. At the end of this time remove the crucible from the furnace. When cold, inspect the contents of the crucible, particularly the inner portions to which the heat would have penetrated least; there should be no unburned charcoal left; a small sample should dissolve with effervescence (hood) in hydrochloric acid and leave no residue more than a slight turbidity.

QUESTIONS

1. Treat a gram of calcium sulphide with 20 cc. of water. Is there any visible change? Filter. Add hydrochloric acid to the filtrate. What is dissolved in the filtrate? What is the substance on the filter? Write equations.
2. Evidently calcium sulphide hydrolyzes extensively. Explain how this is possible without the evolution of hydrogen sulphide. Write equation. Compare this case of hydrolysis with that of aluminum sulphide.

PREPARATION 12

MERCURIC SULPHIDE, HgS

Mercuric sulphide is conveniently made by direct synthesis from the elements. Two modifications of this compound are known, one black, which is formed first in this preparation and also by precipitation of mercuric and sulphide ions; the other a brilliant red (vermilion), which is more stable and into which the black form tends to change.

Materials: mercury, Hg, 20 grams = 0.1 F.W.
flowers of sulphur, 8 grams.
6 *N* KOH, 15 cc.
saturated Na_2SO_3 solution 50 cc.
sodium sulphide solution.

Apparatus: 4-inch porcelain dish.
large porcelain mortar.
warm closet or plate at about 50°.
600-cc. beaker.
glass spatula.
iron ring and ring stand.
Bunsen burner.

Procedure: Place the mercury and the sulphur in a large porcelain mortar, and triturate the mixture, moistening it with sodium sulphide solution. When the globules of metallic mercury seem to have entirely disappeared, add the KOH solution and with it rinse as much as possible of the black paste into the 4-inch dish. Use 10 cc. of water to finish rinsing the material into the evaporating dish. Cover the dish with a watch glass and let it stand in some place at a temperature of about 50°. Replace the water lost by evaporation as often as each day. Stir the mass thoroughly each time with a glass spatula.

When, at the end of about a week, the mass has changed to a pure red color, wash it by decantation (see Note 5 (*b*), page 10) in a 600-cc. beaker. Most of the excess of sulphur is floated off. Then rinse the red sulphide back into the evaporating dish, leaving behind in the beaker any lumps of black sulphide or globules of mercury. Boil the red sulphide with 50 cc. of saturated sodium sulphite solution to remove the last of the uncombined sulphur; wash by decantation with boiling water and collect the mercuric sulphide on a suction filter. Dry the product on the hot plate and preserve it in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Red and black sulphides of mercury have exactly the same composition, as expressed by the empirical formula HgS. Would you regard them as the same or as different substances? Give your arguments.

2. What explanation can you give for the action of potassium hydroxide in facilitating the change of the black to the red modification?

PREPARATION 13

ALUMINUM NITRIDE, AlN

The very active metals are capable of combining directly with nitrogen to form nitrides. In the air the oxide is formed so much more readily, that nitride formation is likely to escape notice; but if the metal is presented in powdered form in a thick mass the oxygen is all combined in the surface layer and only nitrogen penetrates to the interior where pure nitride is formed.

Although aluminum is a very active metal, it enters into many reactions with extreme difficulty on account of a thin, tenacious coating of oxide, which keeps it physically separated from the reacting material. Aluminum powder alone cannot be made to burn in air, but when it is mixed with lampblack and any part is brought to the kindling temperature, which is very high, the combustion spreads throughout the mass. The function of the carbon is to react with this oxide layer. Carbon alone reacts with aluminum oxide to yield the carbide

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO$$

In the presence of nitrogen, however, the nitride instead of the carbide is produced.

$$Al_2O_3 + N_2 + 3C \rightarrow 2AlN + 3CO$$

Materials: finely powdered aluminum, 45 grams. The material sold for use as a pigment and often labeled "aluminum bronze" is nearly pure aluminum and is suitable for the purpose. The small amount of oil which it contains is no disadvantage.
carbon, lampblack, 5 grams.
magnesium ribbon, 4 inches.

Apparatus: 8-inch square of asbestos paper to be laid on a thick iron plate.
large porcelain mortar and pestle.
dark-colored glasses may be worn to protect the eyes from the blinding light.
Bunsen burner.

Procedure: Mix the aluminum powder and lampblack thoroughly in a mortar. Heap up the mixture in as compact a mound as possible on the asbestos paper. The latter must be placed on a thick iron plate and in a safe location, for the heat will be so intense as to burn through the asbestos. Insert the magnesium ribbon 0.5 inch into the top of the pile and light the free end from the gas flame. The temperature of the burning magnesium is high enough to set fire to the mixture, but the spot thus ignited is quite likely to cool off before the combustion can get well started. As soon as the ribbon has burned down to the surface of the pile, play the gas flame over the hot spot, until the combustion is thoroughly under way. Although the Bunsen flame alone is not hot enough to bring the mixture to the kindling point, it prevents the spot heated by the magnesium from cooling rapidly. Watch the combustion spread throughout the mixture, but do not look at the intense light for more than a second at a time unless the eyes are protected with colored glasses. When the ash is cool, break it up, remove as much as possible of the white aluminum oxide crust from the outside, and preserve the nitride in a 4-ounce cork-stoppered bottle.

QUESTIONS

1. Examine the aluminum nitride and describe its appearance.
2. Treat a little with cold water and then with hot water. Is there any reaction?
3. Treat a little with NaOH solution and warm. Is ammonia given off? What type of reaction is this? (See next preparation.)
4. Why does the hydrolysis of aluminum nitride take place in NaOH solution but not in pure water? (See Experiment 9, Chapter II, p. 69.)
5. Heat a little aluminum nitride in the open air to see how easily it can be converted to oxide.

PREPARATION 14

MAGNESIUM NITRIDE, Mg_3N_2

AMMONIUM CHLORIDE, NH_4Cl

Magnesium nitride is prepared by the same general principle as that employed in preparing aluminum nitride (Preparation 13). If, however, a pile of magnesium were allowed to burn freely in the open air, a much greater conversion of nitride into oxide would occur before the reaction died out. The reaction is, therefore, more carefully regulated by being carried out in a crucible which is heated from an external source.

Magnesium nitride differs from aluminum nitride in that it hydrolyzes rapidly with pure water; in fact, it does so with considerable violence. Insoluble magnesium hydroxide and volatile ammonia are formed.

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Materials: powdered magnesium, 10 grams.
dry sand, 50 grams.

Apparatus: iron crucible of 25-cc. capacity and cover.
two 300-cc. flasks.
500-cc. filter flask.
125-cc. separatory funnel.
8-inch U-tube.
4-inch porcelain dish.
thistle tube.
three 2-hole rubber stoppers.
one 1-hole rubber stopper.
asbestos paper.
wire triangle.
iron ring and 2 ring stands.
Bunsen burner.
mortar and pestle.

Procedure: Weigh an iron crucible of about 25-cc. capacity together with the cover. Pack it even full with powdered magnesium, tapping the crucible on the desk to make the powder settle. Weigh the filled crucible; it should hold about 10 grams of the powder. Place the cover tightly on top; surround the crucible on the triangle with a cylinder of asbestos 3 inches in diameter so as to diminish the loss of heat by radiation. Heat the crucible as hot as possible with a Bunsen burner for 45 minutes. After it cools empty the crucible on to a piece of paper and note the white MgO on top and the yellow Mg_3N_2 beneath. Place the material in a mortar, break up the lumps, add 25 grams of dry coarse sand, and mix well. Then place 25 grams of sand in the bottom of a dry 300-cc. flask and pour the mixture from the mortar on top of it.

Use this as the generating flask *A* in Fig. 21. Assemble the rest of the apparatus as shown. Pour 50 cc. of water in the absorption flask *C*. The water should seal the bottom of the thistle tube *h* but should stand about $\frac{1}{4}$ inch below the end of the delivery tube *g*. Place 10 cc. of $6N$ HCl in the absorption tube *D*, and then add enough water to seal the bend. Remove the stopper and fittings from the generating flask *A*. Pour water into the separatory funnel *i* and open the stop cock until the stem of the tube has filled with water. Replace the stopper in the flask and open the stop cock to admit a single drop of water. Add another drop as soon as the reaction subsides, and continue to add a single drop at a time until the reaction becomes less violent. Finally add enough water to make 70 cc. Rock the flask until the contents are thoroughly mixed, then while still rocking it apply a small flame until the liquid boils. Boil gently for 15 minutes. Pour together

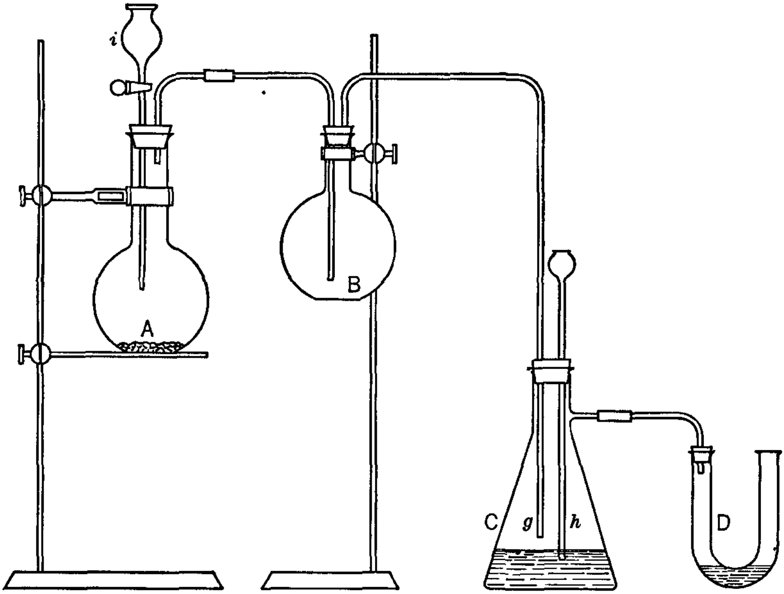


FIG. 21

APPARATUS FOR DISTILLATION OF AMMONIA FROM MAGNESIUM NITRIDE

A = Generating flask. B = Trap to catch solid matter entrained with gas and steam. C = Absorption flask with pure water in bottom. D = Absorption tube, bend sealed with dilute acid.

the contents of the absorption flask and the absorption tube, and, using litmus as an indicator, add enough more 6 N HCl to just neutralize the ammonia in the absorption flask. Evaporate the solution in a porcelain dish on the hot plate to obtain solid ammonium chloride, according to Note 6 (*b*), page 12. Preserve the product in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Burn a little calcium in the air and test the ash for nitride. How?

2. Give reasons for regarding the action of magnesium nitride with water as an example of hydrolysis. Remember that hydrolysis is the exact reverse of neutralization and produces an acid and a base from a salt and water. What is the acid and what is the base in this case?

3. Why is it necessary to mix the magnesium nitride with an inert material such as sand before adding water?

4. The layer from the top of the crucible will often contain a black substance as well as a white, particularly so if the gases from the flame entered under the lid of the crucible. What is this black substance, and why does it form?

5. On the basis that air contains 4 volumes of nitrogen to 1 volume of oxygen and that all the oxygen and nitrogen that enter under the lid of the crucible combine to form solid oxide and nitride, calculate what fraction of the magnesium would be converted to nitride.

Experiments

VALENCE

The elements are divided into two classes, metals and non-metals. Chemically the properties of the metals are as different from those of the non-metals as physically, for the metals form the electropositive constituents of compounds, whereas the non-metals form the electronegative constituents.

It must be remembered that an uncombined element is electrically neutral, but every element, with the exception of the rare gases, has a more or less strong tendency to assume an electrified condition, the strength of which tendency is indicated by the position of the element in the electromotive series. When a metal and a non-metal combine chemically with each other we can conceive of the action as consisting merely of a transfer of electricity so that the metallic constituent becomes positively charged and the non-metallic constituent negatively charged. The electrostatic attraction between the charges holds the constituents rigidly in place in a solid compound, and so the solid substance is a non-conductor. We have seen in Chapter III that many compounds, *viz.*, acids, bases, and salts, when they are dissolved in water give a solution which conducts an electric current. The compounds are *ionized* in the solution. Our idea of ionization by no means signifies that the opposite charges have been separated from each other; it simply regards the single positive constituent as no longer bound exclusively to a particular negative constituent, but as free to wander about through the solution holding under its attractive force first one negative constituent, then another, and so on.

Were it not for the discovery of ionization, we perhaps would never have suspected that the constituents of compounds are electrically charged. This conclusion, however, seems to be well warranted, and it is for this reason that one speaks of metallic elements as positive and non-metallic elements as negative when they are combined, even in compounds that are not ionized.

The number of charges associated with a simple ion as Al^{+++} or Cl^{-} determines its *valence*, the valence of aluminum thus being $+3$ and that of chlorine -1 in the compound aluminum chloride. Such a compound of two elements is called a binary compound, and the constituents are held by the forces of the *primary* valence. It is the purpose of this chapter to study the behavior of the non-metallic elements in binary compounds in which they show their primary negative valence.

OXIDES

Nearly all the elements combine with oxygen forming simple binary compounds.

No divalent negative ion of oxygen, O^{--}, has ever been found; nevertheless the valence of oxygen is believed to be -2 because of the composition of these compounds.

1. Treat a little cupric oxide with hydrochloric acid. The liquid acquires a blue color and the black solid finally disappears entirely. Evaporate the solution and a residue is left which becomes brown on further heating.

The brown residue is anhydrous cupric chloride in which the oxygen of cupric oxide has been replaced by an equivalent amount of chlorine.

$$CuO + 2HCl \rightarrow H_2O + CuCl_2$$

The primary valence of all the elements concerned in this reaction has remained unchanged, the elements have simply "exchanged partners," the type of reaction being metathesis. This instance is typical of the reaction of metal oxides with acids. The oxygen is simply exchanged for an equivalent amount of acid radical and the valence of the metal is not altered.

DIFFERENT BEHAVIOR OF OXIDES AND PEROXIDES

Hydrogen peroxide, H_2O_2, contains, for a given amount of hydrogen, twice as much oxygen as does water, and the additional amount of oxygen is held in an unstable state of combination. Pure hydrogen peroxide is explosive; in dilute solution it gives off one-half its oxygen more or less rapidly but not explosively. In pure solutions this decomposition proceeds so slowly that it is practically imperceptible; but many substances act as catalyzers for the reaction, notably platinum and manganese dioxide.

2. To 10 cc. of a 3 per cent solution of hydrogen peroxide in a test tube, add a pinch of powdered manganese dioxide. Note that a vigorous effervescence ensues and that the escaping gas will cause a glowing splinter to burst into flame.

3. Test for Hydrogen Peroxide. To 2 cc. of 3 per cent hydrogen peroxide solution add 18 cc. of water, thus making the volume 20 cc. Mix thoroughly, pour about 15 cc. of the solution into a test tube, and add 1 cc. of a solution of titanium sulphate.* Note the characteristic yellow color. This is one of the standard tests for hydrogen peroxide. Determine the delicacy of the test by repeating it successively with smaller and smaller amounts of hydrogen peroxide, as follows: take 2 cc. of the remainder of the diluted solution and dilute it to 20 cc. by adding 18 cc. of water. Test 15 cc. of this solution by adding 1 cc. of titanium sulphate, and reserve 2 cc. for further dilution. Proceed in this way with successive dilu-

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* Prepared by fusing 1 part of titanium dioxide with 15 to 20 parts of potassium bisulphate and dissolving the mass in 500 cc. of cold 6 *N* sulphuric acid.

tions according to the powers of 10 until a solution is obtained which shows a distinct yellow color with the titanium sulphate, while the next dilution fails to show the test. In the final tests add 1 cc. of reagent to 15 cc. of pure water and hold this beside the sample being tested, looking through the length of the column of liquid and placing a piece of white paper for a background. By comparing with a " blank " (the pure water plus reagent) in this way the fainter colors may be recognized with much more certainty. Express the sensitiveness of the test as the number of parts of water in which 1 part by weight of hydrogen peroxide can be diluted and still give a distinct test. This test is characteristic for hydrogen peroxide and can be used to differentiate peroxides from simple oxides and dioxides.

We are now going to investigate the behavior of a number of oxides with acids and we are going to use the titanium sulphate reagent to discover whether or not hydrogen peroxide is formed by the action.

4. Peroxides. (*a*) To 1 gram of barium peroxide, BaO_2, in a small beaker add 15 cc. of water and then $6\,N$ HNO_3 drop by drop with continuous stirring until the solid has dissolved. Test the solution for hydrogen peroxide by adding titanium sulphate. In order to convince yourself whether or not the effect could have been caused by the nitric acid, treat 1 gram BaO_2 with 5 cc. of water and 5 cc. $6\,N$ H_2SO_4. Here a clear solution cannot be obtained because insoluble barium sulphate forms. Filter off the insoluble residue and test the filtrate with titanium sulphate. The same yellow color is obtained as before.

(*b*) Test barium oxide BaO in the same way. Since this oxide reacts vigorously with water to form the hydroxide, $Ba(OH)_2$, we might as well use the hydroxide as a starting point, but should bear in mind that it is essentially the same thing as the oxide BaO. No yellow color appears when titanium sulphate is added.

(*c*) Heat a porcelain crucible cover on a triangle to redness; drop upon it a piece of sodium metal the size of a small pea, and remove the flame. The sodium burns to form sodium peroxide Na_2O_2. Place 50 cc. of cold water and 5 cc. of $6\,N$ H_2SO_4 in a small dish; let the porcelain and adhering sodium peroxide cool completely, and then drop it into the dilute acid. Test the solution with titanium sulphate. The characteristic test will be obtained.

(*d*) Prepare another sample of sodium peroxide in the same way. Scrape it off the porcelain into a dry test tube. Add 5 cc. of water. Note the effervescence and that the gas inflames a glowing splinter. Boil the solution until effervescence ceases. Acidify with sulphuric acid and test with titanium sulphate. The test is negative.

In (*d*) an amount of oxygen is evolved corresponding to one-half the oxygen of the Na_2O_2. (See also discussion of Experiment 11, p. 70.) This leaves in the solution the oxide Na_2O or rather NaOH the product of the reaction of Na_2O with water.

$$Na_2O_2 + H_2O \rightarrow 2\,NaOH + \tfrac{1}{2}O_2$$

On acidification we get a simple neutralization:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

In (*c*) the peroxide has not been given a chance to decompose before the treatment with acid. Since hydrogen peroxide was found as a product, the reaction is probably

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

Evaporation of the solution yields crystals of $Na_2SO_4{\cdot}10H_2O$ identical in every respect to the sodium sulphate that can be obtained from (*d*), thus confirming the above equations.

In the same way barium oxide BaO neutralizes an acid, with the formation of water:

$$BaO + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O$$

and barium peroxide yields hydrogen peroxide:

$$BaO_2 + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O_2$$

It is obvious that the reaction of the peroxide with an acid is a metathesis in which the O_2 radical is concerned just as the O is concerned in the neutralization of an ordinary oxide. It is furthermore obvious from the formulas H_2O_2 and Na_2O_2 and BaO_2, if we ascribe the ordinary valence to hydrogen, sodium, and barium, that the valence of the O_2 *radical* is 2.

Thus the peroxides are not really simple binary compounds in which the primary positive valence of the metallic constituent is just equaled by the primary negative valence of the non-metallic constituent. The peroxides could rather be classed with such compounds as nitrates and sulphates in which there is a compound negative radical.

5. Dioxides. To about 1 gram each of manganese dioxide, MnO_2, and lead dioxide, PbO_2, in separate test tubes add 10 cc. of water and 5 cc. of $6N$ H_2SO_4 or HNO_3 and warm for a few moments. Note that the dark-colored powders do not dissolve or change their appearance in any way, nor is there any effervescence. Filter off the insoluble powder and add titanium sulphate to the filtrate. Note that there is no yellow coloration.

These two oxides do not react at all with these acids, and indeed we should not expect on that account to find any hydrogen peroxide produced. These results are merely negative, therefore, and leave us in doubt as to the nature of the oxides, whether they are ordinary binary oxides in which case the valence of the manganese or lead is 4, or whether they are peroxides in which the valence of the metal is 2 like that of barium in barium peroxide.

6. Different Behavior of Dioxides and Peroxides with Hydrochloric Acid. (*a*) Treat 0.5 gram of finely powdered lead dioxide with 5 cc. of ice-cold $12N$ HCl. Note that a yellow solution is formed. Dilute 1 cc. of the solution with 100 cc. of water and add 1 cc. of titanium sulphate. Note that no yellow color is produced. Heat the rest of the solution. Note that yellow gas (chlorine) is given off, that the yellow color of the solution disappears, and that a white crystalline solid settles out as the solution cools. (*b*) Treat 0.5 gram of barium peroxide in the same way with 5 cc. of ice-cold $12N$ HCl. Add cold water until all the crystalline residue is dissolved; dilute 5 cc. of this solution with 100 cc. of water and add 1 cc. of titanium sulphate. The yellow color indicating the presence of hydrogen peroxide is obtained. Warm the remainder of the solution. Note that little or no chlorine is evolved. Dilute 5 cc. of the remaining solution with 100 cc. of water and again add titanium sulphate. Note that the test for hydrogen peroxide is still obtained unless the solution had been heated too long.

In (*a*) the yellow soluble substance is lead tetrachloride $PbCl_4$ and is formed by the reaction

$$PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O$$

Lead tetrachloride is very unstable and decomposes rapidly into the lower chloride $PbCl_2$ and free chlorine. This chloride of lead is the same one that is obtained when lead monoxide is treated with hydrochloric acid:

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O$$

Since the 2 oxygens of lead dioxide are replaced by 4 chlorines, and the lead is exchangeable for 4 hydrogens of the acid, the valence of lead is established as 4 and therefore each of the divalent oxygens is held as a separate unit by the lead.

In (*b*) the barium peroxide acts as we should expect with hydrochloric acid, yielding hydrogen peroxide. Since hydrogen peroxide is unstable, breaking down into water and oxygen, we should expect that it would react, at least to some extent, with the excess of hydrochloric acid and set free chlorine.

$$H_2O_2 + 2HCl \rightarrow 2H_2O + Cl_2$$

This experiment therefore has shown that lead dioxide is an ordinary oxide. The prefix *di* indicates the quantity of oxygen and that the valence of the metal is sufficient to hold all the oxygen in the ordinary manner.

THE HALOGENS

Recall that chlorine is a greenish yellow gas, bromine is a dark red liquid which readily vaporizes to a red gas, and iodine is a nearly black solid which is changed by heat to a beautiful violet-colored gas.

7. Test for the Presence of Iodine. Volatility of Iodine. Place some small crystals of iodine in the bottom of a 2-liter bottle and suspend a piece of filter paper moistened with starch paste in the upper part of the bottle. Cover the whole with a watch glass, allow it to stand 15 minutes or more, and observe that the paper slowly turns blue.

This experiment not only shows the volatility of iodine — it must pass through the space between the solid crystals and the paper as a vapor — but it also illustrates one of the striking properties of free iodine, namely its power of turning starch deep blue. We shall not concern ourselves as to what the blue substance is, but we shall employ starch in testing for iodine, and look for the blue color to indicate its presence.

> **8. Iodide-Starch Paper.** Add 1 cc. of potassium iodide solution to 10 cc. of a starch solution. Wet a number of strips of filter paper with the solution, allow them to dry, and save for use in certain of the following experiments. The test papers thus prepared are colorless.

Free iodine colors starch blue, but iodine in combination has altogether different properties.

> **9. Test for the Presence of Chlorine or Bromine.** Place 5 cc. each of chlorine water and bromine water in separate wide-mouthed bottles. Lower for a moment strips of moistened iodide-starch paper in the mouth of each bottle. The papers are immediately turned deep blue.

Chlorine and bromine are higher in the electromotive series than iodine and thus are able to drive it out of the ionic form

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

> **10. Chlorine from Hydrochloric Acid.** Place about 0.5 gram each of manganese dioxide, lead dioxide, sodium dichromate, and potassium permanganate in separate test tubes. Add about 2 cc. of $6N$ hydrochloric acid to each and test for chlorine by holding iodide-starch paper in the mouths of the tubes. Also after warming a very little observe the odor and color of the gas. Rinse out the tubes immediately at the sink under the hood. Compare the action of the oxides used above with that of copper oxide CuO and lead oxide PbO.

The action of the lower oxides is one of simple metathesis, chlorine and oxygen simply exchange places, no chlorine being set free.

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O$$
$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

In the case of MnO_2 the reaction is one of oxidation and reduction (see page 122).

One atom of manganese changes its valence from +4 to +2, and this is compensated by the change of two atoms of chlorine from −1 to 0, so that algebraically the total changes of valence add to 0.

The reactions of potassium dichromate and potassium permanganate are represented by the equations

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

These are likewise reactions of oxidation and reduction, and the valence changes add up as follows:

$$\begin{array}{llr} 2Cr & +6 \text{ to } +3 & 2 \times (-3) = -6 \\ 6Cl & -1 \text{ to } \ \ 0 & 6 \times (+1) = +6 \\ \hline & \text{Total change} & = 0 \end{array}$$

$$\begin{array}{llr} 2Mn & +7 \text{ to } +2 & 2 \times (-5) = -10 \\ 10Cl & -1 \text{ to } \ \ 0 & 10 \times (+1) = +10 \\ \hline & \text{Total change} & = 0 \end{array}$$

We may summarize this experiment by the statement that free chlorine is liberated from hydrochloric acid by strong oxidizing agents. Whether or not the oxidizing agent is strong enough to do this may perhaps be foretold by considering the element which has the higher than ordinary valence; if the chloride of this element in which the higher valence would be satisfied is unstable, then the oxidizing agent will set chlorine free.

11. Bromine and Iodine from Bromides and Iodides. Test the action of any one of the oxidizing agents used in Experiment 10, say manganese dioxide, on hydrobromic and hydriodic acids.

Add a few drops of chlorine water to 5 cc. of a bromide solution, for example NaBr. Then, in order to find whether bromine has been set free, add 1 cc. of carbon disulphide, shake vigorously, and let the heavier liquid settle to the bottom. The free halogen is more soluble in carbon disulphide than in water, consequently it dissolves in and imparts its characteristic color to it. Note that the globule has acquired an orange-red color.

Likewise add a few drops of chlorine water and of bromine water to separate portions of an iodide solution, for example KI, and test in each case with carbon disulphide. Note that in each case the globule becomes violet colored.

Although this experiment is almost a repetition of Experiment 9, it does illustrate another method of recognizing small amounts of free bromine and iodine. It emphasizes again that, corresponding to their position in the electromotive series, chlorine is more active than bromine and bromine in turn more active than iodine.

Iodine can be liberated from its salts by the weakest oxidizing agents. It should be noted that in this connection the halogens themselves are oxidizing agents; for, in the reaction

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

the bromine has been reduced from a valence of 0 to -1, while the iodine has been oxidized from valence -1 to valence 0.

Fluorine is the strongest oxidizing agent of all. It liberates the other halogens from their compounds. It will even liberate oxygen from water. It is impossible to liberate fluorine from hydrofluoric acid or fluorides by any of the chemical oxidizing agents because there is no other electro-negative element which exceeds it in activity. It is impossible to liberate it from an aqueous solution by electrolysis because the less active oxygen is set free instead. Fluorine can be prepared by electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride. This solution is a good electrolyte, and since it contains no other negative ion than fluoride, it is fluorine that has to be discharged at the anode.

FORMATION AND PROPERTIES OF THE HYDROGEN HALIDES

12. Hydrogen Chloride. Add 2 cc. of concentrated sulphuric acid (36 *N*) to about 0.5 gram of sodium chloride in a test tube and warm it a very little if necessary. The salt effervesces in the concentrated acid. Test for hydrogen chloride gas by blowing gently across the mouth of the tube, by holding moistened litmus in the gas, and by bringing a strip of filter paper moistened with ammonium hydroxide near the mouth of the tube. The gas issuing from the tube creates a dense fog with the breath. The gas turns moistened litmus paper red, and it produces a dense white smoke in the vicinity of the paper moistened with ammonium hydroxide.

The main reaction consists of the displacement of a volatile acid from its neutral salt by means of a non-volatile acid.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$$

Although hydrogen chloride is excessively soluble in water it is not soluble in sulphuric acid.

The fogging of the breath is possible because of the extreme solubility of hydrogen chloride in water. The fog then consists of countless minute globules of hydrochloric acid solution.

The hydrogen chloride of course dissolves in the water in the moist litmus paper and makes hydrochloric acid.

The smoke with ammonia is due to the precipitation of solid ammonium chloride where the gases HCl and NH_3 meet. The ammonium hydroxide dissociates non-electrolytically

$$NH_4OH \rightleftharpoons NH_3 + H_2O$$

and the ammonia combines with the hydrochloric acid

$$NH_3 + HCl \rightarrow NH_4Cl$$

These properties of fogging the breath, reddening litmus, and making a smoke with ammonia are characteristic of volatile acids and particularly of the hydrogen halides.

> **13. Hydrogen Bromide.** Add 1 cc. of 36 N sulphuric acid to about 0.5 gram of powdered potassium or sodium bromide in a test tube. The salt effervesces in the concentrated acid. Apply the same tests as in Experiment 12 then look for other new substances formed, applying the following tests, and towards the last heating the tube a little. Observe the color of the gas and also the effect of lowering iodide-starch paper for *a moment only* into the tube. Continued exposure of iodide-starch paper to strong acid fumes will develop a blue color in any case. Observe the odor, but with great caution. Test the gases with a strip of filter paper moistened with lead acetate solution. The gas evolved fogs the breath even more strongly than hydrogen chloride. It reddens litmus, and it gives a dense smoke with ammonia. The gas is quite strongly tinged with red; it turns iodide-starch paper blue immediately; it does not darken lead acetate paper. Sometimes one is able to distinguish the odor of sulphur dioxide.

The fogging of the breath, litmus test, and smoking with ammonia indicate that hydrogen bromide is freely evolved. The reddish tinge to the gas and the coloring of iodide-starch paper indicate the presence of a rather small amount of free bromine.

The failure to darken lead acetate indicates absence of hydrogen sulphide.

The principal reaction in this experiment is similar to that in the preceding experiment:

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$$

The properties of hydrogen bromide are very similar to those of hydrogen chloride but differ in that hydrogen bromide reduces sulphuric acid to form sulphur dioxide and is itself oxidized to free bromine.

$$H_2SO_4 + 2HBr \rightarrow H_2SO_3 + H_2O + Br_2$$
$$H_2SO_3 \rightarrow H_2O + SO_2$$

The major part of the hydrogen bromide, it is true, escapes from the reaction mixture unaffected, but on bubbling up through the concentrated sulphuric acid a small part of it is oxidized according to the secondary reaction which accounts for the red color of free bromine.

It is recalled from Experiment 11 that bromine is a less active element than chlorine; hence it is but natural that we should find it here displaced from its hydrogen compound by a weaker oxidizing agent. Chlorine is displaced from hydrogen chloride by strong oxidizing agents, MnO_2, PbO_2, $K_2Cr_2O_7$, $KMnO_4$, but bromine is displaced by the comparatively weak oxidizing agent H_2SO_4 which has no action on hydrogen chloride. The sulphur of the sulphuric acid is reduced from valence +6 to valence +4 in sulphur dioxide.

14. Hydrogen Iodide. Add 1 cc. of 36 *N* sulphuric acid to 0.5 gram of powdered potassium or sodium iodide, and apply all the tests enumerated in Experiments 12 and 13; also inspect the walls of the test tube carefully to see if any solid sulphur condenses.

As in Experiments 12 and 13 the solid effervesces in the concentrated sulphuric acid and the gas evolved fogs the breath (even more markedly in this case), turns litmus red, and gives a dense smoke with ammonia. When the tube is warmed, the beautiful purple iodine vapor is seen inside and nearly black crystals collect on the cooler upper walls. Lead acetate paper is colored dark brown. Sometimes a powdery light yellow substance (sulphur) is seen collecting on the walls of the tube.

The primary reaction in this experiment,

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$$

is of the same nature as that in the preceding two experiments. That hydrogen iodide escapes abundantly from the reaction mixture is attested by the fogging of the breath, by the reddening of litmus, and by smoke with ammonia. But that hydrogen iodide enters more extensively into a secondary reaction with sulphuric acid is shown by the abundance of the secondary products. These consist of free iodine, shown by the purple vapor and the black crystalline deposit; hydrogen sulphide, shown by the darkening of lead acetate paper ($PbAc_2 + H_2S \rightarrow PbS + 2HAc$), and the odor; sulphur, shown by the light yellow deposit. Their formation can be accounted for by the equations:

$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2$$

$$H_2S + I_2 \rightarrow 2HI + S$$

Hydrogen sulphide and iodine do not react in the gaseous condition, but where they dissolve in the film of moisture condensed on the cooler walls of the tube they react and this accounts for the deposit of sulphur.

This experiment, taken in conjunction with the preceding two, shows the gradation in properties of the hydrogen halides. The activity of the halogens decreases in the order: fluorine, chlorine, bromine, iodine. Hydrogen fluoride is so stable therefore that no chemical substance can displace fluorine, and hydrogen fluoride is unable to act as a reducing agent in any circumstance. Hydrogen chloride can act as a reducing agent upon the most powerful oxidizing agents. Hydrogen bromide can reduce the comparatively weak oxidizing agent sulphuric acid, but it can only carry the valence of the sulphur down to +4 in sulphur dioxide. Hydrogen iodide can reduce sulphuric acid much more completely, carrying the valence all the way from +6 down to the lowest possible, namely −2 in hydrogen sulphide.

15. Hydrogen bromide and hydrogen iodide might be obtained pure from their salts, provided the latter were treated with a non-volatile acid which would not at the same time behave as an oxidizing agent.

Place about 0.5 gram of powdered sodium bromide in a test tube with a little concentrated phosphoric acid solution, heat, and test the evolved gas for free halogen as well as for hydrogen bromide. Repeat, using sodium iodide in place of the sodium bromide.

In both experiments, fogging of the breath, reddening of litmus, and smoke with ammonia are noted. With the sodium bromide, the gas is entirely uncolored and no test with iodide starch paper is given. With sodium iodide the gas is at first entirely colorless but when the tube is heated strongly the film of moisture condensing on the walls of the tube becomes slightly brown. No test is given with starch paper.

Phosphoric acid is a much weaker oxidizing agent than sulphuric acid, and it fails to oxidize either hydrogen bromide or hydrogen iodide. The brown color, it is true, indicates a trace of free iodine, but this is accounted for by a direct decomposition of hydrogen iodide by heat.

CHARACTERISTIC REACTIONS OF THE HALIDE IONS

The halides of all the metals except silver, lead, mercurous mercury, and cuprous copper are soluble in water, but with the ions of these metals, the halide ions give characteristic precipitates. The precipitates are valuable as tests for identifying either the halogens or the metals in qualitative analysis.

16. (*a*) Add a few drops of silver nitrate solution to a few drops each of hydrochloric, hydrobromic, and hydriodic acid solutions, diluted with 5 cc. of water, in separate test tubes. Let each precipitate settle, pour off most of the liquid, and find whether portions of the precipitate dissolve in a large amount of boiling water. Test also the solubility of each in ammonia.

(*b*) Add lead nitrate solution also to each of the three acids and test the solubility of the precipitates in hot water.

Tabulate the results obtained in (*a*) and (*b*).

The exact figures for the solubility at different temperatures will be found in the solubility table in the Appendix. The solubility of the silver halides in ammonia solution depends on the formation of the complex ion, $Ag \cdot 2NH_3^+$ (see Chapter III, page 118). Silver bromide and silver iodide are decreasingly less soluble in pure water than the chloride, although all three seem by the direct experiment to be completely insoluble. Thus, in a solution containing ammonia, the $Ag \cdot 2NH_3^+$ ion does not dissociate enough for the simple silver ions and chlorine ions to reach the solubility product of silver chloride. The solubility product of silver bromide is sooner reached, and silver bromide is only sparingly soluble in ammonia solution. The solubility product of silver iodide is still smaller, and this accounts for the apparent complete insolubility of silver iodide in ammonia solution.

Relative Activity of the Halogens, Oxygen, and Sulphur

The activity of an element is judged by its power to combine with other elements, or by its ability to pass from the elementary condition into solution in the form of ions, whereby it forces other less active elements out of the ionic into the elementary condition. There can be no doubt as to the relative activity of the halogens as regards their tendency to form simple negative ions. The position of oxygen in this respect is harder to define, for no simple ions of oxygen exist in solution. Under certain conditions chlorine displaces oxygen from water, as in Experiment 10, page 69; yet some substances which give up oxygen readily (oxidizing agents, see Experiment 10 of this chapter) set chlorine free from hydrochloric acid.

> **17.** Observe the color of the stock solution of hydriodic acid, or of a dilute solution of KI acidified with a little H_2SO_4. If this should chance to be fresh and perfectly colorless, pour a few cubic centimeters into the bottom of a beaker and let it stand some time exposed to the air. Apply tests to determine whether the color is caused by free iodine.
>
> Are hydrobromic and hydrochloric acids similarly affected by exposure to the air? Is a solution of potassium iodide so affected?

Hydriodic acid solution can be prepared perfectly colorless and kept colorless so long as it is kept out of contact with the air. In contact with air it becomes brown in a very few minutes and the brown color gradually increases in depth. This color is due to free iodine which is quite soluble in an iodide solution giving a brown solution

$$2H^+ + 2I^- + \frac{1}{2}O_2 \rightarrow H_2O + I_2$$

In the course of this reaction hydrogen ions are used up; it is therefore obvious that the presence of hydrogen ions will aid in the displacement of iodine ions by oxygen. In a neutral potassium iodide solution no iodine is observed and it is thus apparent that the help of hydrogen ions is necessary to accomplish the liberation of iodine.

Chlorine and bromine are not liberated by the action of air on hydrochloric acid and hydrobromic acid, or on neutral solutions of chlorides and bromides.

18. Add a few drops of iodine solution to a little hydrogen sulphide water. The brown iodine solution is immediately decolorized and a white cloudiness (precipitate of sulphur) appears in the solution.

Observe the precipitate which slowly forms in the bottle of hydrogen sulphide water to which air has some access.

Explain the reaction in each case, and place sulphur, oxygen, chlorine, bromine, and iodine in the order of their chemical activity in acid solutions.

From these experiments it is seen that both iodine and oxygen are more active than sulphur. The reactions are quite certainly ionic displacements although it is rather complicated to represent them in intersecting ionic equations.

$$H_2S + I_2 = S\downarrow + 2HI$$
$$H_2S + \frac{1}{2}O_2 = S\downarrow + H_2O$$

From this experiment and the preceding one we should conclude that the non-metallic elements fall in the order F, Cl, Br, O, I, S (fluorine being strongest) with respect to their activity in aqueous solutions containing free acid. This is approximately the order of the electromotive series for these non-metals. If the solution is made neutral the electromotive potential of oxygen is lowered so that the oxygen is no longer able to displace iodine.

In dry gaseous mixtures the order of activity of the non-metals is somewhat altered, oxygen moving up ahead of bromine and chlorine, and sulphur and iodine changing places: F, O, Cl, Br, S, I.

SULPHUR

19. Allotropic Forms. (*a*) Dissolve in a dry test tube a small piece of roll sulphur in 3 to 5 cc. of carbon disulphide. Pour the clear solution on a watch glass and allow it to evaporate spontaneously under the hood. Examine the crystals. This is rhombic sulphur.

(*b*) Heat 10 grams of sulphur in a test tube until it has just melted. Pour the liquid into the cone of a folded filter paper. Then allow the melt to cool very slowly, and when it has partially solidified, and a crust has formed over the surface, break this crust and pour out what is still left in the liquid state. Examine the crystals and compare them with those observed in (*a*). This is monoclinic sulphur.

(*c*) Melt 10 grams of sulphur in a test tube. Heat slowly, and observe all the changes that take place during the heating. When the sulphur boils, pour it into a pan or large beaker of water and observe the condition of the cooled product. It will be found to be quite elastic. This is amorphous sulphur.

Distinguish between the three solid forms of sulphur here observed and discuss the differences in the conditions under which they are formed (see reference book).

20. Hydrogen and Sulphur. (*a*) Prepare hydrogen sulphide by the action of dilute sulphuric acid on ferrous sulphide in a generator bottle (see Note 13 (*a*), page 18). Pass the gas through a drying tube containing a plug of cotton wool, which retains any acid spray, then through a piece of hard glass tube the end of which is drawn out into a capillary jet. Heat a section of the tube to redness and observe that a white deposit is formed on the walls of the cooler part of the tube beyond.

(*b*) Light the gas issuing from the capillary jet and note the products of the freely burning hydrogen sulphide. The odor of sulphur dioxide is unmistakable. If a cold bottle is held over the flame, water condenses inside the bottle. Now thrust a piece of cold porcelain half way into the flame and note the deposit of sulphur.

(*c*) Generate hydrogen gas in exactly the same way as hydrogen sulphide in (*a*). Place about 0.5 gram of sulphur in the end of the hard glass tube nearest the generator. When it is ascertained that the hydrogen coming off is pure, heat the further end of the glass tube to redness and gradually move the flame towards the sulphur until this begins to be volatilized a little. By this arrangement a mixture of hydrogen and sulphur vapor is made to pass through a red-hot tube. Test the escaping gases with lead acetate paper.

Parts (*a*) and (*b*) show that sulphur is deposited when hydrogen sulphide is strongly heated. In the freely burning flame the ultimate products are sulphur dioxide and water:

$$H_2S + \tfrac{3}{2}O_2 \rightarrow H_2O + SO_2$$

But if the unburned vapors in the interior of the flame are cooled by the porcelain before they can burn we find that sulphur is present there. Although we have not directly proved the presence of hydrogen we are justified in thinking that it is the other decomposition product of hydrogen sulphide.

Part (*c*) shows that some hydrogen sulphide is formed when a mixture of hydrogen and sulphur vapor is heated to redness, and it is thus clear that neither the synthesis nor the decomposition of hydrogen sulphide is complete at this temperature but that hydrogen sulphide reaches an equilibrium with its products according to the reversible reaction.

$$H_2S \rightleftharpoons H_2 + S$$

It is instructive to review the properties of the other nonmetals by considering how they would behave in similar circumstances.

Chlorine and hydrogen, passed together into a heated tube, combine completely and with explosive violence; oxygen and hydrogen explode even more violently; and fluorine and hydrogen can hardly be mixed together, even at ordinary temperatures, without exploding. Bromine and hydrogen led through a heated tube combine freely to form hydrogen bromide but without any explosion. Iodine and hydrogen combine to but a limited extent — less than sulphur and hydrogen.

On the other hand, the chemical activity of the non-metal may be judged by the stability of the hydrogen compound, and the stability in turn may be measured by the temperature to which it must be heated before it is perceptibly dissociated. Hydrogen iodide begins to show the violet color of free iodine as low as 180°; hydrogen sulphide does not deposit free sulphur below 310°; hydrogen bromide is first perceptibly decomposed at 800°; hydrogen chloride at 1,800°; water at 2,000°; and hydrogen fluoride is still undissociated at this temperature.

> **21. Ionization of Hydrogen Sulphide.** Pass hydrogen sulphide, which has been filtered through cotton wool, and which has bubbled through one bottle containing water, into distilled water in a flask until the solution is saturated. Test the conductivity of the solution with electrodes *B* (see page 84), and test it with litmus. The conductivity is almost imperceptible; it does not cause the lamp to glow, but it is shown by a slight evolution of bubbles from the electrodes. Litmus is turned towards the red, but not the full red color produced by strong acids.

The effects observed in this experiment are caused by the ionization $H_2S \rightleftharpoons H^+ + HS^-$ to the extent of 0.05 per cent (page 100).

> **22. Hydrogen Sulphide as a Precipitant.** Pass hydrogen sulphide into solutions of salts of the heavy metals acidified with HCl; take for example a solution of copper chloride. A heavy black precipitate is formed.

The precipitate is copper sulphide. The table gives the ionization $HS^- \rightleftharpoons H^+ + S^{--}$ as 0.0002 per cent, but this applies only to a 0.1 equivalent solution of $Na^+ HS^-$ in which all the H^+ ions come from the dissociation in question. In a solution of H_2S containing the H^+ ions of the first dissociation, the concentration of S^{--} ions would be very much smaller. In a solution containing a strong acid like HCl, the concentration of S^{--} which could come from H_2S would be excessively small. But copper sulphide is precipitated from such a solution. The solubility product of copper sulphide must be extremely small.

The solubility of all the heavy metal sulphides is very small; they are all insoluble in water, but some dissolve in hydrochloric acid. The solubility product of these is not quite so small because it is not reached when the ionization of H_2S is driven back by the strong acid.

23. Reducing Action of Hydrogen Sulphide. Dilute 5 cc. of a potassium permanganate solution with 100 cc. of water and add 5 cc. of 6 *N* H_2SO_4. Bring the solution to boiling and pass in hydrogen sulphide. The deep purple color of the permanganate quickly disappears, and a white opalescent precipitate appears.

Although sulphur in hydrogen sulphide has a range of eight possible points in valence, from −2 to +6, to go when it acts as a reducing agent, it usually does not go beyond the zero stage of valence in aqueous oxidizing agents, the obvious explanation being that the free sulphur is precipitated and thus removed from the sphere of action.

$$2KMnO_4 + 5H_2S + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

$$\begin{array}{llr}
2\,\text{Mn} & +7 \text{ to } +2 & 2 \times (-5) = -10 \\
5\,\text{S} & -2 \text{ to } 0 & 5 \times (+2) = +10 \\
\hline
 & \text{Total change} & = 0
\end{array}$$

NITROGEN

Nitrogen is an extremely inactive element, combining directly only with the most active of the metals. Nitrogen forms no simple ions and it is impossible to give it an exact potential in the electromotive series, but it is obvious that it is far less active than sulphur or iodine. Under the influence of electric sparks or of catalysts at about 400° nitrogen does combine sparingly with hydrogen to form ammonia NH_3. It combines quite readily with magnesium to give the nitride Mg_3N_2 which compound bears the same relation to ammonia (its formula should logically be H_3N) that magnesium chloride does to hydrogen chloride.

24. Synthesis of Ammonia. Heat a mixture of 14 grams of iron filings, 0.5 gram of powdered sodium hydroxide, and 0.5 gram of powdered potassium nitrate in a test tube, and test the gas which escapes by holding a rod wet with concentrated hydrochloric acid near the mouth of the tube. A white smoke is formed.

Test the action of iron on sodium hydroxide and potassium nitrate respectively by heating 7-gram portions of iron filings with 0.5 gram of each of these reagents separately.

From sodium hydroxide, a gas that burns with a colorless flame (hydrogen) is evolved. From potassium nitrate a gas that will neither burn nor support combustion (nitrogen) is evolved.

Iron is more active than either hydrogen or nitrogen and displaces them

$$2KNO_3 + 5Fe \rightarrow K_2O\cdot 5FeO + 2N$$
$$2NaOH + Fe \rightarrow Na_2O\cdot FeO + 2H$$

The hydrogen and nitrogen are probably in the atomic state at the moment of liberation. They change at once to ordinary molecular N_2 and H_2 if they find nothing to combine with, but in the presence of each other they combine to form ammonia.

25. Nitrides. Place half a gram of magnesium ribbon rolled into a ball, or half a gram of powdered magnesium, in a small crucible. Heat it until it catches fire, put the cover on to restrict the admission of air, and let the magnesium burn slowly. Transfer the ash to a test tube and add a few drops of water (cautiously). Note the odor of ammonia, and bring a rod wet with concentrated hydrochloric acid near the mouth of the tube, noting the white smoke.

When enough oxygen cannot come into contact with burning magnesium to form the oxide, magnesium combines readily with nitrogen. Of course, prolonged heating in air will convert all nitride into oxide, but if the ash is cooled at once it contains a considerable amount of nitride. Magnesium nitride hydrolyzes very easily according to the reaction

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2H_3N$$

The magnesium nitride may be considered as a salt of the base $Mg(OH)_2$ and the acid H_3N. But since H_3N is so weak an acid that it is not usually considered as an acid at all, the hydrolysis of its salt is correspondingly very complete.

GENERAL QUESTIONS IV

1. What are the distinctive physical and the distinctive chemical properties of the non-metallic elements?

2. Why are the non-metallic elements considered to be the negative constituents of binary compounds?

3. Many binary compounds of non-metals with non-metals are known, but such compounds usually can exist only out of contact with water. For example, phosphorus trichloride is completely hydrolyzed by water. Write the equation for this reaction, and treating it as a metathesis, conclude which element in the phosphorus trichloride is to be regarded as the positive constituent.

4. Arrange the non-metals studied in this chapter in the order of their activity as negative elements, (*a*) when they react in aqueous solution, (*b*) when they react with "dry" substances.

5. Look up the heat of solution of hydrogen iodide and hydrogen sulphide, and state how this factor is able to make iodine more active than sulphur in aqueous solution, whereas sulphur is the more active in the dry state.

CHAPTER V

ALKALI AND ALKALINE EARTH METALS

These metals constitute the left-hand or A families in Groups I and II of the periodic classification of the elements, as shown in the table inside the back cover of the book.

The metals of these two families are studied together because they are extremely active base-forming elements. On account of their great activity they are never found uncombined in nature, and it is only by the aid of the most powerful reducing agencies (for example, by electrolysis of their molten salts) that the metals themselves are extracted from their compounds.

The alkali metals are monovalent. Their hydroxides, MOH, are extremely soluble and are highly ionized as bases; on account of the corrosive properties of the latter they are known as the caustic alkalies — hence the designation, *alkali metals.* The compounds of the alkali metals are, with a very few exceptions, soluble in water, and they are all strong electrolytes.

The radical ammonium, NH_4, is classed with the alkali metals on account of its ability to form the same kinds of compounds.

The alkaline earth metals are divalent; their hydroxides, $M(OH)_2$, are less soluble than those of the alkali metals, but are nevertheless very strongly basic. The compounds of these metals are not so generally soluble as those of the alkali metals, and in particular the carbonates, sulphates, and phosphates are mostly insoluble.

PREPARATION 15

SODIUM CARBONATE BY THE AMMONIA (SOLVAY) PROCESS, Na_2CO_3

The raw materials from which the sodium carbonate of commerce is manufactured are common salt, NaCl, and limestone, $CaCO_3$, but these substances do not spontaneously react with each other, rather a reaction would take place in the opposite direction, as indicated by the arrow.

$$2NaCl + CaCO_3 \leftarrow CaCl_2 + Na_2CO_3$$

Much ingenuity has been exercised by chemists in attempts to effect this change through a series of reactions. In the older Le Blanc soda process sulphuric acid is used in the first step and coal (carbon) in another, and neither of these auxiliary substances is recovered. The soda process which is employed exclusively today is known as the Solvay or ammonia process and uses ammonia as an auxiliary substance. The ammonia is almost 100 per cent recoverable, however, and can be used over and over indefinitely. The successive steps in the process are as follows:

1. Heating limestone in kilns to obtain quicklime and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

2. Passing carbon dioxide and ammonia into saturated brine in an absorption tower:

$$NH_3 + CO_2 + H_2O + NaCl \rightarrow NH_4Cl + NaHCO_3\downarrow$$

3. Collecting the precipitated $NaHCO_3$.

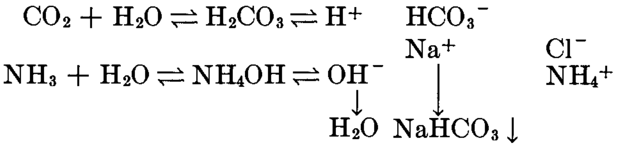
4. Recovery of ammonia by treating the ammonium chloride filtrate with quicklime, expelling the ammonia gas to be used again in step 2, and working up the calcium chloride left behind:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

5. Heating the sodium bicarbonate to obtain sodium carbonate, the carbon dioxide expelled supplying one-half of the amount needed in step 2:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

This preparation stresses particularly the principle involved in step 2. Carbon dioxide produces no precipitate in a neutral sodium chloride solution, the ionization of H_2CO_3 producing too low a concentration of HCO_3^- to saturate the solution with $NaHCO_3$. The presence of the base prevents the accumulation of H^+ and in consequence the carbonic acid may continue to ionize until a sufficient HCO_3^- concentration to precipitate $NaHCO_3$ has accumulated.



$$\begin{array}{lccc}
CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons & H^+ & HCO_3^- & \\
 & & Na^+ & Cl^- \\
NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons & OH^- & \big| & NH_4^+ \\
 & \downarrow & \downarrow & \\
 & H_2O & NaHCO_3\downarrow &
\end{array}$$

Materials: sodium chloride, NaCl, 59 grams 1 F.W.
15 *N* ammonium hydroxide, 80 cc.
carbon dioxide, which can be drawn either from an automatic gas generator (see Note 13 (*c*), page 20), or from a gas holder which is filled as needed from a steel cylinder of liquid carbon dioxide.

Apparatus: bubbling bottle, through which the carbon dioxide is to pass to indicate its rate of flow.
suction filter and trap bottle.
2,000-cc. flask equipped with 1-hole rubber stopper, a delivery tube with a short right-angle bend at the top and reaching to within an inch of the liquid in the flask, and 30 inches of rubber delivery tube.
300-cc. flask with stopper.
funnel and filter.
4-inch porcelain dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Place the salt, the ammonium hydroxide, and 150 cc. of water in the 300-cc. flask and shake vigorously until the salt is nearly dissolved. Pour the solution through a filter into the large flask. Use this flask as the absorption vessel and connect it with the source of carbon dioxide. Loosen the stopper of the flask and let the carbon dioxide expel the air. Then stopper the flask and shake it as vigorously as possible until the absorption of carbon dioxide has slackened. Loosen the stopper again to allow any air that has accumulated in the flask to escape; then continue the shaking until practically no more gas passes the bubbling bottle even with vigorous shaking. If the shaking has been continuous, this point will be reached within 30 minutes.

Pour the suspension of sodium bicarbonate into the suction filter funnel (Notes 3 and 4 (*b*)) and allow it to drain until the surface of the mass in the funnel is firm. Press the surface gently with the blunt end of a test tube to close up any cracks or channels that may have opened and to squeeze out the last possible drops of chloride-containing solution. Stop the suction; pour over the surface of the product 15 cc. of cold distilled water, letting it penetrate uniformly into the mass for 3 minutes. Again apply suction and press out the last possible drops of liquid. Repeat the washing with another 15 cc. of distilled water. The product may now be considered to be "commercially pure" although it still contains an appreciable amount of chloride. Test the preparation for chloride by dissolving about 0.1 gram in 5 cc. of distilled water, adding an excess of dilute nitric acid and a few drops of silver nitrate solution. Transfer the product to a 4-inch porcelain dish, taking care not to include any of the filter paper, and allow it to air-dry completely if it is to be preserved as sodium bicarbonate. If it is to be converted to the carbonate it is not necessary to wait for complete drying. Place the dish on an iron wire gauze on a ring stand, and adjust a gas flame 2 inches high the top of which is ½ inch below the wire gauze. Continue the heating in this fashion until the product appears dry. Then place a watch glass over the dish to retain the heat in the upper layer of the powder and continue the heating with frequent stirring until escape of gas (seething) ceases. One-half hour's heating with the low flame as described should suffice to decompose the bicarbonate (200°) and avoid melting the carbonate (851°) and causing it to cake together and stick to the dish.

Put up the preparation in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. What is the purpose of washing the product with water? How much sodium bicarbonate is lost in the mother liquor and the wash water (see solubility table)?

2. Why must the solution be acidulated with nitric acid before testing with silver nitrate?

3. Why cannot potassium bicarbonate be effectively prepared from potassium chloride by the ammonia process? (Look up the solubility of potassium bicarbonate.) What process may be used to prepare potassium carbonate from this source?

4. Write the intersecting ionic equation for the recovery of ammonia from the ammonium chloride liquors.

5. What becomes of the ammonium chloride still clinging to the sodium bicarbonate preparation when the latter is heated to convert it to the carbonate?

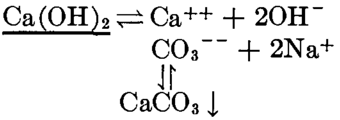
6. Define an acid salt. Compare the acidity of $NaHSO_4$ and $NaHCO_3$. Write equations for reactions in which these acid salts are showing their acid character.

PREPARATION 16

CAUSTIC ALKALI FROM ALKALI CARBONATE, NaOH

CAUSTICIZING REACTION

The industrial process by which large quantities of sodium hydroxide are made consists in treating a 10 per cent solution of sodium carbonate with an excess of calcium hydroxide (milk of lime). After the reaction is complete the mixture is filtered to remove the precipitated calcium carbonate and excess of calcium hydroxide. This process involves a most important application of the principle of solubility product: calcium hydroxide continues to dissolve and calcium carbonate to precipitate according to the reaction



$$\begin{array}{ll} \underline{Ca(OH)_2} \rightleftharpoons & Ca^{++} + 2OH^- \\ & CO_3^{--} + 2Na^+ \\ & \downarrow\uparrow \\ & CaCO_3 \downarrow \end{array}$$

until equilibrium between both solids and the solution is attained.

	Solubility in pure water moles per liter	Solubility product
$Ca(OH)_2$ $CaCO_3$	0 02 0 00013	$0\ 02 \times 0\ 04^2$ $0\ 00013 \times 0\ 00013$

At this point the concentration of both Ca^{++} and CO_3^{--} ions is so small (both close to the value 0.00013) that for practical purposes it is disregarded and the filtered solution is said to be free of either calcium or carbonate. However, with so small a Ca^{++} ion concentration the OH^- ion concentration can be quite large without exceeding the solubility product of $Ca(OH)_2$. In fact the filtered solution has a concentration of nearly 2-molal in NaOH. If, however, the OH^- ion concentration gets above 2-molal, the Ca^{++} ion concentration is depressed to such an extent that an appreciable concentration of CO_3^{--} ions can remain without exceeding the solubility product of calcium carbonate. In other words, if we started with a more concentrated solution of Na_2CO_3 than 10 per cent, a complete conversion to the hydroxide would not be possible.

Materials: anhydrous sodium carbonate, Na_2CO_3, 53 grams = 0.5 F.W.
slaked lime, $Ca(OH)_2$, 50 grams.

Apparatus: 8-inch porcelain dish.
suction filter and trap bottle.
burette with standard HCl.
10-cc. pipette.
300-cc. Erlenmeyer flask.
iron ring and ring stand.
Bunsen burner.
500-cc. bottle with rubber stopper.

Procedure: Dissolve the sodium carbonate in 300 cc. of water, and stir the slaked lime into another 300 cc. of water, making milk of lime. Bring the carbonate solution to boiling in the 8-inch dish and pour the milk of lime slowly with stirring into the boiling solution. Let the mixture boil 15 minutes and then filter, using a suction bottle (see Note 4 (*b*)). Measure the volume of the solution of caustic alkali obtained and preserve it in the rubber-stoppered bottle.

Determine the Strength of the Solution. With a pipette measure 10 cc. of the preparation into a 300-cc. Erlenmeyer flask, add 100 cc. of distilled water, and titrate against standard HCl using phenolphthalein as the indicator. (See Experiment 6, page 75.) Carry out a duplicate titration with a second 10-cc. sample, and take the average of the results to give the normality of the solution. Label the bottle with the number of cubic centimeters of the solution, with its normality, and with the actual amount in grams of the hydroxide.

QUESTIONS

1. The calcium hydroxide used in causticizing is soluble only to the extent of 1.7 grams per liter. Explain how, in spite of its limited solubility, the required amount can enter into reaction.
2. Explain why the solution obtained contains practically no calcium ions although an excess of calcium hydroxide, which is appreciably soluble in pure water, has been used for causticizing.

PREPARATION 17

SODIUM HYDROXIDE BY ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION. FARADAY'S LAW AND THE CURRENT EFFICIENCY

Another widely used commercial method for the production of sodium hydroxide lies in the electrolysis of sodium chloride solution — a method which is economical when the chlorine simultaneously produced can also be utilized.

In this preparation we shall construct a laboratory cell embodying some of the features of the commercial cell and determine the ratio of the actual yield of sodium hydroxide to that theoretically obtainable from the current. We shall use the entire product in making the determination and, therefore, there will be no preparation to be preserved.

The section on electrochemical reactions and Faraday's law, pages 123–126, should be carefully reviewed before proceeding with this preparation.

Coulometer. A cell consisting of copper electrodes immersed in a copper sulphate solution furnishes one of the most reliable and exact methods of measuring the amount of electricity flowing through the circuit into which it is inserted. We shall measure the decrease of weight of the copper anode, rather than the increase of weight of the copper cathode, because some of the copper deposit on the cathode may not be firmly attached, and may powder off in the process of washing, drying, and weighing. It should be remembered that since the Cu^{++} ion has two charges, the equivalent weight of copper is one-half the atomic weight, and 1 faraday will dissolve 31.8 grams rather than 63.6 grams from the anode.

In the commercial electrolysis of brine, carbon anodes and iron cathodes are employed. The anode reaction is mainly the discharge of chlorine ions:

$$2Cl^- \rightarrow Cl_2 + 2\ominus$$

but to a small extent hydroxyl ions are discharged, liberating oxygen:

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2\ominus$$

and a part of this oxygen attacks the electrode, producing CO_2.

The cathode reaction consists almost exclusively in the discharge of H^+ ions furnished by the progressive ionization of water:

$$H_2O \rightarrow H^+ + OH^-$$
$$\ominus + H^+ \rightarrow \tfrac{1}{2}H_2$$

The OH^- ions, which thus accumulate in the cathode compartment, are balanced by the Na^+ ions, which are brought up by the electrolytic conduction. The commercial sodium hydroxide is obtained by evaporating the cathode solution to a high concentration of NaOH, in which NaCl is insoluble. The crystals of NaCl are removed in centrifugal filters, and the purified solution is evaporated until molten NaOH is left. This is poured into molds and allowed to solidify. If the total sodium hydroxide could be recovered, 40 grams would be realized for each faraday. It is the object of this experiment to determine what percentage of this ideal yield can be obtained in a simple cell.

Side Reactions Which Decrease the Yield. The products in the anode and cathode compartments will react if they are allowed to mix.

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

Commercial cells are so designed as to reduce this mixing to a minimum. In our experiment we employ a loose plug of cotton wool to prevent the mixing of the solutions. But even if convection currents are eliminated completely, the unfortunate condition holds that the electrolytic conduction carries OH^- as well as Cl^- ions from the cathode through the cotton wool plug into the anode compartment, where the OH^- ions react with the dissolved chlorine.

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$

(This is identical to the above reaction, except that it is here written ionically.)

Power Efficiency. Since the cost of electricity is based on the energy consumed rather than the amount of electricity, the current efficiency which we are determining is not a measure of the cost efficiency. The energy consumed is proportional to the product of the coulombs and the volts. The minimum voltage to discharge Cl_2 from a normal NaCl solution, and H_2 from a normal NaOH solution, in a cell is 2.17 volts. A somewhat higher voltage must be applied to make a sufficient current flow through the cell. The cell we use in this experiment, however, has a high internal resistance, and more energy will be expended in overcoming this than in bringing about the electrochemical change itself. Hence, we shall not even measure the voltage drop across the cell to determine the power efficiency, but we shall frankly limit our problem to a study of the current efficiency.

Materials: saturated sodium chloride solution.
saturated copper sulphate solution.
standard acid and base.
phenolphthalein solution.
reagent alcohol.

Apparatus: two 8-inch U-tubes.
2 burette clamps.
2 copper electrodes.
iron electrode.
carbon electrode.
brass connector.
100-watt lamp and socket.
ring stand.
cotton wool.
2 burettes.

Data Form:

Duration of Experiment Hour Minute Second
1. Ended (lamp unscrewed) . . . .
2. Begun (lamp screwed in) . . . .
3. Time elapsed . . . . . minutes. . . . . seconds

4. Weight of copper anode, before . . . . grams
5. Weight of copper anode, after . . . . grams
6. Loss in Weight . . . . grams

Titration
HCl
7. Normality of HCl solution . . . .
8. Burette reading after titration. . . . . cc.
9. Burette reading before titration. . . . . cc.
10. Number of cc. used in titration. . . . . cc.

NaOH
11. Normality of NaOH solution. . . . .
12. Burette reading after titration. . . . . cc.
13. Burette reading before titration. . . . . cc.
14. Number of cc. used in titration. . . . . cc.

Procedure: Set up the apparatus as shown in Fig. 22. A carbon anode and a spiral iron cathode are placed in the electrolytic cell at the right. A plug of cotton wool is placed at the bend of the U-tube; it is not packed very tightly, only enough to hinder the bodily mixing of the solutions in the two arms. The electrolytic cell is filled with a saturated solution of common salt. The metal connection on the carbon pole should not touch the solution.

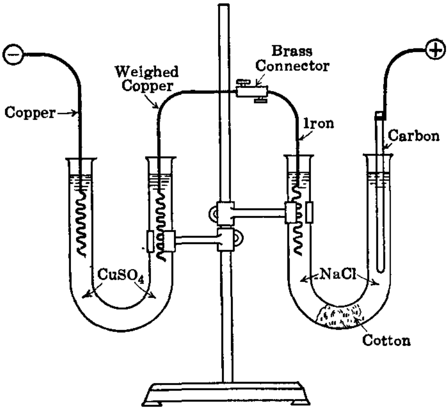


FIG. 22

The coulometer, or left-hand U-tube, should contain saturated copper sulphate solution, which is specially prepared for this experiment. The cathode is made of copper; the anode is a spiral of heavy copper wire free of any coating of oxide. Clean and dry the anode and weigh it.

Connect the two U-tubes "in series," as in the diagram; connect the terminals through a 100-watt lamp with the direct-current laboratory circuit. The current should be turned on or off by unscrewing the lamp from the socket, never by pulling the plug. If the plug is pulled, in re-inserting, the direction of flow of the direct current might be reversed.

Before starting the experiment, the polarity of the terminal posts must be determined by placing across them a strip of pink litmus paper moistened with NaCl solution. The spot touching the cathode turns blue.

Let an instructor approve your arrangement of apparatus. Note the time that the current is turned on.

Allow the current to flow for about 20 minutes. During the flow of the current, prepare two clean beakers, which should be set side by side on the desk, near the apparatus; also have a wash bottle at hand. As soon as the current is turned off, place the iron electrode in one of the beakers; set the carbon pole aside. Pour the solution out of the electrolytic cell, holding it so that the cathode arm will empty into the beaker containing the iron cathode, and the anode arm into the other beaker. Rinse out the cathode arm with three portions of 3 to 5 cc. of distilled water, adding the rinsings to the beaker. Add a few drops of phenolphthalein.

Now carefully remove the anode from the coulometer, and set it in a test tube full of distilled water. Be careful not to bruise it. Then rinse it with alcohol and, after it has dried, weigh it. Return the $CuSO_4$ solution to a bottle marked "Used $CuSO_4$ Solution."

Titrate the cathode solution with the standard acid prepared in Experiment 6, and thus determine the number of equivalents of NaOH produced in the cathode compartment.

From the loss of weight of the copper anode determine the number of faradays of electricity that were used in the cell. The ratio of the number of equivalents of NaOH to the number of faradays gives the current efficiency.

QUESTIONS

1. One coulomb per second is the unit of electric current, and is called the "ampere." From the loss of weight of the anode and the elapsed time, calculate the current that flowed through the cell on the assumption that it was uniform during that time.
2. At the beginning of the electrolysis what ions are transferred through the cotton plug of the U-tube? As the electrolysis progresses and an OH^- ion concentration is built up in the cathode compartment, how is the picture of the ion transference altered?
3. If Na^+ ions are practically the only positive ions which move up to the cathode, how do you explain that H^+ rather than Na^+ ions are discharged at the cathode surface? Describe some form of cell in which sodium metal is actually liberated at the cathode. What is the essential difference between the latter cell and the cell used in this experiment?
4. If the current efficiency of the hydrogen discharge is 100 per cent, calculate from the copper coulometer data the volume of hydrogen escaping.
5. If a silver coulometer had also been inserted in the circuit, what weight of silver would have been deposited on the cathode?

PREPARATION 18

CHEMICALLY PURE SODIUM CHLORIDE FROM ROCK SALT, NaCl

All deposits of salt in the earth are a result of the evaporation either of sea water or of water containing approximately the same salts as sea water. "Rock salt" is the name applied to coarse unpurified salt, and it contains the same impurities as sea salt although usually in lesser amount.

COMPOSITION OF SEA SALT

$NaCl$	77 76%	K_2SO_4	2 46%
$MgCl_2$	10 88%	$CaCO_3$	0 33%
$MgSO_4$	4 75%	$MgBr_2$	0 22%
$CaSO_4$	3 60%		

For most commercial purposes these impurities are not harmful. By careful crystallization of the salt from solution, a product sufficiently free from these impurities can be obtained to be used as table salt. To obtain *chemically pure* sodium chloride, however, more elaborate precautions must be taken. A satisfactory method depends upon the insolubility of sodium chloride in a concentrated solution of hydrochloric acid. A nearly saturated solution of the rock salt is prepared, and, without removing the dirt and insoluble matter, enough pure sodium carbonate is added to precipitate the calcium and magnesium in the solution as carbonates. Into the clear filtrate gaseous hydrochloric acid is then passed until the greater part of the sodium chloride is precipitated, while the small amounts of sulphates and of potassium salts remain in the solution. The precipitate is drained and washed with a solution of hydrochloric acid until the liquid clinging to the crystals is entirely free from sulphates.

Materials: sodium chloride (rock salt), 75 grams.
$36\,N$ sulphuric acid, 95 cc.
$12\,N$ hydrochloric acid, 50 cc.

Apparatus: 2-liter round-bottom flask with 2-hole rubber stopper.
3-necked Woulff bottle with rubber stoppers.
65 mm. funnel.
2 thistle tubes.
delivery tube and connection; see Fig. 23.
600-cc. beaker.
tripod and wire gauze.

Procedure: Dissolve 25 grams of rock salt in 75 cc. of water, hastening the action with gentle heating. To the solution add about 1 gram of sodium carbonate dissolved in a few cubic centimeters of water. Stir, let settle, and add a few drops more of sodium carbonate solution, and if no fresh precipitate is produced in the clear part of the solution no more need be added; otherwise enough more must be added to produce this result. Filter the solution, hot, through an ordinary filter (Note 4 (*c*), page 7). Prepare pure hydrogen chloride by placing 50 grams of rock salt in the generator flask and treating it with the 95 cc. of concentrated sulphuric acid. Observe the directions given under the preparation of hydrochloric acid, page 142, and note particularly the caution as to the disposal of the hot residue. The gas is to be purified by bubbling it through the washing bottle containing about 100 cc. of concentrated hydrochloric acid, and then it is passed through the wide-mouth funnel into the sodium chloride solution in the 600-cc. beaker. When hydrogen chloride ceases to be evolved on heating the generator, collect the pre-

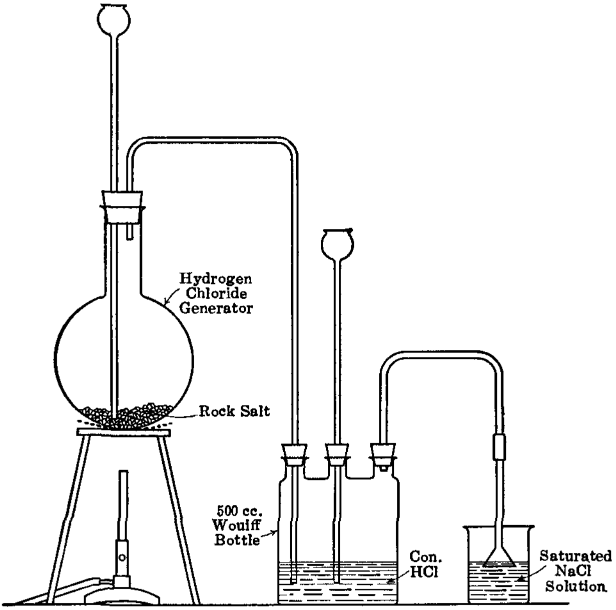


FIG. 23

cipitated sodium chloride on a suction filter. Test the filtrate for sulphate by adding a little barium chloride solution to a small sample of it diluted with water. A positive test will probably be obtained. Now wash the crystals with successive portions of 10 cc. of 6*N* HCl, until the washings show no further test for sulphates. (See Note 5 (*a*), page 9.) Then transfer the crystals to a porcelain dish and heat gently, while stirring, until all decrepitation ceases. Put up the product in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Why must the hydrochloric acid gas be passed through a washing bottle? Why is the safety tube necessary?

2. Why, in the light of the law of molecular concentration, should one expect the solubility of sodium chloride to be lessened by the presence of hydrochloric acid? It may be stated that another effect known as the " salting-out effect " also comes into play here and likewise tends to lessen the solubility of sodium chloride. The great amount of heat liberated when hydrogen chloride dissolves in water indicates a chemical action, and it is very probable that the water and hydrogen chloride unite to form an unstable compound. In the saturated solution then nearly all the water is chemically combined and very little is left to hold sodium chloride in solution.

3. Mention two possible causes for the very considerable amount of heat produced when the hydrochloric acid gas is absorbed by the solution in the beaker.

4. Why does not the solution in the washing bottle also grow hot?

PREPARATION 19

AMMONIUM BROMIDE, NH_4Br

Ammonium bromide could be prepared by the neutralization of ammonium hydroxide with hydrobromic acid,

$$NH_4OH + HBr = NH_4Br + H_2O$$

Since, however, hydrobromic acid is a more expensive material than uncombined bromine, the latter would have the preference as a source of bromine, provided it yielded as satisfactory a product. Bromine reacts upon a cold solution of sodium hydroxide with the formation of sodium hypobromite and sodium bromide.

$$Br_2 + 2NaOH = NaBr + NaBrO + H_2O$$

Sodium hypobromite reacts with ammonium hydroxide according to the equation

$$3NaBrO + 2NH_4OH = 3NaBr + 5H_2O + N_2$$

If now we substitute NH_4 for Na in the last two equations and add the equations we obtain

$$3Br_2 + 8NH_4OH \rightarrow 6NH_4Br + N_2 + 8H_2O$$

which gives the complete reaction of bromine with ammonium hydroxide.

Materials: bromine, Br_2, 12.5 cc. = 40 grams = 0.25 F.W.
15 *N* NH_4OH = 44 cc.

Apparatus: 125-cc. separatory funnel.
300-cc. Erlenmeyer flask.
4-inch porcelain dish.
pan of cracked ice and water.
burette clamp.
ring stand.
mortar and pestle.

Procedure: Lubricate the stop cock of the dropping funnel lightly with vaseline, and secure it in place with a rubber band, so that it will not slip out when in use and let the bromine spurt out over the fingers. Secure the funnel with a clamp to a ring stand so that the bottom of the stem is about 1 inch above the ice water. Place 50 cc. of water and the ammonium hydroxide in the Erlenmeyer flask, float the latter in the ice water, and insert the stem of the funnel in the flask so that it is kept from tipping over. Pour the bromine into the funnel. Now, holding the bulb of the funnel with the left hand, turn the stop cock with the right hand to let one drop of bromine fall into the flask; quickly close the stop cock and with the right hand grasp the flask and rotate its contents. Proceed in this way until all the bromine is added, working as rapidly as possible yet avoiding heating the flask and causing white smoke and bromine vapor to belch out. If, when all the bromine is added, the solution is yellow or red, add ammonium hydroxide, a drop at a time, until the color disappears. Pour the solution into the evaporating dish and evaporate it to dryness on the steam bath (see Note 6 (*b*), page 12). Pulverize the dry salt and put it in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. What products would be formed if bromine were added to a solution of sodium hydroxide instead of ammonium hydroxide (*a*) if the solution were kept cold? (*b*) if it were heated?
2. Add about 10 drops of bromine to 10 cc. of a cold $3N$ sodium hydroxide solution. Add this gradually to a solution of ammonium hydroxide, made by diluting 1 cc. of the $6N$ reagent with 10 cc. of water. Determine what gas is given off.
3. What fraction of the entire amount of ammonium ion used is lost through formation of nitrogen gas when ammonium bromide is made by the action of bromine on ammonium hydroxide?
4. Why cannot hydrobromic acid be prepared from potassium bromide by a method analogous to that used in the preparation of hydrochloric acid?

PREPARATION 20

STRONTIUM HYDROXIDE FROM STRONTIUM SULPHATE, $Sr(OH)_2 \cdot 8H_2O$

One of the most important sources of strontium is the mineral celestite, $SrSO_4$. By reduction with charcoal this can be converted into strontium sulphide,

$$SrSO_4 + 4C = SrS + 4CO$$

and the strontium sulphide, by treatment with copper oxide and water, can be made to yield strontium hydroxide,

$$SrS + \underline{CuO} + H_2O = Sr(OH)_2 + \underline{CuS}$$

Copper oxide is, in the ordinary sense, insoluble; nevertheless, in contact with water it does yield to an infinitesimal extent the ions of cupric hydroxide.

$$\underline{CuO} + H_2O \rightleftharpoons Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^-$$

Since copper sulphide is a far more insoluble substance than copper oxide, it follows that the few Cu^{++} ions from the latter unite with the S^{--} ions from the strontium sulphide to form copper sulphide, which precipitates continuously, while the copper oxide continuously goes into solution to resupply Cu^{++} ions. This action continues until either the copper oxide or the strontium sulphide is exhausted.

Strontium hydroxide crystallizes with 8 molecules of water, $Sr(OH)_2{\cdot}8H_2O$. It is very soluble in hot water, but sparingly soluble in cold water.

Materials: celestite, $SrSO_4$, 61 grams = 0.33 F.W.
powdered charcoal, 35 grams.
copper oxide, 48 grams.

Apparatus: gas furnace.
30-gram clay crucible and cover.
large mortar and pestle.
8-inch porcelain dish.
500-cc. flask.
suction filter and trap bottle.
5-inch watch glass.
400-cc. beaker.
iron ring and ring stand.
Bunsen burner.

Procedure: Grind the powdered celestite in a porcelain mortar until no more grit is felt under the pestle. Add 24 grams of powdered charcoal and continue to grind with the pestle until the two are thoroughly mixed. Place the mixture in a clay crucible, pack it firmly, and cover it with a layer of powdered charcoal $\frac{1}{2}$ inch deep. Cover the crucible with a close-fitting cover and heat it in a gas furnace for 1 hour, at a bright red heat. After the contents of the crucible have cooled, remove the layer of charcoal from the surface and bring the remainder, after crushing it to a powder, into an 8-inch porcelain dish; add 360 cc. of water, bring the mixture to a boil, and while it is boiling add copper oxide, a little at a time, until all of the soluble sulphide has interacted with it — about 48 grams in all. As long as any unchanged strontium sulphide is present the solution will show a yellow color, which may be observed by letting the black solid settle for a moment, and then looking through the upper layers of the clear liquid at the background of the white porcelain dish. As soon as the yellow color has entirely disappeared, the strontium sulphide has all reacted. Crystals of strontium hydroxide separate rapidly from this solution when it cools. Hence it must be filtered quickly in order to avoid having the crystals form in the filter and clog it completely. Heat 50 cc. of water to boiling in a beaker, and keep it at this temperature until it is required. Add hot water to the dish to replace any lost by evaporation, and pour (Note 2, page 4) the hot solution through a large ordinary filter (Note 4 (*c*), page 7), catching the filtrate in a 500-cc. flask, and allowing the main part of the residue to remain in the dish. Add the 50 cc. of hot water to this residue, stir it thoroughly, heating it for a moment over the flame, and then pour solution and residue into the filter and drain out all the liquid. In order to lessen the rate of cooling of the liquid in the filter funnel the latter should be kept covered with a watch glass. Stopper the flask to exclude the air, and wrap it with a towel, so that the solution may cool slowly and larger crystals may be formed. Finally, after several hours cool the solution with running tap water and then collect the crystals on a suction filter. Drain the crystals for a moment, but do not draw too much air through them, as they retain all the carbon dioxide it contains. Wrap the product in paper towels and leave it to dry over night at room temperature. (See Note 9 (*b*), page 15.) Put the product in a 6-ounce cork-stoppered bottle.

QUESTIONS

1. What constituent of the atmosphere must be excluded from the solution while crystallizing and from the crystals while drying? How would it contaminate the preparation?
2. A sample of the preparation should dissolve nearly clear in hot water. What will surely cause a slight cloudiness?
3. How could strontium chloride be prepared from strontium sulphide?
4. Give some other method by which strontium hydroxide could be obtained from strontium sulphide without the use of copper oxide.
5. Starting with the mineral strontium carbonate, how might strontium hydroxide be prepared? Strontium oxide? Strontium chloride?

PREPARATION 21

STRONTIUM CHLORIDE FROM STRONTIUM SULPHATE, $SrCl_2 \cdot 6H_2O$

Strontium chloride might be prepared by treating strontium sulphide, the intermediate product in the last preparation, with hydrochloric acid, but, to avoid the hydrogen sulphide nuisance, and furthermore, to show that strontium sulphate may be attacked without the use of a furnace, we shall employ quite a different method.

The method consists in first converting the sulphate into the carbonate by boiling it with a concentrated solution of sodium carbonate, and then dissolving the carbonate in hydrochloric acid, thereby yielding a solution of the chloride. The conversion of solid strontium sulphate into solid strontium carbonate furnishes an interesting illustration of the solubility product principle, for the solubility of these two salts in pure water is as follows:

	Solubility in grams per 100 cc.	Solubility in mols per liter
$SrSO_4$	0.011	0.0006
$SrCO_3$	0.0011	0.00007

Strontium sulphate would dissolve in the solution of sodium carbonate in the same manner as it would in pure water until it had saturated the solution, and its solubility product, which is equal to 0.0006 × 0.0006, was reached, but for the fact that long before this could occur the solution would be supersaturated with respect to strontium carbonate, the solubility product of which is only equal to 0.00007 × 0.00007. Thus strontium carbonate is precipitated continuously as strontium sulphate dissolves; and since the solution cannot become saturated with the latter as long as a large excess of carbonate ions is present, the solid salt finally remaining will consist entirely of strontium carbonate, provided a sufficient amount of sodium carbonate were employed. The reaction which takes place is, however, reversible, $\underline{SrSO_4} + Na_2CO_3 \rightleftarrows \underline{SrCO_3} + Na_2SO_4$, and, if strontium carbonate were boiled with a solution of sodium sulphate, the solid would change into sulphate until carbonate ions had accumulated in the solution to such an extent as to make the concentration ratio $[CO_3^{--}] : [SO_4^{--}] = 1:74$. When this ratio prevails, both solids are in equilibrium with the solution and no change takes place in either direction.

Materials: celestite, $SrSO_4$, 61 grams = 0.33 F.W.
anhydrous Na_2CO_3, 73 grams.
chlorine water.
6 N HCl, 111 cc.

Apparatus: 8-inch porcelain dish.
600-cc. beaker.
mortar and pestle.
iron ring and ring stand.
Bunsen burner.

Procedure: Grind the powdered celestite in a mortar until it is so fine that it no longer feels gritty under the pestle. Cover it in an 8-inch porcelain dish with 360 cc. of water, add the anhydrous sodium carbonate, and boil the mixture for 30 minutes, stirring it constantly at first. Transfer the solution and solid to a 600-cc. beaker, using 100 cc. of fresh water in rinsing out the last of the residue, and let the solid matter settle for 5 minutes. Decant off the liquid, which is still somewhat cloudy, but from which the essential part of the solid has settled, and wash the residue three times by decantation with 400–500 cc. of water. (See first paragraph, Note 5 (*b*), page 10). The residue is now sufficiently free from soluble sodium sulphate. Transfer about one-tenth of the moist strontium carbonate to another beaker, to be used in a later part of the process. To the remaining nine-tenths add 50 cc. of hot water, and then add hydrochloric acid, drop by drop, while stirring the mixture, until the further addition of a drop of acid produces no more effervescence. This solution now contains a slight excess of acid, and probably a trace of iron chloride as impurity. Add a few drops of chlorine water to oxidize any ferrous to ferric salt, then add the remaining one-tenth of the strontium carbonate and boil the mixture for 5 minutes. The solution should now be perfectly neutral to litmus, in which case all iron will be precipitated as $Fe(OH)_3$. If it is acid, it shows that the hydrochloric acid was added carelessly and that there was thus more than could be neutralized by the strontium carbonate. Filter the perfectly neutral solution, and evaporate the filtrate until a faint scum forms on removing the solution from the flame and blowing vigorously across the surface. Allow the solution to cool, but stir occasionally in order to obtain a uniform crystal meal rather than a cake of crystals. Finally, drain the crystals on a suction filter (Note 4 (*b*), page 6); evaporate the mother liquor to crystallation exactly as at first, and if the second crop of crystals is pure white, add it to the first crop. Wrap the crystals of $SrCl_2 \cdot 6H_2O$ in paper towels and leave them over night to dry

(Note 9 (*b*), page 15). These crystals are efflorescent, hence, as soon as the paper package is unwrapped, place them in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Explain why strontium carbonate, which is less soluble in pure water than strontium sulphate, should dissolve readily in dilute acids, while the latter salt will dissolve scarcely any more in acids than in pure water.

2. If a small quantity of a solution of strontium chloride were added to a solution containing equimolal quantities of sodium carbonate and sodium sulphate, what would be the precipitate formed?

PREPARATION 22

BARIUM OXIDE AND BARIUM HYDROXIDE FROM BARIUM CARBONATE, $Ba(OH)_2 \cdot 8H_2O$

The commercial method of preparing calcium oxide (quicklime) consists in heating calcium carbonate (limestone) in lime kilns. Barium oxide might be made from barium carbonate according to the same principle, except for the fact that the temperature required for the decomposition of barium carbonate is so high as to make such a method almost impracticable. This greater stability of the barium salt is an illustration of the fact that barium oxide is even more strongly basic than calcium oxide. The reaction, $BaCO_3 \rightleftharpoons BaO + CO_2$, is reversible, and in common with other reversible reactions it may be made to progress in one direction or the other by suitably altering the concentration of the substances present in the reacting system. Of the three substances involved in this reaction the only one which can be removed during the course of the reaction is the carbon dioxide. It is, however, not enough to let it merely pass off as a gas, because to escape from the crucible it will have to push back the atmosphere. The pressure of carbon dioxide in equilibrium with barium carbonate at 1350° is seen from the table to be but one-half an atmosphere, that is to say, barium carbonate will decompose until the atmosphere in the crucible contains about 50 per cent of carbon dioxide and then the decomposition will stop. However, at high temperatures charcoal reacts with carbon dioxide to form carbon monoxide

$$CO_2 + C \rightleftharpoons 2CO$$

At the equilibrium point of this reaction the partial pressure of carbon monoxide is many times that of the carbon dioxide; thus it would be much above 1 atmosphere, and carbon monoxide would escape from the crucible. With excess powdered charcoal in the crucible, therefore, both reactions would continue to run until all the barium carbonate had changed to barium oxide. Carbon monoxide does not react with barium oxide.

In the following procedure, in addition to the charcoal, a little rosin is mixed with the charge. On heating, the rosin decomposes forming finely divided carbon which becomes very intimately mixed with the charge.

Temperature	Pressure of CO_2 in equilibrium with	
	$CaCO_3$	$BaCO_3$
700°	22 mm.	——
750	80	——
800	167	——
897	760	——
1000	——	2.7 mm.
1100	8740	——
1350	——	381.

The barium oxide obtained in this way is not pure, but contains particles of charcoal as well as impurities coming from the mineral. It is very suitable, however, for the manufacture of barium hydroxide, into which it is converted by treatment with water. Barium hydroxide is extremely soluble in hot water, but sparingly so in cold water, from which it separates in flake-like crystals of the composition $Ba(OH)_2 \cdot 8H_2O$.

Materials: barium carbonate, $BaCO_3$, 99 grams = 0.5 F.W.; if the mineral witherite is used it should be very finely powdered; the artificially prepared material will react more readily.
powdered charcoal, 25 grams.
rosin, 5 grams.

Apparatus: gas furnace.
30-gram clay crucible, with cover.
8-inch porcelain dish.

5-inch filter funnel and filter.
5-inch watch glass.
500-cc. flask.
iron ring and ring stand.
Bunsen burner.

Procedure: Mix the finely powdered barium carbonate with 10 grams of powdered charcoal and 5 grams of powdered rosin. After mixing the whole mass very thoroughly in a mortar, place it in the crucible, press it down firmly, and cover it with a layer of charcoal at least ½ inch deep. Place a well-fitting cover on the crucible and heat the whole for 1 hour in the gas furnace to as high a temperature as possible. After the crucible has cooled, remove the top layer of charcoal, place the barium oxide in the porcelain dish, and very cautiously add a few drops of water, noting the very violent reaction. Finally add 400 cc. of water, and heat the mixture in the dish to boiling; pour the solution through a large, ordinary filter (Note 4 (*c*), page 7), letting the clear liquid run directly into a 500-cc. flask and keeping the funnel covered with a watch glass to prevent cooling during the filtration. Rinse the residue in the dish with 75 cc. more of boiling water, and pour this upon the filter after the first portion has nearly all run through. Stopper the flask and allow the solution to cool slowly to room temperature; finally, cool it nearly or quite to 0°; collect the crystals on a suction filter; wrap the product in paper towels and leave it over night to dry at room temperature (Note 9 (*b*), page 15). Put the product in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. How does barium hydroxide become contaminated by exposure to the air? Why might this product be dried with less contamination by exposure to the air out-of-doors than to the air of the laboratory?

2. The mineral witherite often contains barium sulphate as an impurity. State what changes this substance would undergo during the above process. How could barium hydroxide be prepared from barium sulphide? (Compare preparation of strontium hydroxide from strontium sulphate, page 194.)

3. Devise a method for preparing barium hydroxide from barium carbonate by which the use of a furnace may be avoided.

Suggestion: Make use of the difference in solubility of barium chloride and barium hydroxide.

Experiments

Very few of the chemical properties of the non-metals are displayed except in conjunction with the metals; in our study of the non-metals in the preceding chapters, therefore, we already have had revealed to us many of the chemical properties of the metals.

> **1.** Place a few small lumps of marble (calcium carbonate) in a small porcelain crucible. Cover the crucible in order to keep in the heat, and heat it strongly for 20 minutes with a Bunsen flame. When the product has cooled, wet each lump with a single drop or two of water and wait a few minutes, if necessary, to observe the effect. The lumps should grow very hot, and steam be driven off. Then wet the product with somewhat more water, and test the reaction of the moist mass towards litmus. The litmus is colored strongly blue by the suspension.

It requires a bright red heat to decompose $CaCO_3$ into CaO and CO_2. The CaO is a strongly basic oxide and combines strongly with water to form the base $Ca(OH)_2$, as is evidenced by the heat evolved. $Ca(OH)_2$ is sparingly soluble but enough dissolves to color litmus strongly blue.

> **2.** Place a few grams of magnesium carbonate in a 4-inch porcelain dish and heat it rather moderately, testing to see if carbon dioxide is being expelled. From time to time test the residue for carbonate by removing a little from the dish, thoroughly wetting it with about 5 cc. of hot water in a test tube, adding acid, and watching for effervescence. Very gentle heating suffices to change the magnesium carbonate so that it no longer effervesces with dilute HCl.

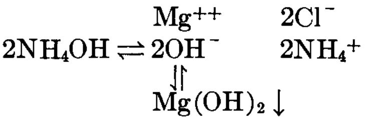
In both calcium carbonate and magnesium carbonate, which may be formulated $CaO \cdot CO_2$ and $MgO \cdot CO_2$, we have the same acid anhydride, CO_2. The tenacity with which the basic anhydrides CaO and MgO hold this acid anhydride is a measure of their basic strength. Magnesium oxide is, therefore, less strongly basic than calcium oxide.

3. Burn a strip of magnesium ribbon, held with iron pincers, and let the ash fall in a porcelain dish. Wet the magnesium oxide with a single drop of water and place the moist mass on a strip of red litmus paper. A small fleck of blue shows on the reverse of the litmus paper when the moist magnesium oxide is applied.

Magnesium has a very strong affinity for oxygen as shown by the intensity with which the metal burns. However, the residual affinity of magnesium oxide for water is much smaller than that of calcium oxide. The solubility of magnesium hydroxide is so small that the saturated solution acts but slowly in turning litmus blue.

4. To some magnesium chloride solution, add (*a*) some ammonium hydroxide; (*b*) some ammonium chloride and then some ammonium hydroxide. In (*a*) a copious white precipitate is observed; in (*b*) no precipitate.

The weakly ionized NH_4OH furnishes a sufficient concentration of OH^- ions to cause the precipitation of $Mg(OH)_2$. However, as the reaction progresses, NH_4^+ ions accumulate in the solution and



$$\begin{array}{lll} & \mathrm{Mg^{++}} & \mathrm{2Cl^-} \\ \mathrm{2NH_4OH} \rightleftharpoons & \mathrm{2OH^-} & \mathrm{2NH_4^+} \\ & \downarrow\uparrow & \\ & \mathrm{Mg(OH)_2}\downarrow & \end{array}$$

cause a continual lessening of the OH^- ion concentration. Since the solubility of $Mg(OH)_2$ although small, is still appreciable (0.0002 F.W. per liter in pure water) it is clear that with the OH^- ion concentration sufficiently depressed a fairly high Mg^{++} ion concentration can prevail without reaching the solubility product of $Mg(OH)_2$.

In part (*b*) an initial addition of NH_4^+ ion depresses the OH^- ion concentration so that no precipitation of $Mg(OH)_2$ at all takes place.

5. Dip a clean platinum wire in solutions of such of the chlorides of the alkali and alkaline earth metals as are at hand, and observe the color imparted to the Bunsen flame when the wire is inserted into the lower part of the flame.

AMMONIUM COMPOUNDS

When ammonium hydroxide dissociates electrolytically it yields the ion NH_4^+. The group of atoms NH_4, which is often spoken of as the ammonium *radical*, resembles in many respects the atom of sodium or potassium. Like these, it can form a monovalent positive ion, or it can form compounds with acid radicals, for example, NH_4Cl, $(NH_4)_2SO_4$; but unlike sodium and potassium, it cannot exist in the uncombined state.

> **6.** (*a*) Place a mixture of dry ammonium chloride and calcium hydroxide in a dry test tube and heat gently. A gas escapes from the tube, which has the odor of ammonia and which turns moist litmus blue.
>
> (*b*) Add a solution of a strong base to a solution of any ammonium salt, warm. The odor of ammonia is at once apparent.

These experiments furnish an example of the displacement of a weak base by means of a strong base. In (*a*) there is doubtless enough moisture condensed on the surface of the solid material so that the reaction can be considered as an ionic one. In this case as well as in (*b*) we have the weak base NH_4OH forming from its ions. The non-electrolytic dissociation of NH_4OH yields the gas NH_3, the odor of which is observed.

7. Gaseous Dissociation of Ammonium Chloride. Like all ammonium salts, ammonium chloride can be volatilized by applying heat. Some of the other salts are permanently decomposed by the process, but the vapor of ammonium chloride can be condensed again to the same solid substance.

> Place 2 grams of ammonium chloride in the middle of a combustion tube, and on either side place loose plugs of asbestos. Outside the asbestos plugs at both ends place moistened strips of both red and blue litmus paper. Support the tube in a slightly inclined position by means of a clamp, and heat the section containing the salt, using a flame spreader. At both ends the red litmus is colored blue at first. Later the color at each end changes to red.

The vapor of ammonium chloride is very largely dissociated non-electrolytically

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

The rate of diffusion of gases, according to Graham's law, is inversely proportioned to the square root of the densities. Thus the ammonia in the mixture will diffuse $\frac{\sqrt{36.5}}{\sqrt{17}}$ or 1.5 times as fast as the hydrogen chloride, and at each end the gas which diffuses through the plugs contains at first an excess of ammonia. The residual gas in the middle is left with an excess of HCl, and when this gas is finally expelled by heat the moist litmus at each end turns red.

> **8. Hydrolysis of Ammonium Salts.** Boil for some time a solution of ammonium sulphate to which has been added a few drops of blue litmus solution. Pass the vapors into a flask of water containing a few drops of red litmus. The litmus in the boiling flask slowly turns red. The litmus in the flask in which the vapors are condensed turns blue.

The neutral salt of a base as strong as ammonium hydroxide is practically not hydrolyzed at all in cold water, certainly not enough to show by the litmus test. Water at 100° is ionized about ten times as much as at ordinary temperature and consequently the hydrolysis of the ammonium sulphate is increased:

$$\begin{array}{rll} & 2NH_4^+ & SO_4^{--} \\ 2H_2O \rightleftharpoons & 2OH^- & 2H^+ \\ & \downarrow\uparrow & \\ & 2NH_4OH \rightleftharpoons 2NH_3 + 2H_2O & \end{array}$$

Even at 100° the hydrolysis is practically negligible except that one hydrolysis product, NH_4OH, is volatile, whereas the other, H_2SO_4, is non-volatile. Thus, since a minute amount of ammonia passes over with the steam, before long the accumulation of NH_4OH in the condensing flask turns litmus blue, and the residue of H_2SO_4 in the boiling flask likewise shows its presence there.

General Questions V

Alkali and Alkaline Earth Metals

1. Make a table of the elements of Group I, Family A, including lithium and sodium, giving in succeeding columns: (1) the symbol of the element; (2) its valence in its compounds; (3) the formula of the oxide; (4) the formula of the hydroxide; (5) the

solubility of the hydroxide in grams per 100 grams of water at 25°; (6) the formula of the sulphate; (7) the solubility of the sulphate at 25°; (8) the formula of the carbonate; (9) the solubility of the carbonate at 25°; (10) the formula of the chloride; (11) the solubility of the chloride at 25°.

2. Make a similar table of the elements of Group II, Family A, including magnesium.

3. Give the same information for ammonium. Discuss the difference between ammonium and ammonia.

4. Make a list of the percentage of ionization of the hydroxides of the alkali metals, of ammonium, and of the alkaline earth metals in 0.1 *N* solution if the substance is soluble to that extent. Give figures for the hydroxyl-ion concentration in 0.1 *N* NH_4OH solution and in saturated solutions of $Ca(OH)_2$ and $Mg(OH)_2$. Describe and discuss the results of Experiment 4 in the light of these figures.

5. An oxy-salt, such as $CaCO_3$ ($= CaO{\cdot}CO_2$), can be broken up by a sufficiently high heat into a basic oxide and an acid oxide — for example, $CaO{\cdot}CO_2 \rightarrow CaO + CO_2$. The higher the temperature necessary to accomplish this, the greater is the chemical affinity between the two oxides, that is, the more strongly basic and acidic, respectively, are these two components; and therefore in a series of salts, all containing the same acidic oxide — for example, $CaCO_3$, $SrCO_3$, $BaCO_3$ — the greater the stability of the salt, the stronger is the basic oxide. Compare the approximate temperatures at which the alkaline earth carbonates are decomposed, and list the alkaline earth oxides in the order of their basic strength.

The carbonates of the alkali metals are practically undecomposable by heat alone. Compare the basic strength of the alkali metal oxides as a family with that of the alkaline earth oxides.

6. More precise information as to the relative basic strength may be given from the molal heats of formation in a series of oxy-salts like the carbonates. In the thermochemical tables sometimes the figure that we want is given, namely, the heat of formation of the salt from the metal oxide and the non-metal oxide, for example, $MgO + CO_2 \rightarrow MgCO_3 + 28{,}850$ calories. But more often we will find only the heat of formation from the elements, for example, $Mg + C + \frac{3}{2}O_2 \rightarrow MgCO_3 + 269{,}900$ calories. We must then look up the heat of formation of mag-

nesium oxide, $Mg + \frac{1}{2}O_2 \rightarrow MgO + 143,400$, and the heat of formation of carbon dioxide, $C + O_2 \rightarrow CO_2 + 97,650$ calories, and subtract the sum of these quantities: $269,900 - 143,400 - 97,650 = 28,850$ calories.

Find in the thermochemical tables the molal heat of formation of the carbonates of sodium, potassium, calcium, and barium from the metal oxide and carbon dioxide, and draw conclusions as to the relative basic strength of the basic oxides.

7. State the colors imparted to a Bunsen flame by vaporized salts (chlorides) of the alkali and alkaline earth metals.

8. Give formulas of the peroxides of sodium and of barium. How do these substances react with cold dilute acids? What is the formula of the peroxide of potassium? Compare the action of the oxides Na_2O, K_2O, and BaO in water with that of the peroxides. What is the valence of the metal in each of the peroxides, and how do you account for the amount of oxygen over that contained in the oxide?

CHAPTER VI

ELEMENTS OF GROUP III OF THE PERIODIC SYSTEM

Boron and aluminum, the first two members of this group, are the only ones which are classed among the common elements. On this account, and also because the difference in properties between Family A and Family B is far less marked than in Groups I and II, the whole group is taken up under one heading.

The characteristics of this group are that the elements possess a valence of 3, and that the oxides, M_2O_3, have but a weakly developed basic character. Boron, in fact, shows practically no base-forming properties, but forms rather a weak acid. The oxide of aluminum displays both basic and acidic properties; that is, it is *amphoteric*. The remaining elements are more distinctly base-forming than aluminum, without, however, approaching in any way the alkaline earth metals in this respect.

PREPARATION 23

BORIC ACID, H_3BO_3

In this preparation, borax, the sodium salt of tetraboric acid, is chosen as the source of boron. Although boron is decidedly a non-metal, still its acid-forming characteristics are not highly developed and its acids are readily displaced by strong acids from solutions of their salts. Thus tetraboric acid, $H_2B_4O_7$, would be set free from borax by hydrochloric acid, but the acid which actually crystallizes is the more highly hydrated orthoboric acid, H_3BO_3.

Materials: borax, $Na_2B_4O_7 \cdot 10H_2O$, 96 grams = 0.25 F.W.
12 N HCl.
methyl orange solution.

Apparatus: 600-cc. beaker.
5-inch funnel.
suction filter and trap bottle.
5-inch watch glass.
iron ring and ring stand.
Bunsen burner.
towel and rubber band.

Procedure: Dissolve 96 grams of borax in 175 cc. of boiling water. Calculate the volume of $12N$ HCl required to liberate the boric acid completely. Add this amount in small portions to the boiling solution, stirring after each addition. When all the acid has been added, test a drop of the solution with methyl orange. If an acid test is not obtained, add $12N$ HCl in 2-cc. portions until a decided pink color is obtained. Finally add an extra 2-cc. portion. Cool the solution in a pan of tap water to 15° or below, and filter, using suction. Press all the liquid possible out of the crystals. Test the filtrate with methyl orange, and if it is not distinctly acid, add enough $12N$ HCl to make it so. Add any boric acid thus precipitated to the main product. Pour 15 cc. of cold water over the cake of crystals in the filter, and allow it to soak in, then drain it off with suction. Dissolve the crystals in 300 cc. of boiling distilled water. Filter hot, without suction, into a clean 600-cc. beaker. (See Note 4 (*c*), page 7.) Heat the solution, and completely dissolve any crystals of boric acid which may have separated. Wrap the beaker in a towel held in place by a rubber band. Cover it with a watch glass, and set it in your locker to crystallize. Collect the crystals and let them dry at room temperature on a paper towel. If the filtrate is evaporated to one-third of its volume, a second crop of crystals will be obtained. Dissolve a small amount of your product in distilled water, and test it for chloride ion.

QUESTIONS

1. Explain the relations between orthoboric acid, metaboric acid, tetraboric acid, and boric anhydride. *Experiment:* Place a few grams of boric acid on a watch glass upon the steam table (100–110°) and leave for $\frac{1}{2}$ hour. What is formed? What would be formed if the acid were heated to 140°? Suspend a little of the acid in a loop of platinum wire, and heat in the Bunsen flame. What is formed?

2. *Experiment:* Place a few crystals of boric acid in a small porcelain dish, cover them with 5 cc. of alcohol, set fire to it. Observe the color of the edges of the flame, especially when stirring and when the alcohol is almost burned out. Repeat, using borax instead of the boric acid, and again, using borax moistened with concentrated sulphuric acid.

What causes the green color of the flame, and why is it not observed with borax alone?

Repeat if necessary the last part of Experiment 1, noticing the color imparted to the flame while the orthoboric acid is first melting, and again when a clear bead of boric anhydride is obtained.

What conclusions can you make from these experiments regarding the volatility of boric acid and of boric anhydride?

3. What effect has a solution of borax upon litmus? Explain what is thus shown regarding the strength of boric or tetraboric acid. Explain why litmus will not be turned a bright red until more than 2 moles of HCl have been added to 1 mole of borax.

4. How can boron chloride be prepared? How does this substance behave when treated with water? How would it behave if boron were a strongly metallic element?

PREPARATION 24

SODIUM PERBORATE, $NaBO_3 \cdot 4H_2O$

At least three boric acids of the definite compositions shown by the formulas H_3BO_3, HBO_2, $H_2B_4O_7$ can be prepared in the solid form. These are all obtainable from the anhydride B_2O_3, and they differ only in the degree of hydration of the B_2O_3.

Hydrogen peroxide differs from water in that it possesses the divalent negative radical O_2 instead of the ordinary divalent O radical of water. (Compare page 160.)

Peroxides such as BaO_2 possess the same O_2 radical as hydrogen peroxide and exhibit similar oxidizing properties. There is also a large number of acids and salts known in which an O_2 group takes the place of the single O atom in the ordinary compound. These also possess the oxidizing properties of peroxides. One of the most easily prepared of these is sodium perborate $NaBO_3$ which bears the same relation to sodium metaborate $NaBO_2$ that hydrogen peroxide does to water. A solution prepared with equiformal amounts of H_3BO_3 and NaOH contains the proportions of acid and base to yield $NaBO_2$. But if this solution is evaporated to the point where crystals separate, we do not obtain $NaBO_2$ but rather borax $Na_2B_4O_7 \cdot 10H_2O$, and the remaining solution contains a higher proportion of base. If, however, H_2O_2 is added to the dilute sodium metaborate solution, the sparingly soluble hydrated sodium perborate $NaBO_3 \cdot 4H_2O$ crystallizes out. This salt when dry keeps fairly well, but if it is left suspended in the solution it gradually loses oxygen and the sodium metaborate goes back into solution:

Materials: borax, $Na_2B_4O_7 \cdot 10H_2O$, 24 grams = 0.0625 F.W.
NaOH, 5 grams.
3 per cent H_2O_2 solution, 283 cc.
alcohol.
ether.

Apparatus: 600-cc. beaker.
suction filter and trap bottle.
pan of ice.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the 24 grams of borax and 5 grams of NaOH in 150 cc. of warm water. Cool the solution to room temperature and add the 283 cc. of hydrogen peroxide slowly. Cool the solution by immersing the beaker in ice water, finally dropping 20 grams of ice into the solution. Stir; after a few minutes fine crystals begin to separate. Stir frequently for the next 20 minutes. Then collect the crystals on a suction filter. Wash the crystals with two successive portions of 25 cc. each of alcohol and then two successive portions of 25 cc. each of ether. Stop the suction before each washing and let the washing liquid sink into the crystals before applying suction again. Dry the crystals on paper towels and preserve them in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. To 50 cc. of water, add 1 cc. of KI solution and 1 cc. of starch emulsion. Note absence of blue color. To half of this starch-iodide solution, add a few crystals of sodium perborate and then a drop or two of acetic acid until a blue color appears. To the other half of the starch-iodide, add a few drops of hydrogen peroxide and note a blue color which disappears when a drop or two of $6N$ NaOH is added. Write equations and compare the action of sodium perborate and hydrogen peroxide.

2. To 50 cc. of water, add 1 gram of sodium perborate and 10 cc. of $6N$ H_2SO_4. Dissolve 0.1 gram of potassium permanganate in 10 cc. of water and add 5 cc. of $6N$ H_2SO_4. Pour this solution

into the first one with stirring and observe the decolorization and the evolution of a gas. Again compare with the action of hydrogen peroxide.

PREPARATION 25

HYDRATED ALUMINUM CHLORIDE, $AlCl_3 \cdot 6H_2O$

A solution of aluminum chloride can be prepared by the action of hydrochloric acid on the metal, but if this solution is evaporated to dryness, the solid that is left is the oxide instead of the chloride. Hydrolysis is prevented by hydrochloric acid, and the hydrated chloride can be crystallized from an acid solution. In this preparation the solution is saturated with hydrochloric acid, which not only drives back hydrolysis but also reduces the solubility of the salt.

Anhydrous aluminum chloride can be prepared by the action of dry chlorine on aluminum; in its properties it is very similar to aluminum bromide, which is the subject of the next preparation.

Materials: aluminum turnings, 13.5 grams = 0.5 F.W.
$12N$ HCl, 125 cc.
rock salt, NaCl, 90 grams.
$36N$ H_2SO_4, 175 cc.
shredded asbestos suspended in water.
sodium hydroxide pellets for the desiccator.

Apparatus: 500-cc. flask.
suction filter and marble.
2-liter flask for generator (Fig. 23 on page 191).
4-inch porcelain dish.
desiccator.
pan of ice and water.

Procedure: Place the aluminum turnings in a 500-cc. flask; add 50 cc. of water and then the $12N$ HCl drop by drop until a vigorous reaction has started and finally as rapidly as may be without producing too violent a reaction. The 125 cc. of acid should just suffice to dissolve the metal. Unless it is perfectly clear, filter the solution through asbestos on a suction filter (Note 4 (*d*), page 8) and return it to the 500-cc. flask. Fit up the hydrogen chloride generator and connections so that the gas will pass first through a washing bottle containing a little $12N$ HCl and provided with a safety tube (Fig. 23, on page 191). The gas will then pass into the flask containing the aluminum chloride solution. The end of the delivery tube dipping into the solution must be at least 1.5 cm. in diameter, else it will become stopped with the precipitated product. To the latter flask fit an exit tube which will lead any waste gas to within ½ inch of the surface of water in a bottle.

Surround the flask of aluminum chloride with cracked ice and water, and pass the gas into the solution until it is saturated. Observe the usual caution about disposing of the hot contents of the generator. Collect the crystalline precipitate in a 5-inch funnel containing a marble and dry it as completely as possible with suction while pressing the crystal mass with the round end of a test tube. Place the product in a 4-inch porcelain dish in the desiccator over solid sodium hydroxide. It will take several days for the excess of hydrochloric acid to evaporate from the crystals. When it is dry put the product in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. Treat some of the aluminum chloride with water. Does it dissolve to give a clear solution? Is there any noticeable heating? Test the solution with litmus. Is the salt hydrolyzed? Is it hydrolyzed extensively? Explain how you reach your conclusion from this experiment.
2. Warm about 1 gram of the preparation in a porcelain dish over a flame until fumes cease to come off. What are the vapors given off, and by what tests do you make your conclusion? Is the residue soluble in water? Of what does it consist?
3. Explain the difference in the extent to which the hydrolysis takes place when the salt is dissolved in a large amount of water and when it is heated with merely its water of crystallization.

PREPARATION 26

ANHYDROUS ALUMINUM BROMIDE, $AlBr_3$

Like aluminum chloride this salt is completely hydrolyzed if its solution is evaporated to dryness. Only the hydrated salt can be prepared by the action of hydrobromic acid solution (see preceding preparation); the anhydrous substance is prepared by the direct action of the elements on each other. The action is one of such extreme violence that it is safe to let the vapor only of bromine come in contact with the metal.

Aluminum bromide melts at 97.5° and boils at 268°. It is very soluble in carbon disulphide without chemical action. It reacts explosively with water, and throughout this preparation extreme caution must be observed not to let any of it come in contact with water.

Materials: aluminum turnings, 9 grams = 0.33 F.W.
bromine, 80 grams = 25 cc. (must be dry and must be measured in a dry graduate).
carbon disulphide.

Apparatus: two 125-cc. distilling flasks.
125-cc. separatory funnel.
600-cc. beaker.
3 clean dry test tubes.
18 inches hard glass tube of 15-mm. diameter.
360° thermometer.
burette clamp.
ring stand.
Bunsen burner.

Procedure: This preparation must be carried out entirely under the hood. Fit the separatory funnel with a rubber stopper into one of the distilling flasks; clamp the latter upright with the bulb immersed in water in a 600-cc. beaker on a ring stand. Fit the side arm of the distilling flask with a rubber stopper into one end of the hard glass tube. The other end of this tube should be thrust loosely into the neck of the other distilling flask. Place the aluminum turnings about in the middle of the hard glass tube. The tube should slope downward toward the receiving flask but not so much that the aluminum will not remain in place. The entire apparatus must be absolutely dry inside. Transfer the bromine to the separatory funnel. Heat the water in the beaker to boiling, and regulate the flame so that it continues to boil gently. Open the stop cock of the dropping funnel and let the bromine drip very slowly into the heated flask and vaporize. Heat the aluminum in the hard glass tube until it begins to glow; then regulate the dripping of the bromine to keep up a vigorous reaction. The reaction will now be self-sustaining if the bromine is perfectly dry. The glass tube may be heated, if necessary, in order to sustain the reaction. Some uncombined bromine will pass the aluminum and escape from the receiving flask. The aluminum bromide will condense and drip into the receiving flask. If any solidifies in the tube it should be melted out.

After this phase of the process is over, clamp the receiving flask in an upright position, using it now as a distilling flask, and close the neck with a rubber stopper carrying a thermometer. Label three dry test tubes and record the weight of each on the label. Support one of these tubes with the side arm of the distilling flask inserted about 3 inches, and start the distillation. At first bromine vapor alone comes over, part of which condenses. As soon as the red color has disappeared from the bulb of the flask, substitute a fresh tube as receiver, and catch 1 or 2 cc. of slightly colored product; then, as soon as the aluminum bromide comes over entirely colorless, change the receiver again, and collect the bulk of the product, which distils at 268°, in the third tube. Stopper all three tubes immediately with rubber stoppers. Hand in the third tube and contents as the preparation. Half fill the second tube with carbon disulphide and restopper it, leaving the aluminum bromide to dissolve. Take the stopper from the distilling flask and observe the dense fumes, caused by the reaction of the aluminum bromide left in it with the water vapor of the air. It is unsafe to pour water into the vessels containing any aluminum bromide. To clean them dissolve the aluminum bromide in a little carbon disulphide, then add water and rinse them out. Carbon disulphide vapor is inflammable and the liquid should not be handled near a flame. If a deposit of aluminum oxide adheres to the inside of the distilling flask add a few cubic centimeters of $12N$ HCl and let it stand over night.

QUESTIONS

1. Place 3 cc. of the carbon disulphide solution of aluminum bromide in a dry 600-cc. beaker. In another beaker place 100 cc. of cold water, and holding it at arm's length with the face turned away, pour it all at once into the first beaker. The effect is startling but not dangerous if one is not too near. Heat the contents of the beaker until all the carbon disulphide is evaporated. Is the aluminum bromide now dissolved in the water? Make tests for Al^{+++} and Br^- ions on separate small portions. How?

Is the solution clear or cloudy? Is the salt in the dilute aqueous solution extensively hydrolyzed?

2. Place another 3 cc. of the carbon disulphide solution in a watch glass. After the carbon disulphide evaporates let the residue stand on a hot plate until it appears dry. Is this residue soluble in water? Of what does it consist?

3. How could hydrated aluminum bromide be prepared?

4. Suggest a method of making anhydrous aluminum bromide, using hydrogen bromide instead of bromine, and state why you think the method might be feasible.

Experiments

> **1. Acid Strength of Boric Acid.** Dissolve 3 grams of H_3BO_3 in 50 cc. of water, thus making a formal solution. Add a few drops of a solution of blue litmus and compare the color with that produced by dilute HCl. Add $1\,N$ NaOH, 1 cc. at a time, noting the gradual change in color, until the litmus is completely blue, and note the amount taken.

It would take 150 cc. of $1\,N$ NaOH to give Na_3BO_3, 50 cc. to give $NaBO_2$, and 25 cc. to give $Na_2B_4O_7$. The fact that the solution becomes alkaline when there is still a large excess of boric acid in the solution (even when it is figured as tetraboric acid, $H_2B_4O_7$) shows how very weak the acid is.

AMPHOTERIC SUBSTANCES

A substance which can behave both as an acid and a base is known as amphoteric. In water such a substance would yield both H^+ and OH^- ions, but the product of the concentrations of these ions could not exceed the ion product of water;

$$[H^+] \times [OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

Amphoteric substances are necessarily extremely weak both as acids and as bases, but they possess the property of reacting with strong acids on the one hand and with strong bases on the other hand.

Aluminum hydroxide is amphoteric; it is itself insoluble, but its salts, such as $AlCl_3$ and Na_3AlO_3, are very soluble; it is therefore most easy to observe whether the aluminum hydroxide reacts with an acid or a base, because if it does it is seen to dissolve.

2. **Aluminum Hydroxide.** Add NH_4OH to an aluminum sulphate solution until a strong odor of ammonia persists after stirring. A gelatinous white precipitate forms. Collect some of this precipitate on a filter and wash it repeatedly with hot water until all excess of ammonia is removed. Then dip red and blue litmus paper into the precipitate and observe that neither is affected.

This experiment shows the insolubility of aluminum hydroxide and the extreme weakness of its acidic and basic properties.

3. **Aluminum Hydroxide Acting as an Acid.** To a little aluminum sulphate solution add NaOH solution a drop at a time until a copious precipitate is observed; continue to add NaOH, and observe that the precipitate soon redissolves.

The precipitate is aluminum hydroxide, $Al_2(SO_4)_3 + 6NaOH \rightarrow \underline{2Al(OH)_3} + 3Na_2SO_4$. That the aluminum hydroxide dissolves in the solution of the base indicates that it has reacted to form a soluble salt and that it is itself an acid. There are two acids of aluminum differing in degree of hydration in the same way as the different boric acids.

$$Al(OH)_3 \rightarrow H_3AlO_3 \text{ (ortho aluminic acid)}$$
$$Al(OH)_3 \rightarrow H_2O + HAlO_2 \text{ (meta aluminic acid)}$$

The soluble salt may be either sodium ortho aluminate, Na_3AlO_3, or sodium meta aluminate, $NaAlO_2$, depending on the amount of NaOH used.

4. **Aluminum Hydroxide Acting as a Base.** To the solution left at the end of Experiment 3 add an acid (say HNO_3) drop by drop until a copious precipitate is observed. Continue to add acid and observe that the precipitate redissolves.

The precipitate is aluminic acid, displaced from its salt by the stronger acid, $Na_3AlO_3 + 3HNO_3 \rightarrow \underline{H_3AlO_3} + 3NaNO_3$. That the aluminic acid dissolves in nitric acid indicates that it reacts to form a soluble salt and is itself reacting as a base.

5. **Comparative Basic and Acidic Strength of $Al(OH)_3$.** Add NH_4OH in excess to an aluminum salt solution, and note that the precipitate does not redissolve in the excess of NH_4OH. Add acetic acid drop by drop. For a time the

precipitate remains unaffected, but after the NH_4OH is all neutralized (shown by the solution ceasing to smell of ammonia after shaking) a little more acetic acid redissolves the precipitate.

Ammonium hydroxide and acetic acid are of equal strength as base and acid respectively. That the $Al(OH)_3$ does not dissolve in excess NH_4OH indicates that it is not a strong enough acid to react with a base of this feeble strength. That it does dissolve in acetic acid indicates that it is a strong enough base to react with an acid of the feeble strength of acetic acid. Thus aluminum hydroxide, although an extremely weak base, is more basic than acidic.

6. Instability of Aluminum Carbonate. Add together solutions of $Al_2(SO_4)_3$ and Na_2CO_3. Effervescence takes place, and the escaping gas can be shown to be carbon dioxide. A gelatinous white precipitate is formed resembling previous precipitates of $Al(OH)_3$. To show whether this precipitate is really the hydroxide, or perhaps the carbonate or basic carbonate, collect some of it on a filter and wash it very thoroughly with water to remove any excess of Na_2CO_3. Then add an acid (say HCl) to the precipitate and observe that it dissolves without a trace of effervescence.

Reference books tell us that aluminum carbonate has never been prepared. In this experiment we brought together the ions of aluminum carbonate and the result showed that this salt cannot exist in solution. The reaction might be described as the hydrolysis of aluminum carbonate:

$$\begin{array}{rll} & \mathrm{2Al^{+++}} & \mathrm{3CO_3^{--}} \\ \mathrm{6H_2O} \rightleftarrows & \mathrm{6OH^-} & \mathrm{6H^+} \\ & \downarrow & \downarrow \\ & \mathrm{2Al(OH)_3} & \mathrm{3H_2CO_3} \\ & \downarrow & \downarrow \\ & \mathrm{2Al(OH)_3}\downarrow & \mathrm{3H_2O + 3CO_2}\uparrow \end{array}$$

That aluminum carbonate is thus completely hydrolyzed indicates that the base and the acid are both very weak.

GENERAL QUESTIONS VI

ELEMENTS OF GROUP III

1. Make a table of all the elements of Group III, giving in succeeding columns: (1) the symbols of the elements in the order of their increasing atomic weights, placing the elements of the A Family in the left of the column, and of the B Family in the right; (2) the formula of the hydroxide, or hydroxides, if more than one is described in reference books; (3) the character of the hydroxide, distinguishing strongly acid, weakly acid, amphoteric, weakly basic, and strongly basic; (4) the formula of the chloride, or chlorides; (5) the degree of hydrolysis of the chloride, distinguishing complete, much, little, or none.

2. Compare aluminum hydroxide with the hydroxides of sodium and magnesium, the corresponding elements in Groups I and II, as regards solubility and degree of ionization.

3. Compare the thermal stability of magnesium and aluminum carbonates — of dry magnesium and aluminum sulphates. What do the facts thus cited show as to the relative basic strength of magnesium and aluminum oxides?

4. Describe the successive observations that are made when NaOH solution is added gradually to an $AlCl_3$ solution until an excess of the base is present. Likewise describe observations when HCl solution is added gradually to an Na_3AlO_3 solution until the acid is in excess. Write fully ionized intersecting equations corresponding to each observation, and explain how the amphoteric character of aluminum hydroxide is manifested in this experiment.

CHAPTER VII

HEAVY METALS OF GROUPS I AND II OF THE PERIODIC SYSTEM

The metals coming under this heading constitute the right-hand or B Families in Groups I and II of the periodic system. They possess high specific gravities, and chemically they are far less active than the metals of the corresponding A Families, reacting but little or not at all with water or air. They are base-forming with the exception of gold, and their oxides yield fairly stable salts with the strong acids; their basic properties, however, are comparatively weak, and the oxides of some of them show very feeble acidic properties as well.

Copper, silver, and gold in Group I show a similarity to sodium and potassium principally in the fact that they form certain compounds of the same type, for example, M_2O and MCl. Zinc, cadmium, and mercury in Group II resemble calcium, barium, and strontium in that they form compounds of the types MO, MSO_4, MCl_2, etc. In other respects, the divergence in the properties of the elements of the A and B Families is at a maximum in these two groups.

PREPARATION 27

CRYSTALLIZED COPPER SULPHATE, $CuSO_4 \cdot 5H_2O$ (BLUE VITRIOL)

On account of the fact that copper has not the power of displacing hydrogen from acids, it is not possible to dissolve it directly in dilute sulphuric acid. But although the metal itself is so difficult to attack with non-oxidizing acids, nevertheless copper *oxide* is readily dissolved by all acids; and thus the problem is to convert copper into its oxide. The cheapest source of oxygen is the atmosphere, and on the commercial scale, the usual method of obtaining copper sulphate from scrap copper is to allow dilute sulphuric acid to drip slowly over the latter, to which air is given free access. Since, however, this method would be too time-consuming for the laboratory, nitric acid instead of air will be employed as the oxidizing agent.

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Materials: copper turnings, 64 grams = 1 F.W.
$6N$ HNO_3.
$6N$ H_2SO_4.

Apparatus: 6-inch iron sand bath.
8-inch porcelain dish.
suction filter and trap bottle.
8-inch crystallizing dish with glass plate.
iron ring and ring stand.
Bunsen burner.

Procedure: Heat the copper turnings in an iron pan until all oily matter is burned off and the metal has become coated with oxide. In an 8-inch porcelain dish treat the ignited copper turnings with the calculated volume of $6N$ H_2SO_4 and $6N$ HNO_3. Warm in the hood for 20 minutes; if any metallic copper remains undissolved, pour the solution off from it and treat it with a few cubic centimeters of fresh nitric acid and twice as much sulphuric acid. If the solution is not perfectly clear, filter it while still at the boiling temperature; then cool as rapidly as possible, stirring to get a crystal meal. Separate the meal from the mother liquor, using the suction filter. Evaporate the mother liquor somewhat, and obtain a second crop of crystals, discarding the mother liquor from this crystallization. Dissolve all the damp product by adding its own weight of water and warming; place the warm solution in the crystallizing dish, add some seed crystals when the temperature is about 35°, cover the dish, wrap it with towels, and leave it to cool very slowly. Remove the crystals, and leave the saturated solution in the crystallizing dish uncovered to evaporate slowly and deposit more crystals. Spread the entire product on paper towels to dry, and hand in the preparation in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. Explain why copper will not dissolve in dilute sulphuric acid.
2. Write the equation for the reaction of copper with con-

centrated sulphuric acid. Analyze this reaction, and show in what manner the copper is oxidized.

3. How can copper sulphate be obtained from copper sulphide on a commercial scale?

PREPARATION 28

CUPROUS CHLORIDE, CuCl

Cupric salts derived from the oxide CuO are stable in contact with air and water and comprise the most used compounds of copper. Cupric ions, Cu^{++}, are present in solutions of cupric salts.

Cuprous salts are derived from cuprous oxide, Cu_2O, and are generally unstable in contact with air and water. No soluble cuprous salts which dissolve in water to give cuprous ions, Cu^+, are known.

The conditions under which cuprous salts can exist may be explained in terms of the equilibrium which establishes itself in the reaction

$$Cu^\circ + Cu^{++} \rightleftarrows 2Cu^+ \qquad (1)$$

When copper metal is dipped in cupric sulphate solution this reaction runs a very small distance to the right until the equilibrium ratio of cuprous and cupric ions is reached. This ratio is very small. The same concentration ratio is reached from the opposite direction when cuprous oxide is treated with dilute sulphuric acid

$$Cu_2O + H_2SO_4 \rightarrow 2Cu^+ \quad SO_4^{--} + H_2O$$
$$2Cu^+ \rightleftarrows Cu^{++} + Cu$$

when nearly all the cuprous sulphate resulting from the neutralization changes to cupric sulphate and copper.

Cuprous ions and chloride ions form two different combinations

$$Cu^+ + Cl^- \rightleftharpoons CuCl \downarrow \qquad (2)$$
$$Cu^+ + 2Cl^- \rightleftharpoons CuCl_2^- \qquad (3)$$

In presence of chloride ions, Cu^+ ions are thus removed and copper can continue to react with Cu^{++} ions as in (1) until the cupric salt is all reduced to cuprous. Increasing concentration of Cl^- favors reaction (3) more than reaction (2), and thus in concentrated HCl we obtain the soluble $H^+CuCl_2^-$. Dilution of the latter reduces the concentration of (Cl^-), which favors the complex ion formation in proportion to its second power, and of the insoluble CuCl only in proportion to its first power. Therefore reaction (3) runs to the left and reaction (2) to the right and white CuCl precipitates.

In the following procedure finely spun copper is placed in a solution of $CuCl_2$ and concentrated HCl and warmed. The clear solution of the complex is poured into a large volume of water, and the precipitate of CuCl is collected, washed, and dried with great precaution to avoid oxidation.

In the presence of dilute HCl cuprous chloride is slowly oxidized by air to soluble cupric salt which can be washed off.

$$\underline{2CuCl} + 2HCl + \tfrac{1}{2}O_2 \rightarrow H_2O + 2CuCl_2$$

Without HCl the dark-colored insoluble basic salt is produced to contaminate the preparation

$$\underline{2CuCl} + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Cu(OH)Cl \downarrow$$

Thoroughly dry cuprous chloride is not oxidized by the air.

Materials: cupric chloride, $CuCl_2 \cdot 2H_2O$, 43 grams = 0.25 F.W.
fine copper ribbon, 25 grams (the material used for domestic scouring pads).
12*N* HCl, 100 cc.
95% alcohol, 30 cc.
ether, 80 cc.

Apparatus: 500-cc. flask.
short-stemmed funnel.
2-liter common bottle.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve 43 grams of crystallized cupric chloride in 100 cc. of water, and filter the solution into a 500-cc. flask. Rinse the filter with 10 cc. of water. Add 100 cc. of 12*N* HCl and then 25 grams of fine copper ribbon. Note the color changes which take place. Suspend a short-stemmed funnel in the neck of the flask to prevent the loss of acid and to exclude air. Heat the mixture with a low flame until it just reaches the boiling point. Then reduce the flame to the smallest possible size and keep the solution just below the boiling point until the color changes to a very light brown. Do not heat more than 15 minutes. While the reduction is taking place, pour 50 cc. of ether and approximately 1,500 cc. of cold water into a 2-liter bottle. (Ether is inflammable. Do not bring it within 3 feet of a flame.) The ether serves to partly expel the oxygen dissolved in the water. Shake the mixture and allow it to stand until the fine bubbles of air have risen to the surface. When the cupric salt in the flask is reduced as indicated by the change to a light brown color, pour it so carefully into the water-ether mixture in the large bottle that all solid particles of copper will be retained in the flask. Rinse the flask with 20 cc. of $3N$ HCl, and pour this with equal care into the large bottle. Let the white precipitate settle. Moist cuprous chloride darkens in direct light, and the bottle should not stand near a window. Pour off most of the liquid, stir up the solid with the rest, and pour the suspension into a suction filter. Use 50 cc. of water, to which 1 cc. of $6N$ HCl has been added, to rinse all the cuprous chloride into the funnel. The solid cuprous chloride will settle on to the filter paper, and most of the liquid can be decanted from the funnel if the filter runs too slowly. Continue the suction until only a *thin film* of water covers the solid; stop the suction. Pour 15 cc. of alcohol in a thin stream around the upper edge of the funnel and let it run down, washing the sides of the funnel and covering the cuprous chloride. Allow the alcohol to soak into the solid, and when it begins to drip through the filter plate, apply suction until only a thin film of alcohol covers the solid. In exactly the same way wash the sides of the funnel and the cuprous chloride with a second 15 cc. portion of alcohol and with two successive 15-cc. portions of ether. Until the second portion of ether is added, the solid cuprous chloride should not be allowed to come in contact with the air. It should always be covered with a thin film of the wash liquid. The second portion of ether should be removed completely by applying suction.

If the cuprous chloride was not dried thoroughly it will turn green on standing. This is due to the formation of basic cupric chloride. The colored impurity may be removed by grinding the preparation in a mortar with enough $0.5N$ H_2SO_4 to make a thin paste. When all the lumps have been removed pour the mixture into 400 cc. of distilled water and repeat the filtration and washings with alcohol and ether.

Transfer the cake of cuprous chloride to a dry watch glass, remove the filter paper, and break up the cake. Rest the watch glass on a wooden ring or on a beaker and set in on the hot plate. As soon as the odor of ether has disappeared, pulverize the product and put it into a 2-ounce bottle which has been thoroughly dried. The product should be pure white.

QUESTIONS

1. Explain why copper does not reduce cupric sulphate to cuprous sulphate.
2. Place 0.5 gram of cuprous chloride in the bottom of a dry test tube. Fill it completely with $6N$ NH_4OH and immediately stopper it tightly, allowing no air bubble to remain at the top. Invert the tube a number of times until the salt is dissolved. At this point, the solution should be nearly colorless, and it would be quite so if the salt had been pure and air had been completely excluded. Pour the solution into an open beaker and note the change in color. Equations?
3. Spread about 0.5 gram of cuprous chloride in a watch glass; moisten it, and let it stand 5–10 minutes. What causes the discoloration? Equation? Rinse the discolored mass into a beaker and add 1–2 cc. $6N$ HCl. What causes the solid to again become white and the solution blue? Equation?

PREPARATION 29

CUPROUS OXIDE, Cu_2O

When metallic copper is heated in the air it becomes coated with a layer of oxide, which, according to conditions, may be cuprous or cupric oxide, or a mixture of the two. Pure cuprous oxide is most conveniently prepared in the wet way by treating an alkaline cupric salt solution with a reducing agent, whereby the red cuprous oxide is precipitated.

Cupric hydroxide is nearly insoluble in NaOH solution alone, but it dissolves when a soluble tartrate is added, the copper going into a complex negative ion similar in color to the ammonio-cupric ion.

Materials: blue vitriol, $CuSO_4 \cdot 5H_2O$, 50 grams = 0.2 F.W.
Rochelle salt, $KNaC_4H_4O_6 \cdot 4H_2O$, 75 grams.
sodium hydroxide, 75 grams.
dextrose, 10 grams.
95% alcohol, 45 cc.

Apparatus: 8-inch porcelain dish.
2-liter common bottle.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the blue vitriol and the Rochelle salt each in 200 cc. of hot water, filter the solutions separately if they are not clear, and when they are nearly cold mix them together in the 8-inch dish. In the meantime dissolve the sodium hydroxide in 200 cc. of water, cool it completely, filter if not clear, and pour it in a thin stream into the mixture in the dish, stirring constantly and being careful not to allow the mixture to get more than barely warm from the reaction. A clear deep blue solution results. Dissolve the 10 grams of dextrose in 100 cc. of water. Heat the cupric salt solution to boiling; add the dextrose solution 10 cc. at a time until the blue color of the cupric salt is discharged. To determine this point it is necessary after stirring to wait a few moments to let the red precipitate of Cu_2O settle so that one can observe the color of the upper layer of solution. Avoid adding more than necessary of the dextrose since this substance is turned brown by the hot alkali and the brilliant red color of the cuprous oxide is dulled. Pour the contents of the dish into about 1 liter of cold water in a 2-liter bottle and mix thoroughly; let settle for about 15 minutes. Although the supernatant liquid still appears turbid at this point, the amount of suspended cuprous oxide is very small. Decant this turbid liquid very carefully so as not to stir up the cuprous oxide. As the bottle is gradually tipped, the heavy cuprous oxide finally settles into the shoulder of the bottle and all but about 100 cc. of the liquid runs over the lip. Fill the bottle again with water, mix, let settle, and decant as before. Transfer the cuprous oxide to the suction filter, and as soon as the last drop of water is sucked into the compacted cake in the bottom, stop the suction. Then wash with 2 successive portions of 15 cc. each of water and 3 successive portions of 15 cc. each of alcohol, following the directions of the preceding preparation. Place the cuprous oxide on a watch glass on the hot plate, and as soon as the alcohol is evaporated, put up the product in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Treat 0.25 gram of the product with 5 cc. of hot 6 *N* H_2SO_4. Note carefully the appearance of the undissolved residue, and whether the solution is blue after the residue has settled. Read the discussion of the preceding preparation and interpret the results observed in this preparation.

2. Treat 0.25 gram of the product with 6 drops of water or enough to moisten it and then add 6 *N* HCl a drop at a time noting the progressive change in the appearance of the residue. Finally see if a considerable amount (5–10 cc.) of the HCl will dissolve the residue. Pour the clear solution into 500 cc. of cold water. Read the discussion of the cuprous chloride preparation and explain the observations made in this experiment.

3. Treat 0.25 gram of the product with 10 cc. of cold 6 *N* NH_4OH and compare the results with those of Experiment 2 under Cuprous Chloride. Could you explain the difference by assuming that cuprous oxide is much more insoluble than cuprous chloride in pure water?

Preparation 30

Ammonio-Copper Sulphate, $CuSO_4 \cdot 4NH_3 \cdot H_2O$

Preparation 3 illustrated the formation of a double salt, ammonium copper sulphate, $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$. In the double salt, *ammonium* plays the part of a positive radical. In the present preparation *ammonia* plays an altogether different role. It does not possess a primary valence, and it enters into a molecular compound with the salt by virtue only of a secondary valence. In fact, the ammonia in this preparation is held in the same sort of a combination as the water in the hydrate $CuSO_4 \cdot 5H_2O$. The molecules of ammonia would appear to be bound to the copper rather than to the sulphate radical, because when the salt is dissolved in water the four ammonia molecules remain in combination with the copper as the complex ion $Cu(NH_3)_4^{++}$, while the sulphate radical appears as the ordinary SO_4^{--} ion. Thus we might say that this salt is the sulphate of the ammonio-copper complex. (Cf. Ammoniates, page 118.)

The salt is exceedingly soluble in water, and therefore, in preparing it, use is made of its insolubility in alcohol. The method adopted of allowing the alcohol to mix with the aqueous solution by slow diffusion is to insure the formation of large, well-defined crystals.

Materials: copper sulphate, $CuSO_4 \cdot 5H_2O$, 25 grams = 0.1 F.W.
6 *N* NH_4OH, 85 cc.
95% alcohol, 165 cc.
ether, 20 cc.

Apparatus: 125-cc. separatory funnel.
8-ounce common bottle.
two 300-cc. flasks.
400-cc. beaker.
4-inch porcelain dish.

Procedure: Pulverize the copper sulphate, place it in a flask and dissolve it in the 85 cc. of cold 6 *N* NH_4OH. (See Note 7, page 12.) Pour the solution through a filter, catching the filtrate in another flask. Place 125 cc. of alcohol in the bottle; fill the stem of the dropping funnel with water; insert it to the bottom of the alcohol, and run in 20 cc. of water to form a layer beneath the alcohol to separate the latter from the ammoniacal copper solution, which is next introduced through the funnel. Allow no bubbles of air to be sucked with the liquid into the stem of the funnel and thus avoid stirring up the solution and mixing the layers. Set the bottle away for at least a week, at the end of which time crystals 2 or 3 cm. long will have formed. The alcoholic and aqueous layers have not yet completely diffused into each other, and when they are mixed, a meal of very small crystals is precipitated. Therefore pour the liquid all at once out of the bottle into a clean beaker. The large crystals adhere to the inside of the bottle. Remove them to a small dish; add 10 cc. of alcohol to which 1 cc. of ammonia has been added; stir thoroughly by rotating the dish, and pour off the alcohol, allowing it to carry with it any of the precipitate of small crystals. Repeat the washing with 10 cc. of alcohol and then with 10 cc. of ether. Spread the crystals on paper towels and leave them until they cease to smell of ether. Then at once stopper them tightly in a 2-ounce cork-stoppered bottle, since they give off their ammonia rather easily. Drain on a suction filter the crystal meal formed in the beaker, and wash it on the filter (Note 5 (*a*), page 9) with the same liquids as were used for the larger crystals. Preserve the large crystals and the crystal meal separately, each in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. What is the reaction between Cu^{++} and OH^- ions? To a little $1N$ $CuSO_4$ add $6N$ NaOH drop by drop, until it is present in excess.

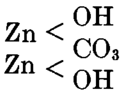
2. Explain what successive reactions occur when ammonium hydroxide is added instead of sodium hydroxide.

3. To 5 cc. of $1N$ $CuSO_4$ add 10 cc. of a molal solution of tartaric acid; then add sodium hydroxide solution, as in (1), and compare the results with those in (1) and (2), but do not attempt to ascribe a definite formula to the complex compound formed.

PREPARATION 31

ZINC OXIDE, ZnO

Zinc oxide is used as a white pigment, for which purpose it has the advantage of not turning black under the action of hydrogen sulphide. It may be obtained directly by burning metallic zinc, or from a soluble zinc salt by precipitating first a basic carbonate and then heating this to convert it into the oxide. Both zinc carbonate and zinc hydroxide are insoluble in water, but the basic carbonate is of still greater insolubility, and therefore precipitates more readily than either of the former when the ions necessary for its formation are brought together. The simplest formula for the basic carbonate is



$$\begin{matrix} & & \mathrm{OH} \\ \mathrm{Zn} & < & \\ & & \mathrm{CO_3} \\ \mathrm{Zn} & < & \\ & & \mathrm{OH} \end{matrix}$$

but the precipitate may be of varying composition according to the conditions of its formation.

If zinc sulphate in solution is treated with sodium bicarbonate, pure zinc carbonate is precipitated, because a sodium bicarbonate solution contains but a minute quantity of OH^- ions. On the other hand, a sodium carbonate solution, in consequence of hydrolysis, contains a considerable quantity of OH^- ions, and thus it furnishes both the CO_3^{--} and OH^- ions necessary for the formation of basic zinc carbonate.

Basic zinc carbonate is decomposed by heat into zinc oxide and carbon dioxide.

Commercial zinc sulphate invariably contains a small amount of iron as an impurity. Since $FeSO_4 \cdot 7H_2O$ crystallizes isomorphously with $ZnSO_4 \cdot 7H_2O$ a preparation of the latter cannot be freed of the former by recrystallization. By addition of chlorine, or its equivalent, to the solution of zinc sulphate, the iron is oxidized to ferric salt; the ferric salt hydrolyzes somewhat, and, if the acid produced by the hydrolysis is neutralized as fast as formed, the hydrolysis proceeds to completion and all the iron is precipitated as $Fe(OH)_3$. In this case, the reagent used to bring about the exact neutrality of the solution is a suspension of basic zinc carbonate. (Compare the similar procedure for removing traces of iron in the preparation of strontium chloride, Preparation 21.)

To obtain the pure white, impalpable powder which is sought it is necessary: to remove the iron salts, which cause a yellow or brown color; to wash entirely free of soluble sodium sulphate, which would give a lumpy product; to avoid getting filter fibers mixed with the material, for these would char and cause darkening; and to avoid overheating the product, which might cause it to react with the glaze of the dish.

Materials: zinc sulphate, $ZnSO_4 \cdot 7H_2O$, 57 grams = 0.2 F.W.
anhydrous sodium carbonate, Na_2CO_3, 24 grams.
bleaching powder or calcium hypochlorite ("H. T. H."), 1 gram.

Apparatus: two 2-liter common bottles.
5-inch filter funnel.
8-inch porcelain dish.
4-inch porcelain dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the $ZnSO_4 \cdot 7H_2O$ in 700 cc. water. Prepare a NaOCl solution as follows: Add 1 gram of calcium hypochlorite or bleaching powder and 1 gram of Na_2CO_3 to 100 cc. cold water. Stir thoroughly and pour through a filter. Add the cold filtrate to the cold solution of $ZnSO_4$ in 700 cc. water in an 8-inch porcelain dish. Heat with a small flame during 10 minutes to a temperature of 100°, when the iron will be completely precipitated as $Fe(OH)_3$. Pour the solution through a filter, collecting the filtrate in a 2-liter common bottle. Dissolve 23 grams of sodium carbonate in 500 cc. of water and filter. Pour the filtrate into the purified $ZnSO_4$ solution. Note if there is any effervescence. The precipitate should be pure white. Stir or shake to aid the escape of carbon dioxide. Fill the bottle to the top with water, stir, and let stand until the white precipitate has settled to one-third or one-fourth the volume of the bottle. This will take about 30 minutes. Draw off the clear solution and wash the remaining precipitate by decantation until it is calculated that it is contaminated with less than 0.1 per cent of the soluble sodium sulphate present at first (see Note 5 (*b*), page 10). Finally, transfer the sludge to a large, ordinary filter (Note 4 (*c*), page 7), and allow it to drain over night. It should now be in the form of a jelly-like cake which holds its shape. Without removing it from the filter lift the latter from the funnel, unfold it without tearing, spread it flat on paper towels, and leave it on the steam table until the material is dry. Do not try to remove the material from the filter until it is absolutely dry; it will then flake off clean when the paper is bent. Heat the basic zinc carbonate in the 4-inch porcelain dish gently with a flame 2 inches high which is held in the hand and played over the bottom of the dish. The material falls to an impalpable powder which seethes, or appears to boil, as long as gases are being expelled. Avoid heating the dish to any faintest sign of visible redness. The product is faintly yellow when hot but it should become pure white when cold. Test the product by wetting 0.1 gram with 2 cc. of water and adding a few drops of $6N$ HCl. The zinc oxide should dissolve, and there should be no trace of effervescence. Put up the preparation in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Why could not the precipitate of basic zinc carbonate have been advantageously freed from the solution by means of a suction filter?

2. Which is more readily decomposed by heat, calcium carbonate or zinc carbonate? Which then is the more strongly basic, calcium oxide or zinc oxide?

3. To a solution of zinc sulphate add a solution of sodium hydroxide, drop by drop, until the precipitate first formed redissolves. How is zinc hydroxide similar to aluminum hydroxide

in respect to its behavior towards strong acids and strong bases? Write ionic equations.

4. Write an equation for the reaction of calcium hypochlorite with sodium carbonate solution. Trace through the reactions and show what impurity would have gone through into the final product if calcium hypochlorite had been used directly instead of sodium hypochlorite.

PREPARATION 32

MERCUROUS NITRATE, $HgNO_3 \cdot H_2O$

Mercury, like copper, will not dissolve in non-oxidizing acids, but it does dissolve in nitric acid. Two oxides of mercury are known, Hg_2O and HgO, corresponding to the mercurous and mercuric salts. In order to obtain the nitrate corresponding to the lower oxide, it is necessary merely to keep mercury present in excess until after the acid is exhausted.

Materials: mercury, Hg, 25 grams = 0.125 F.W.
6*N* HNO_3, 20 cc.

Apparatus: 300-cc. flask.
4-inch porcelain dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Treat 25 grams of mercury in a flask in the hood with 20 cc. of 6*N* HNO_3, warming gently, until no further action takes place. Allow to cool until the flask can be held in the hand, then pour the solution away from any remaining globule of mercury into a small dish, and leave to crystallize until the next day. Spread the crystals out on a filter paper placed on a paper towel and let them dry at room temperature. Put the product in a cork-stoppered test tube as soon as it is dry.

QUESTIONS

1. Treat 0.5 gram of the preparation with 20 cc. of cold water. It does not dissolve to give a clear solution. Note the character of the residue of basic salt. Add dilute nitric acid drop by drop, until a clear solution is obtained. Explain why the presence of a little nitric acid should enable us to get a clear solution.

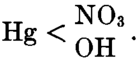
2. The cold dilute nitric acid in Question 1 does not oxidize the mercurous salt. Now add cold dilute hydrochloric acid, drop by drop, until all the mercurous salt is precipitated as white mercurous chloride, HgCl. Look up the solubility of mercurous and mercuric chlorides.

3. Filter off the precipitate obtained in Question 2. The solution will contain any mercuric salt which was present in the sample originally taken. What reagent could you use to test for mercuric salt in this solution? Make the test and report the result.

4. Addition of hydrochloric acid to the solution containing nitric acid gives the strongly oxidizing mixture known as *aqua regia*. What is the chief reason why, if the solution is cold and dilute, the mercurous salt escapes oxidation?

PREPARATION 33

MERCURIC NITRATE, $Hg(NO_3)_2$

When mercury is heated with an excess of nitric acid, mercuric nitrate is produced. This salt is exceedingly soluble in water, and it can be crystallized only with a good deal of difficulty. When a solution of it containing an excess of nitric acid is evaporated, it becomes a thick, heavy sirup, which by further driving off of nitric acid and water becomes a pasty mass, due to formation of small crystals of basic nitrate,  $Hg < \begin{matrix} NO_3 \\ OH \end{matrix}$. If the materials taken for the preparation of this salt are pure, the product can contain no other foreign matter than an excess of nitric acid; consequently, in view of the difficulty of obtaining good crystals, it is convenient to preserve the salt in this pasty condition.

Materials: mercury, Hg, 25 grams = 0.125 F.W.
$6N$ HNO_3, 60 cc.

Apparatus: 300-cc. flask.
125-cc. casserole.
2-ounce glass-stoppered bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Heat 25 grams of mercury in a flask in the hood with 60 cc. $6N$ HNO_3 until it is all dissolved. Test a drop of the solution by adding to it in a test tube 1 cc. of cold water and a drop of dilute hydrochloric acid. A precipitate will probably form, in which case add 10 cc. of concentrated nitric acid to the flask and boil until a precipitate is no longer obtained when tested as above. Pour the solution into a casserole and evaporate in the hood over a very small free flame until the liquid has assumed a sirupy consistency and crystals just commence to form on the surface. Then transfer the whole mass to a warmed sample bottle, which has previously been weighed; let it cool and stopper the bottle.

QUESTIONS

1. To prepare a solution of this salt for use as a laboratory reagent, explain why it is necessary to add nitric acid. (Compare with Question 1 under Mercurous Nitrate, page 232.)
2. To a solution of mercuric nitrate add a little hydrochloric acid. Now add a little stannous chloride solution. What is the precipitate, and what change in the valence of mercury must have occurred before it could form?

PREPARATION 34

MERCURIC SULPHOCYANATE, $Hg(SCN)_2$

In most of its properties the sulphocyanate radical resembles the halogens, with which it is often classed, in the same manner that the ammonium radical, NH_4, is classed with the alkali metals. Mercuric sulphocyanate is insoluble in water, and may be produced by bringing together equivalent quantities of solutions of mercuric nitrate and potassium sulphocyanate, but if a sufficient excess of either of these reagents is used, the precipitate dissolves in it. From a consideration of the principle of solubility product one would predict that an excess of either ion would cause a decrease in the solubility of the salt $Hg(SCN)_2$, but this effect is outweighed by the tendency of $Hg(SCN)_2$ to combine with either Hg^{++} or SCN^- ions to form fairly stable complex ions (see page 119). A very neat expedient may be adopted in this preparation to show when the proper amount of reagent has been added, as follows: ferric sulphocyanate, $Fe(SCN)_3$, is a soluble substance which has an intense red color. If to a given solution of mercuric nitrate a few drops of a ferric salt solution are added, and then to this is gradually added a solution of potassium sulphocyanate, the SCN^- ions will unite with the Hg^{++} ions as long as any of the latter are present, the solution remaining colorless and the precipitate, $Hg(SCN)_2$, forming towards the end; but as soon as the Hg^{++} ions are exhausted, then the SCN^- ions unite with Fe^{+++} ions, producing the red compound, which indicates that the reaction is complete.

Mercuric sulphocyanate has a peculiar property: when ignited it burns with the production of a very voluminous coherent ash, which, from the form it assumes, is called " Pharaoh's Serpent." It should not be burned indoors because of the production of poisonous vapors.

Materials: mercuric nitrate from preceding preparation.
potassium sulphocyanate, KSCN, 25 grams.
ferric chloride for indicator.

Apparatus: 2-liter common bottle.
suction filter and trap bottle.
8-inch porcelain dish.

Procedure: Dissolve the mercuric nitrate in 1 liter of water, adding enough nitric acid to prevent the formation of any basic salt. To this add 10 drops of a ferric chloride solution; then add gradually, with constant stirring, a solution of the potassium sulphocyanate in 500 cc. of water until a red color appears and persists after stirring. Collect the precipitate on a suction filter, and dry it on paper towels.

The dried salt may be made into the so-called Pharaoh's serpent eggs by mixing it with 1.5 grams of dextrine and water to obtain a paste, placing the latter in conical molds about 1 cm. wide and 1 cm. deep, and letting it dry out and harden.

QUESTIONS

1. What is the degree of ionization of the soluble halides of mercury, *i.e.*, $HgCl_2$, $Hg(CN)_2$? Do these salts form, in this respect, any exception to the general rule regarding the ionization of salts?

2. Describe at least three instances which have previously fallen under your observation in which a reagent in limited amount will give a precipitate, but, added in excess, will cause the precipitate to redissolve.

Experiments

Review in Chapter III Experiments 14, 15, 18, 19, pages 91–92 and the discussion of the basic properties of metal hydroxides, page 112, and of complex ions, page 118. In Chapter IV, review Experiments 16 on page 170 and 22 on page 175.

> **1. Stability of the Carbonates.** (*a*) To about 10 cc. each of solutions of $CuSO_4$, $ZnSO_4$, $CdCl_2$, and $AgNO_3$ add 1 N Na_2CO_3 until no further precipitate is formed and notice very carefully whether any bubbles of gas escape. No gas escapes from the cadmium and silver salt solutions; effervescence is noted with the copper and zinc salt solutions. Collect the precipitates from the copper and zinc salt solutions on filters, and wash thoroughly with water until the excess of Na_2CO_3 is removed. This is accomplished when the washings from the filter no longer effervesce when HCl is added. Now pour a few drops of HCl on these precipitates and note that they effervesce when they dissolve.

The escape of carbon dioxide when the Na_2CO_3 is added shows that the copper and zinc carbonates hydrolyze, but the further escape of carbon dioxide when the precipitates are treated with acid shows that the hydrolysis has not been complete. The precipitates then must consist of basic carbonates, such as $Cu(OH)_2 \cdot CuCO_3$. This shows that the basic character of the hydroxides is weak, but not as weak as that of $Al(OH)_3$, because not even a basic carbonate of aluminum can be formed. Since no effervescence took place with the cadmium and silver salts, the precipitates must have been the neutral carbonates, $CdCO_3$ and Ag_2CO_3, which indicates that cadmium and silver oxides are more strongly basic than the others.

> (*b*) Heat a little dry basic copper carbonate by shaking it in a test tube at some distance above a small flame. The light blue powder is quickly changed to black, and the seething of the dry powder shows that a gas is being expelled. A drop of lime water is clouded by the gas. To the residue after it has cooled add 5 cc. of water and then a little HCl and note that the black powder dissolves without effervescence.

The ease with which copper carbonate is decomposed by heat shows further the weakness of the basic character of copper oxide.

2. Hydrolysis of Salts. Recall the fact, or observe by experiment, that the salts $HgNO_3$, $Hg(NO_3)_2$, and $ZnCl_2$ do not dissolve in pure water to give a clear solution but that a flocculent residue of basic salt, $HgNO_3 \cdot HgOH$, $HgOHNO_3$, $ZnOHCl$, is left. The formation of the basic salt is a partial hydrolysis, it leaves the solution faintly acidic; that the hydrolysis is not extensive, is shown by the fact that a moderate amount of the corresponding acid will in each case prevent the formation and precipitation of the basic salt.

3. Hydroxides. In separate test tubes place (*a*) 1 cc. of $1N$ $CuSO_4$; (*b*) 10 cc. of $0.1N$ $AgNO_3$; (*c*) 1 cc. of $1N$ $ZnSO_4$; (*d*) 1 cc. of $1N$ $CdCl_2$; (*e*) 5 cc. of $0.1N$ $HgNO_3$; and (*f*) 5 cc. of $0.2N$ $Hg(NO_3)_2$. To each tube add water to make a volume of 10 cc. and then add $6N$ NaOH, 1 drop at a time, shaking after each drop. Finally add in all 5 cc. of the NaOH.

In every case a precipitate is formed with a small amount of the reagent as follows: (*a*) light blue $Cu(OH)_2$, (*b*) brown Ag_2O, (*c*) white $Zn(OH)_2$, (*d*) white $Cd(OH)_2$, (*e*) black Hg_2O, (*f*) yellow HgO. Those precipitates whose formulas are given as hydroxides are in fact likely to come down as rather indefinite basic salts, that is, as mixtures of the hydroxides and the salt, but for the sake of simplicity in discussion it is allowable to regard them as hydroxides. Silver, mercurous, and mercuric hydroxides do not exist in the solid state; they lose water and form the oxides.

Of the above precipitates, zinc hydroxide alone dissolves freely in excess of the reagent. It forms the soluble salt sodium zincate, Na_2ZnO_2, and it is thus an amphoteric substance like aluminum hydroxide (compare Experiments 2, 3, 4, and 5, page 217).

The copper hydroxide does not dissolve altogether in the excess of the reagent, but the solution acquires a deep blue color which is seen better after the precipitate settles out. This color shows that there must be copper in solution, and that the copper hydroxide possesses amphoteric properties to a slight degree.

4. Basic Strength of Silver Oxide. Collect on a filter the silver oxide precipitate obtained in (*b*) of the last experiment. Wash it thoroughly with hot water. Put part of the moist residue on a piece of red litmus paper and note that the paper is turned blue. Pour 2 cc. of water over the rest of the brown residue; let it run through the filter, and test the filtrate for Ag^+ ions by adding a drop of HCl. A distinct test is obtained.

Test a silver nitrate or a silver sulphate solution with litmus and note that the indicator is not affected.

The brown silver oxide must combine with water to form the hydroxide when it dissolves because of the tests for Ag^+ and OH^- ions that are obtained in the solution. Silver oxide is thus shown to be appreciably soluble and markedly basic. As would be expected of salts of such a base, we find that silver nitrate and silver sulphate are not hydrolyzed. Silver oxide is exceptional for a heavy metal oxide in displaying so marked a basic strength.

5. Ammoniates. Repeat Experiments 3 using $6\,N$ NH_4OH instead of NaOH. Note that in every case a limited amount of reagent produces the same precipitate as NaOH, and that excess of the reagent redissolves all the precipitates except those of the mercury oxides.

Test the resulting ammonia silver salt solution for Ag^+ ions by adding a drop of KCl and note that no precipitate is formed.

The hydroxides dissolve in NH_4OH, not because of any acidic character but because of the ability of the metal ions to form ammoniates (see pages 118–119). Addition of ammonia to the simple metal radical seems to strengthen its metallic character so that it can exist more easily as a positive ion. Thus the hydroxides of the ammonio-metal radicals, excepting those of mercury, are soluble and as highly ionized as the hydroxides of the alkali metals.

6. Complex Negative Ions. (*a*) To 1 cc. $1\,N$ $CuSO_4$ add 10 cc. water and 2 cc. of $1\,N$ KI. Note that the solution turns brown and that a precipitate is formed. Let the precipitate settle, pour off the brown solution and note that a drop of it will turn some starch paste blue, showing the presence of iodine. Wash the precipitate by decantation and note that it is white after the brown solution is removed. To the precipitate suspended in about 2 cc. of water add a small crystal of potassium iodide. This dissolves quickly, giving a fairly concentrated solution. Note that the precipitate dissolves in the KI solution.

The ions of cupric iodide are brought together but cupric iodide is unstable and decomposes into insoluble cuprous iodide, CuI, and free iodine. With excess of KI the soluble salt $KCuI_2$, which is ionized as K^+ CuI_2^-, is formed. Cupric chloride, $CuCl_2$, and cupric bromide, $CuBr_2$, do not decompose in the same way into cuprous salts. (Compare the relative reducing action of chloride, bromide, and iodide, Experiments 12, 13, and 14, pages 166–168.)

(*b*) To 1 cc. of $0.2\,N$ $Hg(NO_3)_2$ add a few drops of $1\,N$ KI and note a bright red precipitate. Add a little more KI and note that the precipitate redissolves to give a colorless solution.

(*c*) To 1 cc. of $0.1\,N$ $AgNO_3$ add a few drops of a saturated NaCl solution. Note the white precipitate. Add 10 cc. of saturated NaCl, shake, and note that the precipitate cannot be seen to dissolve. To show that some does dissolve, filter, and add a large amount of water to the clear filtrate, noting an opalescent precipitate.

Mercuric iodide, HgI_2, is very insoluble but with excess iodide ions it readily forms the complex ion HgI_4^{--}. Similarly silver chloride can, in the presence of a high concentration of chloride ions, form to a limited extent the complex ion $AgCl_2^-$. The latter is very unstable, however, and dilution reduces the Cl^- ion concentration sufficiently to allow the complex ion to dissociate, $AgCl_2^- \rightleftharpoons AgCl \downarrow + Cl^-$, with a reprecipitation of silver chloride.

The above experiments show the strong tendency of the heavy metals of this chapter to enter into the formation of complex negative ions. (See page 120.) The negative radical ions show differing tendencies to enter into these complexes, and in the decreasing order of the strength of this tendency are CN^-, SCN^-, I^-, Cl^-. Sulphate and nitrate ions show very little tendency to join heavy-metal ions in the formation of complexes of this kind, although it may be that the formation of the crystallized double salts like the alums and the double sulphate of potassium and copper is due to such a cause.

7. Sulphides. (*a*) To separate tubes containing diluted heavy-metal salt solutions as in Experiment 3, (*a*) to (*f*), add 2 cc. of $6\,N$ $(NH_4)_2S$ in each case and note the character of the precipitate. Collect each precipitate on a filter, wash it with hot water, and then pour over it a few cubic centimeters of $6\,N$ HCl.

The precipitates are CuS, dark brown; Ag_2S, black; ZnS, white; CdS, yellow; HgS + Hg, black; and HgS, black. Of these only zinc sulphide and cadmium sulphide dissolve in $6\,N$ HCl.

(*b*) To 1 cc. of $1\,N$ $ZnSO_4$ add 10 cc. of water and 1 cc. of $6\,N$ HCl, and pass hydrogen sulphide in until the solution is saturated with the gas. No precipitate is formed. Add 10 cc. of $1\,N$ NaAc and observe the white precipitate.

Zinc sulphide does not precipitate from an acidified solution because the S^{--} ion concentration is repressed by the H^+ ions of the strong acid, $H_2S \rightleftharpoons 2H^+ + S^{--}$, and the solubility product of zinc sulphide cannot be reached. Acetate ions, however, remove H^+ ions, and, the hydrogen sulphide thus being allowed to ionize to a greater extent, the solubility product of zinc sulphide is exceeded and the white precipitate appears. (See Solubility Product, page 131, and Experiment 22, page 175.)

8. Electromotive Series. Review Experiment 19, page 92, and make what further experiments of a similar nature are necessary to determine the relative position in the electromotive series of the heavy metals considered in this chapter.

GENERAL QUESTIONS VII

HEAVY METALS OF GROUPS I AND II

1. Make a table as follows. In column 1 give the symbols of the metals — copper (leave two lines), silver, gold (two lines), zinc, cadmium, and mercury (two lines); in column 2, the formulas of the chlorides; in column 3, the solubility of the chloride, specifying *sol* = soluble, *ins* = insoluble; in column 4, the formula of the oxide corresponding to the chloride in column 2; in column 5, the formula of the corresponding nitrate, if one exists; in column 6, the degree of hydrolysis of the chloride or nitrate, whichever is soluble, specifying none, little, large.

2. Give all available information as to the stability of the carbonates of the metals of this chapter. Compare the base-forming properties of these metals among themselves, and also with the alkali metals, the alkaline earth metals, and aluminum.

3. What is an ammoniate? Give the formulas of the ammonio-ions of copper, silver, zinc, and cadmium. How can crystallized ammonio-copper sulphate be prepared? How would you make a solution of ammonio-copper hydroxide? What is the alkaline strength of such a solution?

4. Discuss the tendency of the heavy metals of Groups I and II to enter complex negative ions; give several examples, at least one for each metal, also examples in which the simple cyanide, thiocyanate, iodide, and chloride ions are involved. Describe experimental facts to illustrate the great stability of potassium argenticyanide, $KAg(CN)_2$, and the instability of sodium argentichloride, $NaAgCl_2$.

5. Compare the metals of this chapter among themselves with regard to their position in the electromotive series, also with the metals of the A families of Groups I and II, and with aluminum.

CHAPTER VIII

THE OXY-ACIDS AND SALTS OF THE NON-METALS

The elements which are distinctly and invariably non-metallic in character are boron in the third group; carbon and silicon in the fourth group; nitrogen and phosphorus in the fifth group; oxygen, sulphur, and selenium in the sixth group; and fluorine, chlorine, bromine, and iodine in the seventh group. Non-metallic elements have already been studied in Chapter IV, in so far as they enter binary compounds in which they act as the negative constituents.

When two non-metallic elements unite, the one which is the less strongly non-metallic is regarded as the positive constituent; it is, so to speak, compelled to play the positive rôle in the compound. For example, sulphur is regarded as the positive constituent of sulphur trioxide. Although in such a compound the primary valence of each element seems to be satisfied — sulphur, $+6$, and oxygen, -2, in sulphur trioxide — there must be a large residual combining power (secondary valence) because the compound combines so readily with other *saturated* compounds. The oxides of non-metals thus unite with metal oxides to form salts, and with water to form acids, for example, $SO_3 + Na_2O \rightarrow Na_2SO_4$; $SO_3 + H_2O \rightarrow H_2SO_4$. When such salts or acids ionize, the non-metal always appears as a constituent of the complex negative ion. In the sulphate ion the combination of 1 sulphur, with a valence of $+6$, and 4 oxygens, with a valence of -2 each, would leave the unbalanced valence of -2 for the whole ion; this is the actual valence of the ion. Hence we conclude that elements present in molecular compounds and in complex ions still possess the same primary valence as in the simple compounds.

Although all the non-metals except oxygen and fluorine show positive primary valences in some of their compounds, nevertheless it is the most characteristic property of the non-metals that they do not form positive ions. In ions they are always combined with enough of an electronegative element to furnish a surplus of negative charges for the whole ion.

An inspection of the periodic arrangement of the elements shows that non-metals do not occur at all in the first and second groups;

that they occur only at the top in the third, fourth, and fifth groups; and that in the sixth and seventh groups they comprise all the well-known members of the B families. It is true in these families, as might be expected by recalling characteristics of preceding groups, that the strength of the non-metallic character grows weaker, and that the approach towards metallic character grows more evident, as the atomic weight increases.

The characteristic valences of the sixth and seventh groups are 6 and 7, respectively, and the corresponding oxides are EO_3 and E_2O_7. In these oxides and in the compounds derived from them, there is little dissimilarity between the A and B families. Thus perchlorates and permanganates are analogous to each other, as are also sulphates and chromates. In the lower states of valence, the elements of the B families are entirely different from those of the A families, the B family elements forming exclusively negative ions, S^{--}, SO_4^{--}, whereas the A family elements form positive ions, Cr^{++}, Cr^{+++}.

PREPARATION 35

POTASSIUM BROMATE AND POTASSIUM BROMIDE, $KBrO_3$ AND KBr

Bromine, like chlorine, hydrolyzes to a considerable extent according to the reversible reaction:

$$Br_2 + H_2O \rightleftharpoons HBr + HBrO \qquad (1)$$

In presence of a base both acids are neutralized as fast as formed and reaction (1) proceeds to completion. Thus the complete reaction in presence of KOH is:

$$Br_2 + 2KOH \rightarrow KBr + KBrO + H_2O \qquad (2)$$

Hypobromites are unstable, and, at boiling temperature, and particularly in slightly acid solution, undergo an action of oxidation and reduction, the total result of which is:

$$3KBrO \rightarrow KBrO_3 + 2KBr \qquad (3)$$

Multiplying equation (2) by 3 and adding equation (3) the equation

$$3Br_2 + 6KOH \rightarrow KBrO_3 + 5KBr + 3H_2O \qquad (4)$$

is obtained. This equation represents the sum total of the chemical changes occurring in the process, and on it the calculation of quantities of materials and products is to be based.

The reaction represented in (3) does not take place to an appreciable extent in alkaline or neutral solution, but when the neutral point is overstepped by a mere trace of acid the reaction readily completes itself in a few minutes at the boiling temperature. A little excess of bromine, shown by a reddish color, gives, by virtue of the hydrolysis above mentioned, the requisite degree of acidity. The following train of equations gives an idea of the way in which this trace of bromine promotes the reaction. It will be noticed that in equation (9) the bromine used in equation (5) is regenerated, so that a trace of bromine working over and over again suffices to convert all the hypobromite into bromate. The addition of all the equations (5) to (9) in the train gives the equation (10) for the total net change which is identical to equation (3)

$$\begin{array}{rcll}
Br_2 + H_2O & \rightarrow & HBr + HBrO & (5) \\
HBr + KBrO & \rightarrow & KBr + HBrO & (6) \\
2HBrO + KBrO & \rightarrow & KBrO_3 + 2HBr & (7) \\
HBr + KBrO & \rightarrow & KBr + HBrO & (8) \\
HBrO + HBr & \rightarrow & Br_2 + H_2O & (9) \\
\hline
3KBrO & \rightarrow & KBrO_3 + 2KBr & (10)
\end{array}$$

Materials: potassium hydroxide, 0.5 F.W. = 28 grams; this material should be as nearly free from carbonate as possible. Since it is very deliquescent it will doubtless contain water, and a somewhat greater weight than 28 grams will have to be taken. Take 31 grams if the analysis of the material is not known.
bromine, 40 grams = 12.5 cc. = 0.25 F.W. Br_2
charcoal, 5 grams.

Apparatus: 300-cc. Erlenmeyer flask.
400-cc. iron crucible.
suction filter and trap bottle.
2.5-inch funnel.
4-inch porcelain dish.
50-cc. graduate.
asbestos paper.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the potassium hydroxide in 100 cc. of water in a 300-cc. Erlenmeyer flask. At the hood obtain the liquid bromine in a measuring cylinder and perform all the operations with bromine under the hood. Cool the KOH solution to room temperature and pour the bromine into it, about 1 cc. at a time, rotating the contents of the flask until the bromine has dissolved after each addition. When all the bromine is added, it should be in slight excess, which is shown by a distinct reddish tint in the solution, not merely a yellow color.

Now heat the contents of the flask to boiling and boil until the excess of bromine has been expelled. Then cool to 15° or lower. Collect the crystals on a suction filter. Preserve the filtrate to obtain the by-product, potassium bromide.

Dissolve the crystals in four times their weight of hot water. Unless the solution is perfectly clear, filter it hot, and without suction, to remove dirt, rinsing the filter with about 5 cc. of boiling water.

Cool the filtrate to below 15° as before, and collect the crystals. Add the mother liquor to that reserve for obtaining the by-product.

Dissolve 0.05 gram of the crystals in 2 cc. of hot water; add 1 drop of $AgNO_3$ solution. A precipitate while the solution is at the boiling temperature is silver bromide and shows that the product has not been purified from bromide. Repeat the recrystallization as many times as necessary to obtain a pure product.

Potassium Bromide. Combine all the mother liquors, evaporate in a porcelain dish until a pasty mass is obtained, mix this thoroughly with 5 grams of powdered charcoal, and dry the mass completely. Pulverize the dry mixture in a mortar and heat it to redness, for 20 minutes, in an iron crucible surrounded by an asbestos mantle. Extract the product with 60 cc. of hot water, filter, wash the residue and filter with an additional 15 cc. of hot water, and evaporate the solution to dryness to obtain potassium bromide. The solution of potassium bromide "creeps." If it has to be set away over night the vessel containing it should be placed in a clean large dish to catch any of the salt that creeps over the edge of the smaller vessel.

Test the product for absence of bromate by dissolving some in a little water and acidifying with sulphuric acid. If no bromate is present, no free bromine will be produced, *i.e.*, the solution will remain colorless and odorless.

Put up the two products in separate cork-stoppered bottles.

QUESTIONS

1. When the bromate is tested with silver nitrate why is it necessary to have the solution hot? (Look up solubility of silver bromate.)

2. How does dilute H_2SO_4 react with a pure bromate? Explain, with reactions, the test for the presence of bromate in the bromide.

3. Explain why it would not be possible to free a preparation of potassium bromide of a little bromate by recrystallization.

4. Explain why potassium bromate can be readily freed of bromide by recrystallization.

PREPARATION 36

POTASSIUM CHLORATE, $KClO_3$

Read the discussion of the hydrolysis of bromine in the preceding preparation. About one-third of the chlorine in chlorine water is hydrolyzed. The bleaching power of chlorine is due directly to the oxidizing action of the hypochlorous acid produced by the hydrolysis. The formation of chlorate in this preparation is also a result of the oxidizing action of hypochlorous acid.

In the action of chlorine with an alkali hydroxide, six equivalents of the latter must react in order to produce one equivalent of alkali chlorate. To economize in potassium hydroxide, which is more expensive than sodium hydroxide, we shall use one equivalent only of the former and five equivalents of the latter. The five equivalents of sodium chloride which could be recovered as a by-product is not of great value, and we shall discard it in this preparation.

Materials: potassium hydroxide, 16 grams
sodium hydroxide, 44 grams } the pellet form of these hydroxides, as free of carbonate as possible, should be used. Allowing roughly 10 per cent as water gives the net amounts: KOH, 0.25 F.W.; NaOH, 1.25 F.W.

chlorine, from a cylinder or generated from granular manganese dioxide and 12*N* HCl.

Apparatus: 500-cc. flask with 2-hole rubber stopper.
chlorine generator, use 2,000-cc. round-bottomed flask.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Calculate the amount of manganese dioxide and $12N$ HCl required to generate the chlorine necessary to react with the alkalies. Take 10 per cent in excess of this amount and fit up the chlorine generator. Dissolve the potassium and sodium hydroxides together in 70 cc. of water in the 500-cc. flask, but do not filter the solution, even if it is not entirely clear. Arrange a wide delivery tube to bubble chlorine into the alkali solution in the flask, which is supported on a lamp stand so that it can be heated. The exit tube from the flask is prolonged to a bottle containing $6N$ NaOH to absorb any excess chlorine. Pass chlorine into the alkali solution until the latter is saturated with it. Let the reaction heat the solution. Finally make sure that the solution is saturated with chlorine. Remove the generator fittings, close the flask with a solid rubber stopper, and shake vigorously; if the upper part of the flask still contains chlorine gas the solution is saturated. Boil the contents of the flask gently, avoiding " bumping," until the excess of chlorine is expelled; then pour it all, still at boiling temperature, on to the suction filter. Stop the suction before any air has been drawn into the layer of crystals; add 15 cc. of water to the flask, heat it to boiling, pour it on to the salt crystals in the filter, and, after it has soaked in, apply the suction. In this way nearly all the potassium chlorate is washed into the filtrate. Cool the filtrate to 0° and collect the potassium chlorate crystals on the suction filter. Dissolve the moist crystals in three times their weight of water. If the solution is not clear, pour it through a small common filter, rinsing the filter with 10 cc. of boiling water to carry through any potassium chlorate which crystallized in the filter. Purify by recrystallization until the product is free from chloride. Preserve it in a 2-ounce cork-stoppered bottle.

A product of 15 grams is to be regarded as satisfactory. The mother liquors should all have been saved to work over again if the recrystallizations have not been skilfully enough carried out the first time.

QUESTIONS

1. Tabulate the solubilities at high and low temperatures of the salts concerned, and arrange a flow sheet of the method to be followed if the mother liquors are worked over.

2. The commercial method of making potassium chlorate is by the electrolysis of a potassium chloride solution. What are the primary products formed at the two electrodes? Explain how, when the primary products are allowed to mix in the cell, the reactions are similar to those of this and the preceding preparations.

PREPARATION 37

POTASSIUM IODATE, KIO_3

As is well known, the chemical affinity of the halogens for hydrogen or positive elements decreases in passing from fluorine to iodine; but the affinity for oxygen *increases* in this order, so that iodates and iodic acid (I_2O_5) are more stable than chlorates and chloric acid (Cl_2O_5). Use is made of this fact in the following preparation, in which the total change is represented fairly closely by the equation

$$KClO_3 + \tfrac{1}{2}I_2 \rightarrow KIO_3 + \tfrac{1}{2}Cl_2$$

The actual reaction, however, is not so simple as this. The presence of a small amount of acid is necessary to make it take place. This acid gives rise to a little free chloric acid, which is a far stronger oxidizing agent than potassium chlorate, and oxidizes iodine to iodic acid. The latter acid reacts with more potassium chlorate and thus chloric acid is regenerated. It will be noticed that in carrying out the following directions more iodine is taken than is necessary to react with the potassium chlorate according to the equation given above. This excess of iodine is oxidized to iodic acid by a part of the free chlorine which is represented in the equation as escaping.

Materials: potassium chlorate, $KClO_3$, 31 grams = 0.25 F.W.
iodine, 36 grams.

Apparatus: 1,000-cc. flask.
short-stemmed funnel.
pan of cold water.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve 31 grams of potassium chlorate by warming it with 100 cc. of water in a 1000-cc. flask. Add 36 grams of powdered iodine and hang a small funnel in the neck of the flask to prevent, to some extent, the escape of iodine vapor. Place a pan of cold water close at hand; then add 1 cc. of 6 *N* nitric acid to the flask, and warm rather carefully until a brisk reaction commences. Then allow the reaction to proceed so that violet vapors fill the flask, but if iodine starts to escape through the funnel, check the reaction by dipping the flask for a moment in the cold water. After the reaction has moderated warm the solution until the iodine color has disappeared, and then boil it for about 10 minutes to expel most of the free chlorine. The solution now contains a considerable quantity of iodic acid in addition to the potassium iodate. Add a solution of potassium hydroxide until the neutral point is just reached (test by dipping a stirring rod in the solution and touching it to litmus paper). Allow the solution to cool, collect the crystals of potassium iodate, and evaporate the mother liquor to obtain another crop of crystals. Purify the entire product by dissolving it in four times its weight of hot water, cooling, and collecting the crystals. Dry the product and preserve it in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Explain the secondary reaction of the foregoing preparation in which chlorine reacts with iodine.
2. From knowledge of the reactions of chlorine and bromine predict how iodine would react with a KOH solution. Find from reference books whether this prediction is borne out by the facts.

PREPARATION 38

IODIC ACID; IODINE PENTOXIDE, I_2O_5

Iodine pentoxide is a white solid substance that, at ordinary temperatures, is entirely stable. It cannot be prepared by direct synthesis from iodine and oxygen, because when cold the elements combine too slowly, and when heated the compound is unstable. It may be readily prepared by the direct oxidation of iodine by means of strong oxidizing agents, such as concentrated nitric acid or chlorine. One method for the oxidation of iodine has already been illustrated under the preparation of potassium iodate, but there the conditions were such that a salt of iodic acid was obtained rather than the free acid or its anhydride. Starting with this salt, however, the free acid is obtained by metathetical reactions which depend on the insolubility of barium iodate and the still greater insolubility of barium sulphate.

Materials: potassium iodate, KIO_3, 43 grams = 0.2 F.W.
barium nitrate, $Ba(NO_3)_2$, 26 grams = 0.1 F.W.
$36N$ H_2SO_4, 8 cc.
$16N$ HNO_3

Apparatus: 600-cc. beaker.
750-cc. casserole.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the potassium iodate and the barium nitrate, separately, each in 250 cc. of hot water, and mix the two solutions at the boiling temperature while stirring well. Cool the mixture, let the heavy precipitate settle, decant off the clear liquid, and wash the salt twice by decantation with pure water. Drain the barium iodate on a suction filter, and wash it on the filter with cold water. Then remove it to a porcelain casserole, suspend it in 250 cc. of water, heat to boiling, and stir in a solution of 8 cc. $36N$ H_2SO_4 in 100 cc. of water. Keep this mixture well stirred at the boiling temperature for at least 10 minutes, since the conversion of solid barium iodate into solid barium sulphate is a reaction that requires some time. Filter the solution and rinse the last of the iodic acid from the solid barium sulphate by washing two or three times on the filter with small portions of water. Evaporate the solution in a casserole to a small volume, and finally, holding the casserole in the hand, keep the contents rotating, so that the whole inside of the dish is continually wet. Continue evaporating until solid iodic acid separates in some quantity. Cool completely and rinse the crystals with three successive portions of 10 cc. each of $16N$ nitric acid, triturating the crystals thoroughly with each portion of the acid. Warm the casserole carefully until the product is perfectly dry and ceases to give off acid vapors. This warming will convert the iodic acid to a large extent into the anhydride I_2O_5. Place the iodine pentoxide at once in a 2-ounce cork-stoppered bottle.

To obtain completely anhydrous iodine pentoxide, the product could be heated for some time in an oven at about 200°. Crystallized iodic acid could be obtained by dissolving the product in a very little water, in which it is extremely soluble, and allowing the solution to evaporate slowly.

QUESTIONS

1. Dissolve a little of the iodine pentoxide in water. Test the solution to show whether it contains a strong acid. How?
2. Heat 0.5 gram of iodine pentoxide in a dry test tube. Insert a glowing splinter in the tube. Note whether the entire substance can be volatilized; also if any of the original substance deposits in the cooler part of the tube.

PREPARATION 39

POTASSIUM PERCHLORATE, $KClO_4$

When potassium chlorate is heated to about 400° it may decompose according to either of the following independent reactions:

$$4KClO_3 = KCl + 3KClO_4 \qquad (1)$$

$$KClO_3 = KCl + 1\tfrac{1}{2}O_2 \qquad (2)$$

The second reaction is accelerated by catalyzers, such as manganese dioxide or ferric oxide, or in fact any material with a rough surface. Too high a temperature also causes reaction (2) principally to take place. On the other hand, if the temperature is maintained at the right point, the salt is free from dirt, and the inside of the crucible is perfectly clean and free from roughness, the decomposition proceeds mainly according to reaction (1). Potassium perchlorate is very sparingly soluble in cold water and may be separated from potassium chloride and any undecomposed potassium chlorate by crystallization.

Material: potassium chlorate, $KClO_3$, 61 grams = 0.5 F.W.

Apparatus: 100-cc. porcelain crucible and cover.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Place 61 grams of potassium chlorate in a dry, clean 100-cc. porcelain crucible, the glaze of which is in perfect condition.

Cover the crucible to prevent loss of particles of the salt by decrepitation, and heat gently until the charge just melts. Then remove the cover and keep the melt just hot enough to maintain a brisk evolution of oxygen, but do not increase the temperature when the mass shows a tendency to grow solid. At the end of about 20 minutes the melt should begin to stiffen around the edges and become more or less pasty or semi-solid throughout; when this point is reached, let the contents of the crucible cool completely, then cover it with 200 cc. of water, and let it stand until it is entirely disintegrated. Collect the undissolved potassium perchlorate on a suction filter and wash it with two successive portions of 15 cc. of cold water (see Note 5 (*a*), page 9). Redissolve the salt in hot water (see solubility table) and allow it to recrystallize. About 30 grams of potassium perchlorate should be obtained. A few crystals of the product should give no yellow color (Cl_2) when treated with a few drops of $12N$ hydrochloric acid. The product should be entirely free from chloride (test with silver nitrate).

QUESTIONS

1. Why is manganese dioxide added when oxygen is prepared by heating potassium chlorate?
2. What is the reaction of hydrochloric acid with hypochlorous, chloric, and perchloric acids, respectively?
3. What are the four oxy-acids of chlorine? Compare their stability.
4. To what extent are hydrochloric, hypochlorous, chloric, and perchloric acids ionized in dilute solution?
5. How could pure perchloric acid be prepared from potassium perchlorate?
6. What is the solubility of silver chlorate and of silver perchlorate? How may preparations of chlorates and perchlorates be tested for the presence of chlorides?

PREPARATION 40

SODIUM THIOSULPHATE, $Na_2S_2O_3 \cdot 5H_2O$

Sodium sulphite is a salt of the lower oxide of sulphur, and may thus be regarded as unsaturated with respect to oxygen; it is, in fact, capable of slowly absorbing oxygen from the air and thereby going over into sulphate. If it is allowed to react with sulphur, the latter enters into the compound in much the same way as oxygen, and *thio*sulphate instead of sulphate is formed. The sulphur so taken up certainly plays a different function from the sulphur already contained in the compound, although it is perhaps a question whether the thiosulphate is exactly the same compound as sulphate, except that one oxygen atom is replaced by a sulphur.

Sodium sulphite is conveniently prepared by allowing sulphur dioxide (sulphurous acid) to react with sodium carbonate. It is practically impossible, however, to distinguish the exact point at which the normal sulphite (Na_2SO_3) is formed; therefore it is more expedient to divide a given amount of sodium carbonate into two equal parts, to fully saturate one part with sulphur dioxide, whereby sodium bisulphite, $NaHSO_3$, is formed, and to add the other half of the sodium carbonate, thereby obtaining the normal sulphite, Na_2SO_3.

Materials: anhydrous sodium carbonate, Na_2CO_3, 106 grams $=1$ F.W.
sulphur dioxide; this gas is most conveniently drawn from steel cylinders in which liquid sulphur dioxide is held under pressure. It can be prepared by the action of copper turnings on $36\,N$ H_2SO_4.
sulphur (powdered roll sulphur), 48 grams.

Apparatus: two 500-cc. flasks with 2-hole rubber stoppers and delivery tubes.
600-cc. beaker.
5-inch funnel.
8-inch porcelain dish.
4-inch crystallizing dish.
5-inch watch glass.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve 53 grams of the sodium carbonate in 300 cc. of hot water, and place about five-sixths of the solution in one flask and the remainder in another flask. Connect these flasks in series so that sulphur dioxide gas may be passed first into the larger volume of solution, and what is there unabsorbed may pass on through the second flask. Pass a vigorous stream of the gas into the solutions. After a short time a marked frothing occurs in the first flask, due to the escape of carbon dioxide, and after this frothing ceases a similar frothing soon commences in the second flask. When the latter ceases, pass the gas a little while longer until sulphur dioxide escapes freely from the second bottle. Then place the solution of sodium bisulphite in a 600-cc. beaker, and cautiously add the remaining 53 grams of sodium carbonate. Boil the solution uncovered for 15 minutes, replacing water lost by evaporation; weigh and record the weight of the sulphur in the note book; then add the sulphur, cover the beaker with a watch glass, and keep the mixture gently boiling for an hour and a half or longer, again replacing all the water boiled off. Filter the solution without suction. Rinse the residual sulphur onto the filter with 15 cc. of water, catching the drainings with the filtrate. Then wash the sulphur, dry it, and weigh it to find whether the calculated quantity has reacted. Evaporate the filtrate in a porcelain dish to 200 cc., let it cool to 30°; if any unchanged sodium sulphite is left it will separate as a crystal meal which is to be filtered off. Leave the solution uncovered at room temperature in an 8-inch crystallizing dish until an abundant crop of crystals is obtained; discard the final 30 cc. of mother liquor. Sodium thiosulphate can remain in highly supersaturated solution; it is best therefore to add some seed crystals to the solution set to crystallize. Wrap the product in paper towels and leave it over night to dry. Preserve it in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. Dissolve 0.5 gram of the product in 5 cc. of water and add 2 cc. of hydrochloric acid. Observe the odor and the precipitate. What is the free acid corresponding to the salt, sodium thiosulphate? What can be said regarding the stability of this acid?

2. What is the valence of sulphur in each of the salts: sodium sulphide, sodium sulphite, and sodium sulphate? State in each case whether the sulphur plays the part of a positive or negative element.

3. Distinguish between the parts played by the two atoms of sulphur in sodium thiosulphate.

4. When sulphur dioxide was passed into the sodium carbonate

solution the following distinct stages in the process were noted: (*a*) The gas passed into the solution in distinct bubbles and was in large part absorbed. (*b*) Effervescence took place with minute bubbles arising from every part of the solution. (*c*) Effervescence ceased, and the gas entered the solution again in clear, distinct bubbles, but still it was for the most part absorbed. (*d*) The gas passed through the solution in distinct bubbles and was entirely unabsorbed. Look up the degree of ionization of both hydrogens, both of sulphurous and carbonic acids. Write equations for the reactions taking place during each of the stages enumerated above.

Experiments

The behavior of the halogens with aqueous solutions of bases, in fact even with seemingly dry bases such as calcium hydroxide in which a trace of moisture is present, can best be accounted for when it is taken into account that they hydrolyze extensively. Thus in chlorine water, that is, water nearly saturated with chlorine at atmospheric pressure, chlorine comes to equilibrium with its hydrolysis products HCl and HOCl with about two-thirds of the chlorine present as Cl_2 and one-third in the form of equimolal amounts of HCl and HOCl.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

A similar condition exists in water solutions of bromine and iodine except that iodine is much less soluble than either chlorine or bromine.

> **1. Hypochlorites.** (*a*) To 10 cc. of freshly prepared chlorine water, which has a distinct yellow color, add 6*N* NaOH until the yellow color has disappeared. Close the test tube and shake thoroughly, and then note that the odor of chlorine has also disappeared.

Since two-thirds of the chlorine in chlorine water is in the form of Cl_2, the yellow color is apparent in spite of the fact that one-third of the total chlorine exists in the form of the colorless compounds HCl and HOCl. Addition of sufficient base neutralizes both the acids, upsetting the equilibrium, and the hydrolysis runs to completion. The salts NaCl and NaOCl are both colorless.

(*b*) Stir 5 grams of bleaching powder with 5 cc. of water. It cannot be seen to dissolve at all. Add 1 cc. of the suspension to 100 cc. of water, and note that it imparts a cloudiness to the whole so that it cannot yet be told whether any has dissolved. Pour the rest of the undiluted suspension into a filter and collect the filtrate. To 1 cc. of the filtrate add a few drops of $6\,N$ HCl. The color and odor of chlorine are perceived.

Bleaching powder is prepared by treating slaked lime, $Ca(OH)_2$, with chlorine, and it is essentially a mixture of equivalent amounts of calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$. The formula of the solid material is written $CaOCl_2$, indicating the belief that it is not a mixture of two salts, but rather a mixed salt in which each molecule contains a chloride and a hypochlorite radical.

Calcium chloride and calcium hypochlorite are both extremely soluble; but bleaching powder always contains a considerable excess of calcium hydroxide which has not reacted with the chlorine, and also a good deal of calcium carbonate. That hypochlorite and chloride dissolve freely out of the bleaching powder is shown by the action with hydrochloric acid.

$$2HCl + Ca(OCl)Cl \rightarrow CaCl_2 + H_2O + Cl_2$$

(*c*) Soak a piece of colored cotton cloth in one-half of the filtrate obtained in (*b*). Different colors bleach with varying ease, but it is probable that this one will decolorize hardly perceptibly. Remove the cloth with the solution still clinging to it and immerse it in very dilute H_2SO_4 (1 cc. of $6\,N$ acid to 50 cc. of water). The color now rapidly disappears.

Add 5 cc. of $6\,N$ NaOH to the other half of the filtrate from the bleaching powder suspension. A voluminous white precipitate is formed. Soak another piece of cloth in this suspension and note that it is not bleached at all.

It is a well-known fact that dry chlorine does not bleach dry cloth, but that chlorine water bleaches it easily. It is known that chlorine hydrolyzes (see Preparation 36), and the bleaching is attributed to the hypochlorous acid, which, on account of its instability, is a strong oxidizing agent and oxidizes the colored substance to a colorless one.

The hypochlorite solution contains OCl^- ions, and the fact that this solution does not bleach rapidly indicates that the ions are not the principal bleaching agent. Addition of sulphuric acid produces un-ionized hypochlorous acid, $H^+ + OCl^- \rightarrow HOCl$, the ionization of this acid in 0.1 N solution being 0.06 per cent. Thus it is clear that HOCl must be the principal bleaching agent. That the hypochlorite solution did bleach the cloth slowly might have been due to a slow action of the OCl^- ion, or perhaps to a small amount of HOCl produced by hydrolysis of the salt, or set free by the action of carbonic acid from the air. That no bleaching occurs after adding the NaOH settles this point, because no free HOCl can remain in presence of the base.

This experiment shows that the salt of hypochlorous acid is more stable than the acid itself.

2. Hypobromites. Add a few drops of bromine to 2 cc. of 6 N NaOH diluted with 5 cc. of water. The red color of the bromine disappears. Dip colored cloth and litmus paper in this solution and then in dilute H_2SO_4, to show that it bleaches in the same way as a hypochlorite solution.

Add a part of the solution to 2 cc. of NH_4OH and notice that there is effervescence, the escaping gas being non-combustible and a non-supporter of combustion (nitrogen). (See Preparation 19.)

Add the rest of the solution to a solution of 0.25 gram of urea in 5 cc. of water and notice a similar effervescence.

Hypobromites are very similar in properties to hypochlorites and oxidize organic coloring substances. Ammonia and urea are oxidized, even in alkaline solution, by hypobromite,

$$3NaOBr + 2NH_3 \rightarrow 3NaBr + 3H_2O + N_2$$

$$3NaOBr + CO(NH_2)_2 \rightarrow 3NaBr + CO_2 + 2H_2O + N_2$$

3. Chlorates and Bromates. The formation of chlorate and bromate by heating hypochlorite and hypobromite, respectively, is illustrated in Preparations 35 and 36. Test-tube experiments may be tried, adding excess of chlorine and bromine respectively to hot 6 N KOH, boiling a little and cooling, whereupon the sparingly soluble potassium chlorate and potassium bromate crystallize out.

4. Bromic and Iodic Acids. To a globule of carbon disulphide in a test tube add a few drops of bromine water until, after shaking, the globule has assumed a distinct red color. Add 5 cc. water and then chlorine water, a few drops at a time, shaking after each addition. The red color bleaches and finally disappears altogether.

Repeat, substituting iodine for bromine, and note that the deep violet color, which the free iodine imparts to the globule of carbon disulphide, is likewise bleached on shaking the globule with chlorine water.

Recall Experiment 11, page 165, which showed that chlorine oxidizes bromide and iodide respectively to free bromine and iodine. The present experiment carries the oxidation still further and raises the valence of each element to +5.

$$5Cl_2 + Br_2 + 6H_2O \rightarrow 2HBrO_3 + 10HCl$$

$$5Cl_2 + I_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

Bromic and iodic acids are colorless; they are very soluble in water, and highly ionized.

5. Properties of Potassium Chlorate. (*a*) Heat some potassium chlorate in a test tube. It melts and soon afterwards the melted salt effervesces. A glowing splinter thrust into the gas bursts into flame.

(*b*) Place a very small crystal of potassium chlorate on a watch glass, (Danger! use of a larger amount may cause a violent explosion), place 2 drops of $36\,N$ H_2SO_4 on an adjacent part of the glass and let it flow until it touches the crystal. The latter dissolves with effervescence, a deep yellow gas with a very strong odor somewhat resembling that of chlorine being formed. Part of this gas dissolves in the sulphuric acid coloring it a deep brownish yellow.

(*c*) Add $6\,N$ H_2SO_4 to a dilute potassium chlorate solution.

In (*c*) the ions of chloric acid are brought together and thus a solution of chloric acid containing also the ions of potassium sulphate is obtained. Chloric acid is a soluble, highly ionized acid of a stability comparable to that of nitric acid.

In (*b*) chloric acid is formed, but the concentrated sulphuric acid acts as a dehydrating agent.. The oxide Cl_2O_5, which is obviously the anhydride of chloric acid, however, does not appear; it breaks down into the oxide ClO_2, which is the dark yellow gas, and free oxygen. Chlorine dioxide is not the anhydride of any known acid, but it dissolves in water and forms equivalent amounts of chlorous and chloric acids, in which the valence of chlorine is +3 and +5 respectively,

$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

Chlorine dioxide is extremely explosive, and it is very dangerous to make larger amounts of it than that directed in this experiment.

The instability of the oxy-compounds is further shown in (*a*) in which chlorine is reduced from a valence of +5 to −1.

6. Reduction of Iodic Acid. (*a*) Dissolve a little potassium iodate in water and add some starch paste. No color is observed. Add a little potassium iodide to part of the mixture, and still no color is observed. Now add an acid, for example, HNO_3, and observe that instantly the solution turns deep blue.

Iodate and iodide ions alone have no action on each other, but with hydrogen ions present a mutual oxidation and reduction of the iodine takes place.

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

No oxidation or reduction of the hydrogen occurs, but the hydrogen ion is used up, which explains why the presence of acid is necessary to make the reaction take place.

(*b*) Dip filter paper in the rest of the potassium iodate-starch mixture and suspend it in a bottle containing a little sulphurous acid. A deep blue color immediately appears in the paper. If the paper remains in the bottle the blue is very quickly bleached, leaving the paper white again.

The sulphur dioxide escaping from the solution dissolves in the water on the paper and the sulphurous acid reduces the iodate to free iodine which gives the blue color.

$$H_2SO_3 + 2KIO_3 \rightarrow K_2SO_3 + 2HIO_3$$
$$2HIO_3 + 5H_2SO_3 \rightarrow 5H_2SO_4 + H_2O + I_2$$

The iodine is then reduced by more sulphurous acid to hydriodic acid, which is colorless,

$$I_2 + H_2O + H_2SO_3 \rightarrow H_2SO_4 + 2HI$$

7. Sulphur Dioxide. Burn some sulphur in a deflagrating spoon in a bottle. Note the characteristic odor of the gaseous product. Lower into the bottle a piece of filter paper soaked in potassium iodate-starch solution and note the same effects as in Experiment 6.

Sulphur burns forming sulphur dioxide SO_2. The effect with the potassium iodate-starch paper constitutes a convenient test for sulphur dioxide.

8. Sulphurous Acid. (*a*) Bubble sulphur dioxide into a bottle of water and note that it dissolves freely. The solution colors litmus red and it conducts electricity fairly well.

(*b*) **Test for Sulphurous Acid.** To 5 cc. of sulphurous acid add 1 cc. of $6N$ HCl and 2 cc. of $BaCl_2$ solution. A small precipitate or a slight clouding will probably occur at this point, for the sulphurous acid solution invariably contains some sulphuric acid if it has stood exposed to the air. Pour the liquid through a filter; the filtrate may come through cloudy, in which case pour it repeatedly through the same filter until it is clear. To this filtrate add bromine and note that the red color disappears and a white precipitate is formed.

Sulphurous acid is a rather weak acid, and presence of the strong acid HCl prevents the formation of SO_3^{--} ions in sufficient concentration to precipitate with Ba^{++} ions. The first precipitate removes all the sulphuric acid. Then the addition of bromine oxidizes the sulphurous acid to sulphuric acid and another precipitate of barium sulphate is produced.

$$H_2SO_3 + Br_2 + H_2O \rightarrow H_2SO_4 + 2HBr$$

9. Reducing Action of Sulphurous Acid. To 5 cc. of potassium permanganate solution add sulphurous acid. The deep purple solution becomes colorless.

$$5H_2SO_3 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O$$

10. Oxidizing Action of Sulphur Dioxide and Sulphurous Acid. (*a*) Fill a 250-cc. wide-mouth bottle with sulphur dioxide and lower into the gas a burning strip of magnesium ribbon held by pincers. The magnesium continues to burn brilliantly, forming the same white smoke as if it burned in air. There is also noticed a yellowish deposit on the glass (sulphur).

(*b*) Pass hydrogen sulphide into a solution of sulphurous acid. A milky precipitate is formed.

Although sulphur has considerable affinity for oxygen, its strength in this respect is far less than that of the active metal magnesium.

In (*b*) we have another case similar to that in Experiment 6 (*a*) in which an element existing in different states of oxidation mutually oxidizes and reduces itself.

$$H_2SO_3 + 2H_2S \rightarrow 3H_2O + 3S \downarrow$$
$$4 + 2(-2) = 0$$

11. Dehydrating Action of Sulphuric Acid. Add 10 cc. of $36N$ H_2SO_4 to 5 grams of sugar in a porcelain dish. If necessary warm the mixture a little to start a reaction. Once started the reaction proceeds vigorously giving off a good deal of heat, and the sugar swells up and grows black. Finally, there is left a bulky brittle charcoal-like mass.

The formula of sugar, $C_{12}H_{22}O_{11}$, shows that it contains hydrogen and oxygen in the proportion to form water. The affinity of sulphuric acid for water is so great that it causes the sugar to decompose so as to yield carbon and water.

12. Oxidizing Action of Sulphuric Acid. In separate test tubes heat sulphur, charcoal, and copper turnings with $36N$ H_2SO_4, and hold potassium iodate-starch paper in the mouth of each tube. In each case the test paper is turned blue.

Concentrated sulphuric acid is an oxidizing agent (cf. Experiments 13 and 14, pages 167–168), it being reduced usually to sulphurous acid (SO_2).

$$2H_2SO_4 + S \rightarrow 3SO_2 + 2H_2O$$
$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O$$
$$\left\{\begin{array}{l} H_2SO_4 + Cu \rightarrow CuO + SO_2 + H_2O \\ CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \end{array}\right.$$

This experiment should be compared with Experiments 6 (*b*), 8 (*b*), and 9, in which sulphurous acid reduces iodic acid, bromine, and permanganate, it itself being oxidized to sulphuric acid. The latter is not an oxidizing agent in dilute solution.

> **13. Nitric Acid as an Oxidizing Agent.** (*a*) To 3 grams of copper turnings in a test tube add 5 cc. water and 5 cc. of 6 *N* HNO_3. Fit the stopper with a delivery tube leading to a trough of water. Heat the test tube a very little to start the reaction; let the gas go to waste until it appears colorless in the test tube, then collect a test tube full of it at the water trough. Note that the gas is colorless and that it is not soluble in the water. Remove the test tube from the trough, turn it mouth up, and hold a sheet of white paper behind it; a red gas is seen where the gas in the tube meets the air. Note the suffocating odor of this gas.

Non-oxidizing acids have no effect on copper but they dissolve copper oxide. Dilute nitric acid first oxidizes copper, it itself being reduced to nitric oxide, $3Cu + 2HNO_3 \rightarrow 3CuO + H_2O + 2NO$; before any further oxidation of the copper occurs, the nitric acid acts as an acid with the copper oxide giving the soluble copper nitrate, and it is for this reason that we see no direct evidence of the intermediate reaction. Nitric oxide has the most remarkable property of combining spontaneously with oxygen at ordinary temperature, forming the deep reddish brown gas nitrogen dioxide, $NO + \frac{1}{2}O_2 \rightarrow NO_2$.

> (*b*) To 2 grams of granulated zinc in a test tube add 20 cc. of water and 2 cc. of 6 *N* HNO_3. Warm the mixture but not to boiling; then let it stand 5 minutes. Test the solution by pouring it from the undissolved zinc, adding sodium hydroxide in excess, and warming, when the odor of ammonia becomes apparent.

Zinc is a much more powerful reducing agent than copper: furthermore, zinc displaces from an acid, hydrogen, which, at the moment of its displacement, is in the atomic or " nascent " condition, and especially active. Under these conditions the nitrogen is reduced to its lowest valence, which is shown in ammonia. The ammonia does not escape from the solution because it combines with the excess of nitric acid.

$$\begin{array}{l}
4Zn + 8HNO_3 \rightarrow 4Zn(NO_3)_2 + 8H \\
\quad HNO_3 + 8H \rightarrow 3H_2O + NH_3 \\
\underline{NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad\qquad\qquad\qquad} \\
4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3
\end{array}$$

$$\begin{array}{llr}
4Zn & 0 \text{ to } +2 & 4 \times (+2) = +8 \\
1N & +5 \text{ to } -3 & \underline{\qquad\qquad = -8} \\
 & & \text{Total change} = \ \ 0
\end{array}$$

Explain how the final step in the experiment is an example of the displacement of a weak base from its salt by a stronger base and that it involves no change in the primary valence of any of the elements.

14. Nitrous Acid. (*a*) Dissolve 0.5 gram of sodium nitrite in 5 cc. of ice water and add 1 cc. of cold 6 *N* H_2SO_4. A blue solution results which at 0° effervesces very slowly. Add a few drops of this solution to a half test tube of water containing a few drops of iodide-starch solution. An intense blue color is produced. Add a few drops of sodium nitrite solution alone, of sulphuric acid alone, and of nitric acid alone to tubes made up with a similar amount of iodide-starch, and note that in none of these cases is any color produced. (To produce no effect the nitric acid must be free from nitrous acid and it should be taken from a special bottle prepared for this experiment.)

Allow the rest of the potassium nitrite-sulphuric acid mixture to warm up to room temperature. Note that it effervesces rather strongly, giving off a reddish brown gas, and that the blue color quickly disappears.

Nitrous acid is of about the same strength as acetic acid, and it is blue in color. It is formed when its ions are brought together. It is very unstable, decomposing mainly according to the equation

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

the NO giving the reddish brown color when it comes in contact with air. Nitrous acid is an oxidizing agent, liberating iodine from hydriodic acid,

$$2HNO_2 + 2HI \rightarrow 2H_2O + 2NO + I_2$$

Since nitric acid does not liberate iodine under similar circumstances, the nitrous acid is shown to be the more vigorous oxidizing agent. This is quite in accord with what we have already found in other cases, namely, that the stability of the acid is greater the higher the valence of the principal element. It is also seen that the nitrite ion alone is not the oxidizing agent; the presence of hydrogen ions is necessary.

> (*b*) **Reducing Action of Nitrous Acid.** To about 0.1 gram of sodium nitrite and 100 cc. of cold water in a beaker add 10 cc. of $6\,N$ H_2SO_4. To this solution add drop by drop with constant stirring 0.1 formal $KMnO_4$, until the pink color produced by each drop disappears more and more slowly and finally 1 drop more produces a permanent pink color.

The permanganate oxidizes the nitrous acid to nitric acid,

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$$

The reaction proceeds so sharply to completion, and the intense color of the permanganate serves as such an excellent indicator, that it is very easy to estimate the amount of nitrite from the volume of a solution of $KMnO_4$ of known strength that it will decolorize.

GENERAL QUESTIONS VIII

THE OXY-ACIDS AND SALTS OF THE NON-METALS

1. Make a table, in the first column of which place the formulas of hypochlorous acid, chlorous acid, chloric acid, perchloric acid, hypobromous acid, bromic acid, hypoiodous acid, iodic acid, two per-iodic acids differing in degree of hydration, sulphurous acid, sulphuric acid, nitrous acid, nitric acid. In the second column give the valence of the element in the particular acid; in the third column the formula of the anhydride; in the fourth column the word gas, liquid, solid, or hyp., according to the state of aggregation of the anhydride at ordinary temperature, hyp. signifying hypothetical or non-existent; in the fifth column the percentage ionization of the acid in $0.1\,N$ solution — if no exact figure can be found specify whether very weak, weak, or strong.

2. Give the names of the oxides having the formulas N_2O, NO, NO_2, ClO_2. Give a brief account of the properties of each, including state of aggregation, stability, ability to support combustion, behavior with water.

3. When an element forms a series of oxy-acids, what rule seems to hold connecting the valence with the acid strength?

4. Compare the affinity of sulphur dioxide and sulphur trioxide for water, giving whatever data you can find. Make a similar comparison of Cl_2O and Cl_2O_7, N_2O_3 and N_2O_5. Can any general rule be stated to cover these cases?

CHAPTER IX

ELEMENTS OF GROUP IV OF THE PERIODIC SYSTEM

This group stands in the middle of the Periodic Table of the elements, and in it the difference in properties between the elements of Family A and Family B is at a minimum. Like Group III, therefore, the whole group is considered under one heading.

The elements of this group which come most to our attention in everyday life are carbon, silicon, tin, and lead. Carbon and silicon are the first two members and are exclusively acid-forming elements, although the acids formed are not strong ones. Tin and lead are the last two members of Family B and are in the main base-forming; they are comparable in this respect with the heavy metals already considered under Groups I and II. In this group the elements of low atomic weight are exclusively acid-forming, and the elements of high atomic weight are almost entirely base-forming. Between these extremes there is an almost regular gradation of properties.

Preparation 41

Precipitated Silica, SiO_2

Carbon dioxide and silicon dioxide are chemically very similar to each other in that both form weak acids, that of silicon, the heavier element, naturally being the weaker acid. On the other hand, these oxides are very dissimilar in their physical properties, one being a gas, and the other a solid with an extremely high melting point.

The mineral quartz is crystallized silicon dioxide. Sea sand consists mostly of rounded grains of broken quartz. If finely ground quartz or sand is fused for a long time with sodium carbonate, the weaker, but non-volatile, acid anhydride displaces the carbon dioxide, and sodium silicate is obtained. This is a glass-like substance, which, however, can slowly be dissolved by water heated under pressure. The solution so obtained is evaporated to a sirup-like consistency and is sold on the market under the name of " water glass." Several grades of water glass of different ratios $Na_2O:SiO_2$ are sold, but perhaps the most common grade approximates the composition $Na_2Si_4O_9$ (= $Na_2O \cdot 4SiO_2$ = $Na_2SiO_3 \cdot 3SiO_2$).

The addition of an acid to a sodium silicate solution causes a separation of silicic acid which appears as a jelly-like substance. Orthosilicic acid has the composition H_4SiO_4, metasilicic acid, H_2SiO_3; the acid corresponding to the sodium salt of the above formula, $H_2Si_4O_9$. Suspended in water these different silicic acids are more or less easily interchangeable one into another, but, if silicic acid is heated, it loses all its water and becomes the anhydride. The anhydride practically will not take on water again to form acids.

The very finely divided anhydride prepared by precipitating and drying silicic acid is more reactive than the most finely powdered quartz, and it finds use as a reagent in certain analytical tests.

Materials: water-glass, 25 cc.
6 *N* HCl.
12 *N* HCl.

Apparatus: 8-inch porcelain dish.
600-cc. beaker.
suction filter and trap bottle.
hot plate.

Procedure: To 25 cc. of water glass in a porcelain dish add 25 cc. of water and slowly stir in 6 *N* HCl until the acid is in excess. The liquid first coagulates to a jelly, then the jelly hardens and breaks up on stirring into seemingly dry lumps, and later after an excess of acid is added (about 30 cc. in all) the mass grows partially fluid again. Place the dish on a water bath or a hot plate to evaporate to complete dryness. If a hot closet or hot plate at 130° is available the dish and contents should be baked for 1 hour at this temperature. Otherwise heat the dish over a flame for 15 minutes, avoiding, if possible, letting any part of the contents get above 150° as this would render traces of iron oxide very difficult to redissolve in acid. While the dish is still warm moisten the contents completely with 12 *N* HCl. Let it digest for 15 minutes. Wash the contents of the dish into a 600-cc. beaker and let the silica settle. Wash by decantation several times and collect the silica on the suction filter, washing it well on the filter. Dry the product and put it up in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Quartz can be melted like glass, but at a much higher temperature, and many kinds of chemical apparatus are made of fused quartz. Dishes made of fused quartz are used for boiling concentrated sulphuric acid. Why cannot they be used equally well for concentrating caustic alkalies?
2. Mix 0.5 gram of the precipitated silica with 1 gram of powdered calcium fluoride. Place the mixture in a test tube, moisten it with 36 N H_2SO_4, and warm it gently under the hood. Dip a stirring rod in water and lower it, with a drop adhering, into the gas in the test tube. Note the precipitate that forms in the drop of water. Write equations for all the reactions, and state what rather unusual properties are shown by this experiment to be possessed by hydrofluoric acid and by silicon tetrafluoride.

PREPARATION 42

STANNOUS CHLORIDE, $SnCl_2 \cdot 2H_2O$

This salt can be prepared by the action of hydrochloric acid upon metallic tin, but since the action is exceedingly slow, it is hastened by the addition of a very small quantity of nitric acid, which oxidizes the tin. Nitric acid is ordinarily reduced only to the oxide NO by its action upon a metal; but in the course of this preparation no red fumes of oxides of nitrogen are found to escape, because, under the influence of tin and stannous chloride, the reduction does not stop at nitric oxide, but continues to the lowest possible step, which is ammonia or in this case its salt, ammonium chloride. Stannous salts are oxidized quite readily to stannic by the oxygen of the air; to prevent this happening during the evaporation of the solution, an excess of metallic tin is kept in the liquid.

Materials: feathered tin, 100 grams.
12 N HCl, 175 cc.
6 N HNO_3, 25 cc.
750-cc. casserole.

Apparatus: shredded asbestos suspended in water.
suction filter and trap bottle.
8-inch porcelain dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Place 100 grams of feathered tin in a 750-cc. casserole, cover with 175 cc. of $12N$ HCl, and add (at the hood) 25 cc. of $6N$ HNO_3, a little at a time, during a period of 10 minutes. Then concentrate the solution, by boiling over a free flame, to a volume of 90–100 cc., at which point a crystal scum will form on blowing on the surface of the hot liquid. There should still be left a small amount of undissolved metal. If at any time during the evaporation all the tin becomes used up, add a little more. Prepare an asbestos filter (Note 4 (*d*), page 8), moisten it with concentrated hydrochloric acid, and filter the concentrated stannous chloride solution before it has cooled to below 60–70°. Finally, rinse out the casserole with 15 cc. of concentrated hydrochloric acid and pour this liquid through the filter, letting it mix with the main part of the solution. If during the filtration the liquid stops flowing, due to crystals separating in the filter, add 5–10 cc. of boiling water. Pour the solution into an 8-inch porcelain dish, and leave it to evaporate slowly at room temperature in a place exposed to the air but protected from dust. (The solubility of stannous chloride decreases very rapidly with decreasing temperature. Hence it is advantageous to carry out the crystallization in as cool a place as possible.) When a good crop of crystals has formed, pour off the liquid into another dish; spread the crystals on paper towels and allow them to dry. It is to be remembered that stannous chloride is extremely soluble in water and that the composition of the mother liquor is not far different from that of the crystals of $SnCl_2{\cdot}2H_2O$ which separate. Heat the remaining solution carefully just to the boiling temperature, but do not allow it to boil more than a moment. In this way sufficient water and hydrochloric acid are expelled to allow another crop of crystals to form. If too much hydrochloric acid is expelled by the evaporation and an indistinctly crystalline precipitate of basic salt separates on cooling, add a few drops of hydrochloric acid and redissolve the salt by warming. Set the solution aside to cool and evaporate, as before, and collect another crop of crystals. By repeating this process once or twice more, almost the entire mother liquor should be used up and nearly the calculated yield of stannous chloride should be obtained.

QUESTIONS

1. Explain why during this preparation no red oxides of nitrogen are seen to escape in consequence of the reduction of nitric acid by the metal. If nitric acid is reduced to NH_3, show how many more equivalents of oxygen it will yield for the oxidation of the tin than if it were reduced only to NO.

To test for the presence of ammonium salt in the product, take about 1 gram of the crystals; dissolve in 10 cc. of water in a small beaker. Add sodium hydroxide solution until the precipitate first formed redissolves. Place over the beaker a watch glass, on the under side of which is stuck a piece of moistened red litmus paper. Place some cold water in the hollow of the watch glass, and warm the solution in the beaker very gently. What observation will indicate the presence of ammonium salt, and why?

2. Dissolve 1 gram of stannous chloride crystals in 1 to 2 cc. of cold water. Then add a considerable amount of water. What is the precipitate? What can be added to prevent its formation?

3. To a cold solution of stannous chloride add sodium hydroxide until it has redissolved the precipitate first formed. Write the equation. Save the solution.

4. Pour the solution saved from Experiment 3 over a little bismuth hydroxide on a filter paper. (The bismuth hydroxide can be precipitated for the occasion.) Compare the action with that of stannous chloride on mercuric chloride.

5. Prepare a very concentrated cold solution of sodium stannite: Dissolve 1 gram of stannous chloride in 1 cc. of water. Dissolve a small lump of sodium hydroxide in its own weight of water, and add this solution, a drop at a time, to the first solution — cooling all the while under the water tap — until the precipitate at first formed redissolves. Then heat the solution. Compare the action with that in Experiment 4.

6. In preparing a solution of stannous chloride for a laboratory reagent, what is the necessity of adding hydrochloric acid and of placing a piece of metallic tin in the bottle?

PREPARATION 43

STANNIC SULPHIDE (MOSAIC GOLD), SnS_2

Stannic sulphide, SnS_2, is the higher sulphide of tin, and can be prepared by direct combination of the metal or, still better, of the lower sulphide, SnS, with sulphur. Under ordinary conditions these two substances will not react at a temperature below that which will decompose stannic sulphide. If, however, they are mixed with ammonium chloride the presence of this substance makes possible the combination at a lower temperature. The stannic sulphide formed in this way appears as soft, glistening, yellow crystals. It is used as a bronzing powder, and is known under the name of mosaic gold. In physical properties it is very different from the stannic sulphide which can be precipitated by hydrogen sulphide from a solution of stannic chloride.

Stannous chloride, the raw material, if it is fresh, is completely soluble in a very little water; with much water it hydrolyzes somewhat with precipitation of basic stannous chloride, Sn(OH)Cl. If the stannous chloride is old, it has probably become partially oxidized to stannic chloride, and the latter extensively hydrolyzed to insoluble stannic acid H_2SnO_3. A clear solution is therefore not obtained when the stannous chloride is treated with a large amount of water. Nevertheless the addition of ammonium sulphide converts all the tin to sulphide, the sulphides being very much less soluble than the products of the hydrolysis.

Materials: stannous chloride, $SnCl_2{\cdot}2H_2O$, 45 grams = 0.2 F.W.
hydrogen sulphide (Note 13 (*c*), page 20).
powdered sulphur.
ammonium chloride.

Apparatus: 2-liter common bottle.
hydrogen sulphide generator.
250-cc. beaker.
5-inch filter.
mortar and pestle.
8-inch test tube, stopper, and glass tube.
6-inch sand bath and sand.
iron ring and ring stand.
Bunsen burner.

Procedure: Stannous Sulphide. Place the stannous chloride in a beaker and treat it with its own weight of water. If it dissolves completely pour it into a large common bottle and dilute it with 1,500 cc. of hot water. If it does not all dissolve decant the solution into the bottle, crush any hard lumps with a pestle, and treat the residue successively with small amounts of water pouring the easily floatable suspension each time into the bottle. Make up the volume to 1,500 cc. and, under the hood, pass hydrogen sulphide in through a delivery tube leading to the bottom of the bottle. Continue this treatment until the solution is saturated with the gas, when, after vigorous shaking, it will smell of hydrogen sulphide. Let the precipitate settle, decant off the clear solution and transfer the sludge on to a gravity filter. Do not wash the sludge; merely let it drain thoroughly. Without tearing the filter, remove it from funnel and spread it out on paper towels on the hot plate. Pulverize the product when it is dry.

Stannic Sulphide. Save 2 grams of stannous sulphide for an experiment. Grind the rest together with one-half its weight of sulphur and 0.4 its weight of ammonium chloride. Bring the mixture into an 8-inch test tube. Close the tube with a stopper bearing a short piece of glass tube drawn out to a capillary and bend downward at right angles. The capillary is to relieve any pressure caused by heating and at the same time prevent outside air entering the tube during the heating. Lay the tube in a sand bath pan containing a ¼-inch layer of sand. Then heap sand over the part of the tube containing the charge. Heat the sand bath, first rather moderately for 15 minutes, then for 1 hour so that the bottom of the iron pan is bright red. Cool, break the tube, separate the layer of stannic sulphide from the dirty-colored material on top, pulverize the product and put it up in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. *Experiment:* Treat 0.25 gram powdered stannous sulphide with sodium sulphide (Na_2S) solution, warming for about 3 minutes. Does the solid dissolve? Then add about 0.1 gram of powdered sulphur and warm a little longer. Does the stannous sulphide now go into solution? Write equations and explain how the sulphur could have caused the stannous sulphide to dissolve.

Finally acidify the solution. What is the precipitate? Equation? Test portions of this precipitate to see if it will dissolve in

$6N$ HCl — in warm Na_2S. Does the mosaic gold dissolve in these reagents? Can you explain the difference?

2. Write ionized equations for (*a*) the precipitation of basic stannous chloride SnOHCl, when a solution of $SnCl_2$ is diluted with a large amount of water; (*b*) the conversion of SnOHCl to SnS when this precipitate is treated with Na_2S solution.

PREPARATION 44

ANHYDROUS STANNIC CHLORIDE, $SnCl_4$

Anhydrous stannic chloride, $SnCl_4$, is prepared by the action of dry chlorine gas upon metallic tin. It is a colorless, very mobile liquid which boils at 114°. At ordinary temperature it has a considerable vapor pressure, and the vapor, reacting strongly with the water vapor of the air, gives rise to dense fumes. With liquid water stannic chloride reacts violently. If a limited amount of water is added with caution it is possible to obtain solid hydrates of the composition $SnCl_4 \cdot 3H_2O$, or $SnCl_4 \cdot 5H_2O$. These hydrates dissolve to form apparently clear solutions, but the salt is very extensively hydrolyzed, the rather complex hydrolysis products remaining for the most part in a colloidal condition.

Materials: feathered tin, 119 grams = 1 F.W.
chlorine (from a cylinder or generated from granular MnO_2 and $12N$ HCl).
tin foil.

Apparatus: 350-cc. tubulated retort or distilling flask.
five 8-ounce wide-mouth bottles.
chlorine generator (2,000-cc. flask) or cylinder of liquid chlorine.
36-inch condenser.
250-cc. distilling flask.
150-cc. container for stannic chloride: the neck must be previously drawn out to a narrow tube that can be quickly sealed off in blast flame.
delivery tubes, connectors, and rubber stoppers as in diagram.
tripod.
2 ring stands.
2 iron rings.
clamp and fastener.
2 Bunsen burners.

This preparation is to be attempted only if 4 consecutive hours are available in the laboratory, and even then, the apparatus should be assembled at a previous exercise.

Fit up a chlorine generator with a 2,000-cc. flask in which place 33 per cent in excess of the calculated quantity of manganese dioxide. The gas is to be passed through first one wash bottle containing water, and then two wash bottles containing concentrated sulphuric acid. Place 119 grams of feathered tin in a tubulated retort, and place the retort on a sand bath. The neck of the retort should pass into a long condenser which should empty into a 250-cc. distilling flask, in which has been placed some tin foil. Connect the side arm of the flask with a bottle containing sodium hydroxide solution to absorb the waste chlorine. The tube entering the bottle should not dip into the liquid, but should reach down to near its surface; a safety tube should be supplied, and the exit tube should dip into a solution of sodium hydroxide in another bottle. Into the retort should be fitted the tube supplying chlorine from the generator and wash bottles, and this should reach nearly to the center of the surface of the tin, which is to be melted before the action is started. Glass tubing is to be used throughout, and where connections are made with rubber the ends of the glass tubes should be brought close together. Before beginning to generate the chlorine, the whole apparatus must be proved to be tight, so that none of this gas can escape into the laboratory.

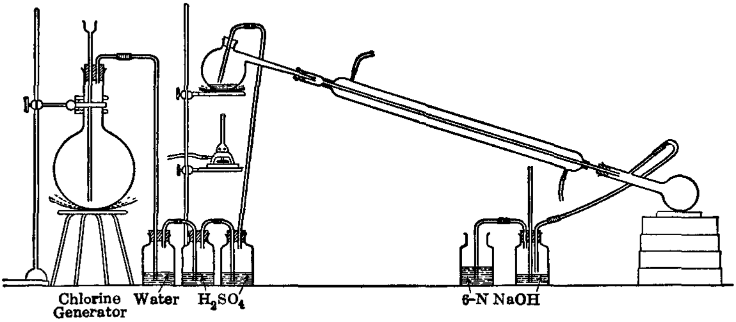


FIG. 24

Procedure: Melt the tin. Commence the generation of chlorine, and regulate it so that the tin in the retort can be seen to burn quietly. Continue the action until all the tin has disappeared and the tin tetrachloride has been caught in the receiving flask. Remove the neck of the retort from the condenser, and insert instead a stopper with a tube leading to the bottles already used for absorbing waste chlorine. Close the side arm of the receiving flask and, with the condenser still in the same position, boil the tin tetrachloride until it is colorless (it contains a large amount of dissolved chlorine and, on boiling, this reacts with the tin foil). Change the position of the flask and condenser, and distil the tin tetrachloride into the prepared container. During the distillation this container should not be open to the air, but should be connected by a tube to the absorbing bottles already used. When the liquid is all distilled, seal the neck of the container at a blast lamp, so that the preparation can be preserved out of contact with the air.

QUESTIONS

1. What is the purpose of the wash bottles as arranged for the chlorine gas?
2. Suggest how hydrated stannic chloride, $SnCl_4 \cdot 5H_2O$, might be made, starting with stannous chloride.
3. What happens if hydrated stannic chloride is heated? (Compare aluminum chloride and bromide, Preparations 25 and 26.)

PREPARATION 45

ANHYDROUS STANNIC BROMIDE (TIN TETRABROMIDE), $SnBr_4$

(This preparation must be started at the beginning of the laboratory period and must be completed the same day. Perform under the hood.)

There are two series of compounds of tin and the halogens; those related to stannous oxide, SnO, in which the metal has a valence of 2 (stannous salts), and those related to stannic oxide, SnO_2, in which it has a valence of 4 (stannic salts). The compounds with lower valence are usually prepared by the action of the halogen acids on the metal. Stannous chloride, for example, is formed when hydrochloric acid reacts with tin. Stannic salts, on the other hand, are prepared by the reaction of tin and the free halogen. In this preparation stannic bromide results from the reaction of bromine and tin. The reaction between the two elements is a vigorous one, and usually it is necessary to cool the mixture to prevent the loss of bromine. Stannic bromide boils at a relatively low temperature (203°), and it can be purified by distillation. Since stannic bromide reacts with water, care must be taken to exclude moisture during the distillation, and the product must be preserved in a dry, well-stoppered tube.

Materials: bromine, 12.5 cc. = 40 grams = 0.25 F.W. Br_2.
feathered tin, 25 grams.

Apparatus: 125-cc. separatory funnel.
125-cc. distilling flask.
thermometer, 250°.
Pyrex test tubes.
ring stand.
burette clamp.
Bunsen burner.

Procedure: Place 24 grams of feathered tin in a 125-cc. distillling flask which has been warmed to expel all moisture. (Save 1 gram of the smallest pieces of tin for use later in the preparation.) In a 125-cc. separatory funnel place 12.5 cc. of bromine. (Before pouring the bromine into the separatory funnel, make sure that the stop cock has been lubricated and that the bore is not obstructed.) Insert the stem of the funnel in the neck of the flask. Regulate the stop cock of the separatory funnel so that the bromine falls at the rate of 1 or 2 drops a second. Observe the tin when a drop of bromine first falls on it. If bromine vapor comes out of the side arm, stop the addition of bromine and immerse the bulb of the flask a moment in a pan of water.

When all the bromine has been added, shake the flask and allow it to stand 5 minutes. Then add the gram of tin saved at the beginning of the preparation and allow it to stand 5 minutes. If the mixture commences to boil, cool the flask again with water. When the reaction is apparently complete, replace the separatory funnel with a 250° thermometer arranged so that the bottom of the mercury bulb is 1 inch below the side arm of the distilling flask. Adjust the clamp holding the flask so that the side arm of the flask dips into a dry test tube. Warm the stannic bromide in the flask with a very low flame until it begins to boil. Gradually increase the temperature until uncombined bromine has been expelled and the liquid begins to distil slowly into the tube. The first part of the distillate is usually dark colored and boils around 150°. It should be rejected. Watch the color and boiling point of the distillate; when it becomes colorless and the temperature reaches 200°, change the receiver to a weighed, dry, 6-inch Pyrex test tube. This should be done without interrupting the distillation. If the distillation is not too rapid, all the vapor will condense in the side arm of the flask and the test tube. When the distillation is complete, immediately stopper the test tube and allow it to stand in an upright position until the stannic bromide has crystallized.

The product should be colorless. If a satisfactory result is not obtained, the stannic bromide may be redistilled from a clean, dry flask, to which one or two small pieces of tin have been added.

QUESTIONS

In each of the following experiments record your observation and write an equation.

Make a solution of stannic bromide by mixing in a graduated cylinder 1 cc. of your preparation of anhydrous stannic bromide, 4 cc. of 6 *N* HCl, and 15 cc. of water. Shake the mixture until solution is complete. Use this solution for the following tests.

1. (*a*) To 3 cc. of the solution add a few drops of 6 *N* NaOH. Then add an excess of NaOH.

(*b*) To 3 cc. of the solution add a few drops of 6 *N* NaOH. Then add an excess of 6 *N* HCl.

(*c*) Repeat (*a*) using stannous chloride solution.

(*d*) Repeat (*b*) using stannous chloride solution.

2. (*a*) To 3 cc. of mercuric chloride solution add an equal volume of the stannic bromide solution.

(*b*) To 3 cc. of mercuric chloride solution add an equal volume of stannous chloride, and then 3 cc. more stannous chloride.

Compare the reducing properties of stannous and stannic ions.

3. (*a*) To 3 cc. of stannic bromide solution add a few drops of sodium sulphide, and then an excess of sodium sulphide.

(*b*) To 3 cc. of stannous chloride add a few drops of sodium sulphide, and then an excess. To the mixture add sodium polysulphide, Na_2S_x.

Name the different compounds of tin formed in these reactions.

PREPARATION 46

LEAD NITRATE, $Pb(NO_3)_2$

Lead nitrate is one of the most readily prepared salts of lead, since it is of moderate solubility and can be obtained in well-formed anhydrous crystals, $Pb(NO_3)_2$. In it lead appears in its usual state of oxidation, which corresponds to that of the oxide PbO; indeed, the salt is actually prepared by treating this oxide (litharge) with nitric acid.

A saturated solution contains for each 100 grams of water the given number of grams of lead nitrate

Temperature	0°	10°	18°	25°	50°	100°
$Pb(NO_3)_2$	36	44	51	56	79	127

Materials: litharge, PbO, 56 grams = 0.25 F.W.
6 *N* nitric acid.

Apparatus: 400-cc. beaker.
8-inch crystallizing dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Take 56 grams, or 0.25 F.W., of litharge, PbO. Calculate the amount of 6 *N* nitric acid which would be necessary to convert it into lead nitrate and the amount of water needed to dissolve the salt thus formed. Proceed to prepare lead nitrate, striving to obtain good crystals of as large a size as possible.

The solution which is set to crystallize should be slightly acid — enough to redden litmus. If insufficient nitric acid was used, the excess of PbO would have dissolved somewhat in the hot concentrated $Pb(NO_3)_2$ solution forming the basic salt $PbOHNO_3$ which would separate as a fine granular or flaky precipitate when the solution cooled.

QUESTIONS

1. Explain why lead nitrate should be less soluble in dilute nitric acid than in pure water.

2. Add a few drops of ammonium hydroxide to 1 cc. of lead

nitrate solution. Then add an excess of the reagent. Repeat, using sodium hydroxide instead of ammonium hydroxide. Write equations and explain the amphoteric character of lead hydroxide.

3. Are lead salts (nitrate or chloride) appreciably hydrolyzed in aqueous solution? Compare the basic strength of the hydroxide of divalent lead with that of aluminum hydroxide.

4. Precipitate a little lead chloride by adding hydrochloric acid to a solution of lead nitrate. Describe its properties and compare them with those of lead tetrachloride (reference books). To what oxide of lead does lead tetrachloride correspond?

PREPARATION 47

LEAD DIOXIDE, PbO_2

The compounds of lead in which its valence is 2 are the most stable, but with strong oxidizing agents the valence may be raised to 4. The oxide PbO_2 is very much less basic than the lower oxide, and, furthermore, it is very insoluble — either the anhydrous oxide or its hydrated forms, $Pb(OH)_4$ or $PbO(OH)_2$. The effect usually observed when a salt of divalent lead is oxidized is a precipitation of dark brown lead dioxide. This precipitate can be obtained by oxidizing an alkaline solution containing a lead salt with chlorine, but it cannot be obtained in an acid solution with this oxidizing agent because hydrochloric acid reduces lead dioxide (see Experiments 10 and 6, Chapter IV, pages 162 and 164). In an acid solution containing no reducing agent, that is in a nitric acid or a sulphuric acid solution, lead dioxide can be formed by the action of a very strong oxidizing agent, as for example, by the electrolytic oxidizing action at the anode of a lead storage battery. It is to be noted that nitric acid does not oxidize lead to the tetravalent condition.

In this preparation we shall make use of bleaching powder in a slightly alkaline solution as the oxidizing agent. This is chosen in preference to chlorine because it is easier to handle and no precautions need be taken to avoid escape of objectionable chlorine into the laboratory. It should be recalled that the effect of bleaching powder is the same as that which would be obtained by passing chlorine into an alkali. The precipitate finally obtained after the bleaching powder has acted contains the greater part of the lead in the form of lead dioxide; but it may also contain a small residue of unoxidized lead, as $Pb(OH)_2$, as well as calcium hydroxide and calcium carbonate from the bleaching powder. By treating this precipitate with nitric acid everything except the lead dioxide is dissolved or decomposed, and practically pure lead dioxide remains.

The packages of bleaching powder are labeled with the percentage of available chlorine. This is the percentage by weight of chlorine which would be given off if the material were treated with dilute H_2SO_4.

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

It is to be noted that bleaching powder may contain unavailable chlorine (*e.g.*, $CaCl_2$). Calculate the weight of bleaching powder with the given content of available chlorine (assume 30 per cent if the package is not marked) that would be required to oxidize the lead acetate used for this preparation. The so-called high-test hypochlorite, $Ca(OCl)_2$, which has recently become available in the chemical market, may be used in place of bleaching powder.

Materials: lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, 95 grams = 0.25 F.W.
sodium hydroxide, NaOH, 25 grams.
bleaching powder containing 30 per cent available chlorine, 66 grams, or calcium hypochlorite, 40 grams.
6 N HNO_3, 250 cc.

Apparatus: 8-inch porcelain dish.
2-liter common bottle.
suction filter and trap bottle.
mortar and pestle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve the lead acetate in 200 cc. of cold water in the 8-inch porcelain dish; add a solution of the sodium hydroxide in 100 cc. of water, stirring well, and into the mixture, which should not be warmer than 30°, stir a paste made by rubbing 66 grams of bleaching powder or 40 grams of calcium hypochlorite in a mortar with a little water. Warm the mixture slowly to the boiling temperature, stirring frequently, and finally boil it for 30 minutes, replacing water lost by evaporation. Transfer the contents of the dish to a 2-liter common bottle and wash the sludge by decantation with cold water (see Note 5 (*b*), page 10) until over 99 per cent of the soluble chloride is removed. Then transfer the sludge again to the dish, add 250 cc. of 6 *N* HNO_3, and boil it for 10 minutes. Wash the residue of lead dioxide by decantation until the wash water is no longer acid; transfer the product to a filter and let it drain without suction (Note 4 (*c*), page 7). After the lead dioxide has drained, remove the filter and contents carefully from the funnel, unfold the filter, and spread it on paper towels on the steam table to dry. When completely dry, detach the lumps of lead dioxide from the paper, and pulverize them in a mortar. Put up the product in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Why could not lead dioxide be prepared equally well by treating a solution of lead chloride with chlorine?
2. Compare the reaction of lead dioxide and of lead monoxide with hydrochloric acid.
3. Compare the action of lead dioxide with that of manganese dioxide upon hydrochloric acid.
4. Why should not lead dioxide and manganese dioxide dissolve in dilute nitric acid as well as in hydrochloric acid?

PREPARATION 48

RED LEAD, Pb_3O_4

Of the oxides of lead, the monoxide PbO is the most stable when heated to a high temperature, and in fact all the other oxides are converted into this one when they are heated strongly in contact with the air. At a moderate heat, however, the monoxide is capable of taking on more oxygen from the air until the composition approximates that of the formula Pb_3O_4. This substance is not to be regarded as a simple oxide of lead, but rather as a compound of PbO and PbO_2, in which the monoxide is the basic component and the dioxide the acidic. It may thus be regarded as the salt, lead orthoplumbate, $2PbO \cdot PbO_2 = Pb_2(PbO_4)$. This view is strengthened by the behavior of the substance when treated with nitric acid — part of the lead dissolves to give lead nitrate, while the other part is left as lead dioxide,

$$Pb_2(PbO_4) + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + H_4(PbO_4)$$
$$H_4PbO_4 \rightarrow PbO_2 + 2H_2O$$

The following procedures should yield a product of nearly the composition Pb_3O_4. This substance, under the commercial name of minium, finds use as a red pigment.

Dry Method

Material: lead monoxide (massicot), PbO, 25 grams.

Apparatus: iron or aluminum plate 2–4 mm. thick.
ring burner.
iron spatula.

Procedure: Spread 25 grams of lead monoxide in a thin layer on an iron or aluminum plate 2–4 mm. thick. Either use the variety of lead oxide which has not been fused and is known under the name of massicot, or use lead carbonate, which on being heated yields a very pure and finely divided lead monoxide. Heat the lead oxide over a ring burner so adjusted that the flames do not quite touch the metal plate. The plate must be kept just below a perceptible red heat. Continue the heating for 6 hours or more and turn over the powder frequently with an iron spatula. When the change is complete, the product is dark brown when hot, a bright scarlet-red when partly cooled, and a somewhat less brilliant red when entirely cold.

Wet Method

Materials: lead monoxide (litharge) PbO, 33 grams = 0.15 F.W.
lead dioxide PbO_2, 24 grams = 0.1 F.W.
6 *N* NaOH.

Apparatus: 600-cc. beaker.
5-inch funnel.
150-cc. casserole.
iron ring and ring stand.
Bunsen burner.

Procedure: It is rather difficult to adjust the temperature successfully for the dry method. Place 33 grams litharge, 24 grams of lead dioxide and 50 cc. of 6 *N* NaOH in a 600-cc. beaker. Stir thoroughly and leave in a warm place (80°), striring when convenient and adding water whenever the mass becomes dry, until the contents have become bright red. Finally wash the red lead thoroughly by decantation, and rinse on to a gravity filter in a 5-inch funnel. Let it drain over night. Lift the filter intact from the funnel, open it out on paper towels, and leave it on the hot plate until it is entirely dry. Detach the red lead from the paper by bending the paper; transfer the dry material to a 150-cc. casserole and heat it in a flame about 2 inches high, holding the casserole in the hand and rotating it in the flame. At the correct temperature (350–400°) the material becomes a dark reddish brown; after cooling it is a much more brilliant red than before heating. Great care must be taken to keep the material stirred during the heating so that the under layers do not become superheated and changed to PbO. Preserve the preparation in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. If it is assumed that Pb_2O_3 and Pb_3O_4 are lead metaplumbate and lead orthoplumbate, respectively, write formulas to express these facts. Write the formulas of the corresponding meta- and orthoplumbic acids.
2. Warm a little of the red lead with nitric acid. What is the residue, and what soluble salt is formed? Filter the mixture and test the filtrate by diluting and adding a few drops of sulphuric acid.
3. Heat a little of the red lead to a dull red heat on a thin piece of iron.

PREPARATION 49

CERIC OXIDE FROM CEROUS OXALATE, CeO_2

Cerous oxalate, $Ce_2(C_2O_4)_3 \cdot 10H_2O$, is formed in the Welsbach treatment of Monazite sands in the production of thorium nitrate, and is the starting point in the preparation of nearly all cerium salts. Since ceric oxide is more easily acted upon by common reagents, it is often prepared as the first step in making other salts from the oxalate.

If cerous oxalate is strongly heated in air, the water of crystallization is first driven off, then the cerous oxalate decomposes into cerous oxide and oxides of carbon. The cerous oxide is oxidized by the oxygen in the air to ceric oxide.

Material: Cerous oxalate, $Ce_2(C_2O_4)_3 \cdot 10H_2O$, 72.5 grams = 0.1 F.W.

Apparatus: 6-inch iron sand bath.
iron ring and ring stand.
Bunsen burner.

Procedure: Pour the cerous oxalate into the clean iron sand bath. Support the pan on an iron ring and heat with a long blue flame with no cone. The flame should be long enough to be in contact with all parts of the pan, but it should not appear above the rim. The solid should be stirred frequently to insure complete decomposition. When the solid is no longer white, the temperature should be increased and the pan heated for 10–15 minutes with a hot flame. Cool, weigh the pan plus the solid, and heat again until the weight is approximately constant. Put the product in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. Pour 4–5 cc. concentrated hydrochloric acid on 0.5 gram of the product. Equation?
2. Heat 0.5 gram of the product in a test tube with 5 cc. concentrated nitric acid. Equation? To what is the color due?

PREPARATION 50

CEROUS OXALATE, $Ce_2(C_2O_4)_3 \cdot 10H_2O$

In the quantitative determination of cerium, use is made of the fact that cerous oxalate is insoluble in neutral and acid solution. Since a quantitative yield is not necessary in this preparation, some of the cerium is sacrificed to insure complete removal of any iron that may be present. In order to have a neutral solution for the hydrolysis of the iron, a slight excess of ceric oxide is used.

From the discussion of the preparation of ceric oxide it is evident that the cerous oxide, Ce_2O_3, which would be the direct product of the decomposition of cerous oxalate, is readily oxidized by the oxygen of the air to ceric oxide, CeO_2. In contact with the air therefore ceric oxide is the stable oxide. The salts of ceric oxide, however, are in general not stable and go over rather easily to cerous salts. This is particularly true of ceric chloride, $CeCl_4$, which decomposes spontaneously into cerous chloride, $CeCl_3$, and free chlorine.

Materials: Crude CeO_2, 22.2 grams = 0.1 F.W. + 5 grams.
12 *N* HCl, 34 cc. = 0.4 F.W.
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, 20 grams.
3 *N* sodium carbonate.
ammonium oxalate solution.

Apparatus: 2-liter common bottle.
300-cc. flask.
5-inch funnel.
8-inch porcelain dish.
400-cc. beaker.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dilute 34 cc. of 12*N* HCl to 50 cc. and pour it into the 300-cc. flask. Add the ceric oxide under a hood. Warm gently until the reaction starts. Stop heating until the reaction slows down, then heat cautiously to boiling and keep at that temperature for 5 minutes. Cool; filter without suction directly into the large bottle. Dilute to 700 cc. The iron is now to be precipitated as $Fe(OH)_3$. Add 5 cc. of 3 *N* Na_2CO_3. If the precipitate is light colored, showing that it consists in the main of white cerous carbonate, no more Na_2CO_3 need be added, otherwise add 3-cc. portions of this reagent until the new precipitate shows no brownish color of ferric hydroxide (best let the precipitate settle and pour some of the nearly clear liquid into a beaker in order that the color may be observed when the reagent is added). Stir the whole suspension in the bottle and let it settle. Decant the clear liquid through the filter directly into an 8-inch evaporating dish, finally pouring the sludge on to the filter and letting it drain. Add 5 cc. of 12*N* HCl to the filtrate; boil down to 75–100 cc. Pour into the beaker. Dissolve the oxalic acid in

50 cc. of boiling water, filter if necessary, and pour into the hot solution of cerous chloride while stirring. Boil for 1 minute, filter hot, using suction. Wash the precipitate on the filter with two successive 10-cc. portions of ammonium oxalate solution. Dry on paper towels, weigh, and put up in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Explain at what point in the preparation and how the ceric compound was reduced to cerous.
2. Explain how the separation of iron depends on the difference in the extent to which ferric and cerous salts hydrolyze. Which is more basic, $Fe(OH)_3$ or $Ce(OH)_3$?

PREPARATION 51

CEROUS CHLORIDE, $CeCl_3 \cdot 7H_2O$

Ceric oxide dissolves in hydrochloric acid, forming cerous chloride and evolving chlorine. (Read the discussion of Preparation 50.) The cerous chloride hydrolyzes to only a slight extent in neutral solution. By evaporating and cooling the solution, crystals of $CeCl_3 \cdot 7H_2O$ may be separated if hydrolysis is prevented. A saturated solution at room temperature contains 128 grams of $CeCl_3 \cdot 7H_2O$ in 100 cc. of solution, and the solubility increases rapidly with rise in temperature. The salt is soluble in its own water of crystallization at a temperature below the boiling point.

Materials: CeO_2, 48 grams = 0.25 F.W. + 5 grams.
12 *N* HCl, 84 cc. = 1 F.W.
sodium carbonate, anhydrous.

Apparatus: 2-liter common bottle.
500-cc. flask.
5-inch funnel.
8-inch porcelain dish.
4-inch crystallizing dish.
5-inch watch glass.
iron ring and ring stand.
Bunsen burner.

Procedure: Dilute 84 cc. of 12 *N* HCl to 125 cc. and pour it into the 500-cc. flask. Add the ceric oxide under a hood. Warm gently until the reaction starts. Stop heating until the reaction slows down, then heat cautiously to boiling, and keep at that temperature for 5 minutes. Cool, filter without suction into the 2-liter bottle. To remove iron from the solution proceed according to the same principle as in the preparation of cerous oxalate.

Prepare cerous carbonate by adding an excess, about 5 grams, Na_2CO_3 to one-tenth of the cerous chloride solution. Wash the cerous carbonate by decantation (see Note 5 (*b*), page 10) until the soluble sodium chloride is completely removed. Add the cerous carbonate suspension to the main part of the cerous chloride solution; digest with frequent stirring for 15 minutes or longer. Remove the ferric hydroxide and excess cerous carbonate by filtering, add 5 cc. $12\,N$ HCl to the filtrate, and evaporate in the 8-inch porcelain dish to 70 cc. Pour into a small crystallizing dish, cover with a 5-inch watch glass, cool slowly. Remove the crystals; dry them on a watch glass. Allow the solution to evaporate in an uncovered dish to obtain an additional crop of crystals. Put up the product in an 8-ounce cork-stoppered bottle.

QUESTIONS

Answer the questions under Cerous Oxalate.

Experiments

1. **Carbon Dioxide.** From a generator (Note 13 (*a*), page 18) fill with carbon dioxide several test tubes inverted in a pan of water, and use them in the following experiments.

(*a*) Place the thumb over the mouth of a test tube of carbon dioxide and transfer it to a beaker of freshly drawn water. Clamp it in position and note the level of the water at intervals of about 15 minutes.

(*b*) Stick a gummed label on a second test tube of the gas, and make a light pencil mark at the middle point of the length of the tube. Place the thumb over the mouth of this tube, remove it from the water, and turn it upright. Draw some fresh water from the tap, and, removing the thumb sufficiently, pour water into the tube until the level stands at the pencil mark. Close the tube again tightly with the thumb, invert the tube, and place a heavy mark at the level of the surface of the water, calling this mark 1 (it will of course nearly if not quite coincide with the light mark). Shake the tube vigorously for 60 seconds, then place the mouth of the tube under water in the pan, remove the thumb, and mark the level to which the water rises, calling this mark 2. Now measure with a graduate, first, the volume between the closed end of the tube and mark 1, thus giving the volume of carbon dioxide taken; second, the volume between marks 1 and 2, thus giving the volume of carbon dioxide, measured under atmospheric pressure, dissolved by the water; third, the volume between mark 1 and the open end of the tube, thus giving the volume of water in which the carbon dioxide was dissolved. Take the temperature of the water in the pan. The undissolved gas was under a pressure less than atmospheric just before the thumb was removed from the end of the tube. Calculate this pressure according to Boyle's law from the volume. Then calculate the volume of carbon dioxide that would be dissolved at the temperature of the experiment in 1 volume of water if the gas were at atmospheric pressure, applying Henry's law that the quantity of a gas dissolved in a liquid is proportional to the pressure.

At 15° 1 volume of water will dissolve 1 volume of carbon dioxide under 1 atmosphere pressure.

(*c*) Take a third tube of the gas, introduce 5 cc. of 1 *N* NaOH, and shake as in (*b*). Note that except for a small bubble, which is doubtless air introduced when the NaOH was poured in, the gas is entirely dissolved by the solution.

The carbonic acid, which in (*b*) comes to equilibrium with the carbon dioxide in the gas phase, is in this experiment neutralized by the base,

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$$

and since 5 cc. of 1 *N* NaOH reacts, according to the equation, with carbonic acid equivalent to 56 cc. of carbon dioxide, all the gas is dissolved.

(*d*) Repeat (*c*) using 5 cc. of 1 *N* Na_2CO_3 instead of NaOH. Note that the gas is nearly if not all dissolved. If the experiment is repeated and the shaking is continued for a longer time the gas is entirely dissolved.

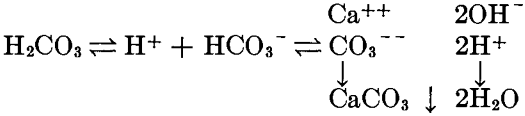
According to the equation, $Na_2CO_3 + H_2CO_3 \rightarrow 2NaHCO_3$, 56 cc. of carbon dioxide should be dissolved in this experiment.

(*e*) Repeat (*c*) using 10 cc. of lime water (saturated $Ca(OH)_2$ solution) instead of 5 cc. of 1*N* NaOH. Note the appearance of the solution during and after the absorption.

Write equation to account for this appearance. What volume of CO_2 should 10 cc. of saturated $Ca(OH)_2$ be able to absorb (the $Ca(OH)_2$ is 0.02 molal) if (1) $CaCO_3$ is formed, (2) $Ca(HCO_3)_2$ is formed?

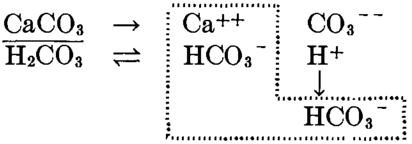
(*f*) Bubble carbon dioxide slowly into a test tube of lime water. A white precipitate forms at once but very soon redissolves and the solution then remains clear.

As long as the base is in excess both stages of the ionization of carbonic acid can proceed to completion because of the removal of H^+ ions (see Ionization of Polybasic Acids, Chapter III, page 116),



$$\begin{array}{rcc} & Ca^{++} & 2OH^- \\ H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons & CO_3^{--} & 2H^+ \\ & \downarrow & \downarrow \\ & CaCO_3 \downarrow & 2H_2O \end{array}$$

but, as soon as the carbon dioxide is in excess, the concentration of H^+ ions from the first hydrogen of the carbonic acid is greater than can exist in equilibrium with the CO_3^{--} ions in a saturated solution of calcium carbonate; hence the carbonate ions are removed progressively and the solid continues to dissolve until the solution is again clear.



$$\begin{array}{cccc} \underline{CaCO_3} & \rightarrow & Ca^{++} & CO_3^{--} \\ H_2CO_3 & \rightleftharpoons & HCO_3^- & H^+ \\ & & & \downarrow \\ & & & HCO_3^- \end{array}$$

The components boxed in by the dotted lines represent the ionized salt calcium bicarbonate present in the final solution.

2. Combustibility of Carbon Compounds. Place successively a few drops of gasoline, carbon disulphide (CS_2), carbon tetrachloride (CCl_4), and chloroform in a porcelain dish and apply a lighted match.

Make mixtures of gasoline and carbon tetrachloride in the proportion of 5 cc. and 1 cc.; 4 cc. and 2 cc.; 3 cc. and 3 cc.; 2 cc. and 4 cc.; 1 cc. and 5 cc., and under the hood apply a lighted match to each. If the mixture does not at once catch fire, heat it to its boiling point and try again.

Place 1 cc. of gasoline and 5 cc. of water in the dish and apply a lighted match.

Gasoline is a mixture of hydrocarbons, that is compounds of carbon and hydrogen, of which hexane C_6H_{14}, heptane C_7H_{16}, and octane C_8H_{18}, are the principal ones. Gasoline and carbon disulphide are very combustible. Carbon tetrachloride and chloroform do not burn.

Carbon tetrachloride and gasoline are mutually soluble in each other in all proportions. The vapor pressure of gasoline is lowered by the admixture, and furthermore the vapor that escapes is mixed with non-combustible carbon tetrachloride vapor; it is thus understandable that the combustibility of gasoline is lessened by large admixture with this substance.

Gasoline and water do not mix, but the former will float in a layer over the latter; water is of little effect in extinguishing a gasoline fire.

3. Carbon Monoxide. Place a plug of shredded asbestos *loosely* 2 inches from one end of a combustion tube. Fill the tube with granulated (not powdered) charcoal for a length of about 4 inches, and insert another plug of asbestos. Join this tube to a carbon dioxide generator, and let the gas flow until air is completely expelled from the apparatus. Draw out the end of a delivery tube to a fine capillary in order that it may deliver very small bubbles of gas, and connect this by means of a rubber tube with the other end of the tube containing the charcoal. Place a little $6N$ NaOH in a shallow dish; fill a test tube with the same solution, and invert the tube in the solution in the dish. Have the generator delivering a *very slow* stream of carbon dioxide, and insert the delivery tube under the mouth of the test tube. The carbon dioxide should be completely absorbed in rising through the NaOH solution. If it is not, it must not be delivered so rapidly by the generator. Now heat the charcoal as hot as possible, using the flame spreader, and note if now any gas issues from the delivery tube which is not absorbed by the NaOH. Test the gas for its combustibility.

Carbon dioxide is reduced by hot carbon to carbon monoxide which is not an acidic oxide because it does not react with the base. Carbon monoxide is combustible.

4. Carbides. (*a*) The aluminum nitride made in Preparation 13 contains a considerable amount of carbide Al_4C_3. Treat some of this product, or some commercial aluminum carbide, with 6 N NaOH in a test tube with a delivery tube. Collect some of the gas over water, which will dissolve all the ammonia. Test the combustibility of this gas and find that it burns with a nearly colorless flame.

(*b*) Drop a little calcium carbide, CaC_2, into water in a test tube; note that a gas is evolved and that this gas will burn with an intensely luminous and very smoky flame.

Nearly all the metals form carbides which will hydrolyze more or less readily. The hydrolysis products of aluminum carbide are methane and aluminum hydroxide

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

from which it is concluded that in aluminum carbide the carbon is acting as a simple negative radical with a valence of 4. Note that the maximum negative valence of carbon is 4 as well as the maximum positive valence (in CO_2) and the arithmetical sum of the maximum positive and negative valences is 8. No element is known for which this sum exceeds 8, and, with a large number, the value of 8 is equaled.

The hydrolysis product of calcium carbide is acetylene

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

The weight of 22.4 liters of acetylene is 26 grams, which is equal to the formula weight of C_2H_2. It thus appears that there is present in calcium carbide the complex carbon radical C_2 with a negative valence of 2 for the whole radical.

5. Silicon Dioxide and Silicic Acid. (*a*) Wet a little silicon dioxide (very finely powdered quartz, or better the product of Preparation 41), test with litmus, and note that litmus is not affected. Add Na_2CO_3 solution and warm gently, noting that there is no effervescence.

(*b*) Collect a little of a mixture of anhydrous potassium carbonate and sodium carbonate (the mixture melts more easily than either salt alone) in a loop on the end of a platinum wire and melt it in the Bunsen flame to a clear bead. Dip the bead into powdered silicon dioxide and melt it again. Note that the liquid bead effervesces until the silica has dissolved.

(*c*) Dilute 5 cc. of water glass, sodium silicate solution, with 5 cc. of water in a beaker, and add 6 *N* HCl, drop by drop, with stirring, noting that the solution coagulates to a stiff, apparently dry jelly.

Repeat, diluting 5 cc. of water glass with 100 cc. of water and noting that coagulation does not take place on acidifying.

Silicon dioxide is the anhydride of silicic acid, but when it is entirely dehydrated its action with water is almost imperceptible. It does not react with a solution of the salt of the weak carbonic acid. Silicic acid is in fact a far weaker acid than carbonic. With melted sodium carbonate, however, silicon dioxide reacts, $SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2 \uparrow$, but this does not necessarily show that silicon dioxide is more strongly acidic than carbon dioxide; the effect is due rather to the greater volatility of the carbon dioxide. Water glass is obtained by dissolving the sodium silicate melt in hot water under pressure. From it ordinary acids displace the weak silicic acid in *colloidal* form. This colloidal silicic acid appears as a jelly in concentrated solutions. In dilute solution it remains *dispersed* so that its formation is not apparent. When the colloidal silicic acid is heated it is changed to the anhydride, which will not again take up water.

6. Hydrolysis of Stannous Salts. Dissolve 0.5 gram crystallized $SnCl_2 \cdot 2H_2O$ in a few drops of water. A clear solution can be obtained if the preparation is fresh. Dilute the solution with water and note the white precipitate. Add a little HCl and note that the precipitate redissolves.

Stannous salts in which tin displays the lower valence of 2 are derivatives of the hydroxide $Sn(OH)_2$. That salts, such as the chloride, nitrate, and sulphate, can exist in solution indicates that stannous hydroxide is basic; but that the salts hydrolyze very easily, with precipitation of basic salt, $SnCl_2 + H_2O \rightleftharpoons SnOHCl \downarrow + HCl$, indicates that the base is a weak one.

7. Reducing Action of Stannous Salts. (*a*) Add $SnCl_2$ solution drop by drop, to 2 cc. of $HgCl_2$ solution diluted with 10 cc. of water. Notice the white precipitate which turns gray and then black with more of the reagent.

(*b*) To 2 cc. $FeCl_3$ solution diluted with 10 cc. of water add $SnCl_2$ until the solution appears colorless. Then test for ferric ions by adding KSCN to a part and note that there is no red color. Test for ferrous ions by adding a freshly prepared solution of $K_3Fe(CN)_6$, and note the deep blue precipitate.

Tin has a marked tendency to develop the valence 4 characteristic of the group, and in consequence stannous compounds are strong reducing agents.

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + 2HgCl \downarrow$$
$$SnCl_2 + 2HgCl \rightarrow SnCl_4 + 2Hg \downarrow$$
$$SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$$

8. Lead Salts. (*a*) Dissolve a little pure crystallized lead nitrate in water and test with litmus noting that it is not affected. Dilute the solution and note that there is no precipitate of basic salt.

(*b*) Moisten some litharge (PbO) with water and test with litmus, noting that the litmus is turned blue. Boil the litharge a few minutes with 10 cc. of water, filter, and add hydrogen sulphide solution to the filtrate, noting a little black precipitate.

That lead monoxide is soluble enough to give a precipitate of lead sulphide and that the solution is alkaline enough to color litmus blue marks it as exceptionally basic for a heavy-metal oxide. The absence of hydrolysis of the lead salts is a further evidence of the distinctly basic character of $Pb(OH)_2$.

9. Amphoteric Character of the Hydroxides of Tin and Lead. Dilute 2 cc. of $1\,N$ $SnCl_2$ with 10 cc. of water. From a 10-cc. graduate add $6\,N$ NaOH, noting the amount required to produce the maximum precipitate and again the amount necessary to redissolve the precipitate.

Repeat using 2 cc. of 1 N $Pb(NO_3)_2$ instead of $SnCl_2$ and note that a very much larger volume of the NaOH is necessary to redissolve the precipitate.

$Pb(OH)_2$ is much more basic than $Sn(OH)_2$; it is correspondingly more weakly acidic, as is shown by the greater excess of base required to convert it to the soluble salt.

$$\underline{H_2SnO_2} + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$$
$$\underline{H_2PbO_2} + 2NaOH \rightarrow Na_2PbO_2 + 2H_2O$$

Sodium stannite and sodium plumbite both hydrolyze easily but the latter much more so, consequently the greater amount of base to overcome its tendency to hydrolyze.

10. Stannic Acid. Heat 0.5 gram of tin in a casserole with a little 16 N HNO_3. Note that red gases are evolved, that the metal disintegrates, and that a white powder insoluble in the nitric acid, and later insoluble in water, is formed.

Concentrated nitric acid oxidizes tin to the dioxide which, in a hydrated form, usually called meta-stannic acid (approximately H_2SnO_3), is left as the white insoluble residue.

11. Thio-Salts of Tin. Perform Experiment 1 under Preparation 43. Stannous sulphide does not dissolve in Na_2S solution. Addition of sulphur causes it to dissolve. Addition of HCl to the solution produces a yellow precipitate and an evolution of hydrogen sulphide.

Sulphur and oxygen are interchangeable in sulphides and oxides. Metal oxides (basic) and non-metal oxides (acidic) combine to form salts. Likewise metal sulphides may combine with sulphides of weakly metallic or non-metallic elements to form salts, the so-called thio-salts, or sulpho-salts. Thio-salts of a few of the elements, notably tin, are very well defined. Stannous sulphide does not form a thio-salt; but addition of sulphur converts it to stannic sulphide which does form a soluble thio-salt with the sulphide of an alkali metal.

$$Na_2S + \underline{SnS_2} \rightarrow Na_2SnS_3$$

In the same way that the higher oxide SnO_2 is more acidic than SnO, the higher sulphide SnS_2 is more acidic and reacts more easily with the basic sulphide, Na_2S.

Addition of an acid displaces the very weak thio-stannic acid from its salt solution, $2HCl + Na_2SnS_3 \rightarrow 2NaCl + H_2SnS_3$; this acid is very unstable and decomposes into stannic sulphide, the yellow precipitate, and hydrogen sulphide, $H_2SnS_3 \rightarrow H_2S \uparrow + SnS_2 \downarrow$.

12. Lead Dioxide. (*a*) To 2 cc. of $Pb(NO_3)_2$ solution add 5 cc. of water and 6 *N* NaOH until the precipitate first formed redissolves. Then add chlorine water and note the dark brown precipitate.

(*b*) Collect the precipitate on a filter, wash it with water, break the tip of the filter, and wash the precipitate with a jet from the wash bottle into a test tube. Shake the test tube and divide the suspension equally among four tubes. Add to the respective tubes (1) 6 *N* HNO_3, (2) 6 *N* H_2SO_4, (3) 6 *N* HCl, (4) 6 *N* NaOH, and note that nitric and sulphuric acids have no effect, hydrochloric acid dissolves the brown precipitate with evolution of chlorine, and sodium hydroxide has no effect.

Chlorine in alkaline solution oxidizes the divalent lead to tetravalent, the latter appearing as the very insoluble brown PbO_2

$$Na_2PbO_2 + Cl_2 \rightarrow 2NaCl + PbO_2 \downarrow$$

This highest oxide of lead has practically no basic properties and it does not react with nitric and sulphuric acids. Neither are its acidic properties highly developed, for it does not react with NaOH in solution. The action with HCl has already been discussed; it depends on the reducing action of this acid. The next experiment, however, throws a little more light on this subject.

13. Lead Tetrachloride. Cool to 0° 5 cc. of 12 *N* HCl in a test tube, and keeping the solution cold add about 1 gram of dry lead dioxide a little at a time with shaking. Note that a clear yellow solution is formed. Add a drop or two of this solution to 500 cc. of cold water in a large beaker and note an opalescent brown precipitate which rather slowly becomes visible. Let the rest of the yellow solution grow warm and note that chlorine gas is evolved and that a crystalline white precipitate separates.

The yellow solution contains lead tetrachloride. It is puzzling to explain why lead dioxide will not react with two of the strong acids tried, yet does react with hydrochloric acid to give what is apparently a salt, $PbCl_4$. The explanation lies in the character of lead tetrachloride, which is practically un-ionized, and therefore is hardly to be classed as a salt. In the anhydrous condition it is a liquid like carbon tetrachloride. Furthermore it combines with excess HCl to form the complex acid H_2PbCl_6, of which the ammonium salt $(NH_4)_2PbCl_6$ can be crystallized. By comparison, if nitric acid reacted with lead dioxide, the tetranitrate, $Pb(NO_3)_4$, would be the product; this presumably would be highly ionized like all nitrates, which means that it would have to hydrolyze completely.

With a large amount of water the lead tetrachloride hydrolyzes

$$PbCl_4 + 4H_2O \rightarrow Pb(OH)_4 \downarrow + 4HCl$$
$$Pb(OH)_4 \rightarrow PbO_2 + 2H_2O$$

giving the brown precipitate. In concentrated solution it decomposes into chlorine and $PbCl_2$, the white crystalline precipitate.

14. Stability of Lead Carbonate. (*a*) To a neutral lead nitrate solution add Na_2CO_3 solution drop by drop, noting the white precipitate and the absence of effervescence.

(*b*) Heat a little dry white lead carbonate in a test tube and note that it changes to a yellow powder when it has become moderately hot. The temperature is much higher than that required to decompose copper carbonate. Treat some of the residue with dilute HNO_3 and note that it dissolves without effervescence.

The facts that lead carbonate $PbCO_3$ will precipitate without hydrolyzing to a basic carbonate, and that lead carbonate must be heated moderately hot to be decomposed, both confirm the conclusion, already made, that PbO is a distinctly basic oxide.

General Questions IX

1. Arrange a table of the dioxides of the elements of Group IV: column 1, the formulas of the dioxides, placing those of the A family at the left and those of the B family at the right of the column; column 2, the character of the dioxide specifying, *a.* = distinctly acidic, *w. a.* = weakly acidic; *ind.* = indifferent; *w. b.* = weakly basic; *b.* = distinctly basic; *amph.* = amphoteric; column 3, the formula of as well defined a salt as possible of the dioxide; column 4, the extent of hydrolysis of this salt, specifying much, little, or none.

2. Make a similar table embracing the lower oxides, CO, SnO, Ce_2O_3, PbO.

3. Make a table for the tetrachlorides of all the elements of Group IV: column 1, the formula of the tetrachloride; column 2, its state of aggregation, specifying, gas, liquid, or solid; column 3, its boiling point at atmospheric pressure, specifying *dec* if it decomposes before the boiling point is reached; column 4, the equation for its reaction with a large amount of water.

Judging from the decreasing metallic properties in the series, Pb, Sn, Si, C, we should expect the tetrachlorides to hydrolyze more readily as we progress in this order. Two factors modify this effect: the tendency to form a complex acid such as H_2SnCl_6 with the anion $SnCl_6^{--}$, and the insolubility or total lack of ionization of the tetrachloride. Explain from this point of view why carbon tetrachloride and carbon disulphide are without perceptible action with water.

4. Find out what elements of Group IV form carbonates, and give the formulas of the carbonates and approximately their relative stability.

5. What is a thio-salt? Describe how a thio-salt of tin can be formed, and discuss its properties and its relation to the corresponding oxy-salt.

CHAPTER X

ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM

In this group, as in Groups III and IV, the difference in properties between the elements of Families A and B is not so striking as in Groups I and II (or as in Groups VI and VII), and the whole group is considered under the same heading. It is also true that the elements of Family A, that is, vanadium, columbium, and tantalum, are of comparatively infrequent occurrence, and are given no attention in this course. On the other hand all the elements of Family B are of frequent occurrence and considerable importance.

The characteristic valence of the group is 5, corresponding to the oxide M_2O_5, but the elements likewise exhibit a valence of 3 in the oxide M_2O_3. It is noteworthy that the valence is nearly always either 3 or 5.

It is true in this group, as well as in Group IV, that the acid-forming properties are most marked in the elements of low atomic weight (nitric acid is one of the strongest acids), and decrease with increasing atomic weight, whereas the base-forming properties are most strongly developed with the elements of high atomic weight.

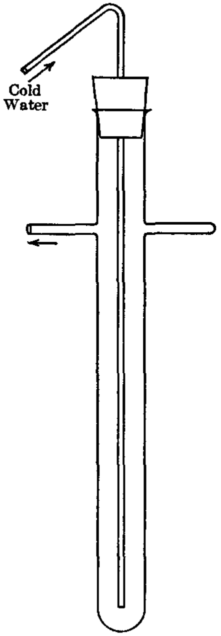


FIG. 25

PREPARATION 52

ORTHO-PHOSPHORIC ACID, H_3PO_4

Pure phosphoric acid is prepared commercially by burning phosphorus in air to form phosphorus pentoxide and then treating this compound with water. On a laboratory scale it is more convenient to oxidize the phosphorus with a solution of nitric acid.

The solution first obtained by the action of dilute nitric acid

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upon phosphorus contains a considerable quantity of phosphorous acid, H_3PO_3; but upon concentrating this solution, a point is reached at which a rather vigorous reaction takes place, which consists of an oxidation of the phosphorous to phosphoric acid by means of the nitric acid still present.

Commercial phosphorus often contains a small quantity of arsenic. This on the treatment with nitric acid is oxidized to arsenic acid, which would contaminate the preparation of phosphoric acid unless removed by hydrogen sulphide.

Phosphorous acid may always be present in the product if the oxidation with nitric acid has not been complete, and its presence may be detected by its ability to reduce silver nitrate and give a black precipitate of metallic silver,

$$H_3PO_3 + 2AgNO_3 + H_2O = 2HNO_3 + 2Ag \downarrow + H_3PO_4$$

Materials: red phosphorus, P, 31 grams = 1 F.W.
$6N$ HNO_3, 295 cc.
$16N$ HNO_3, 20 cc.
seed crystal of H_3PO_4.

Apparatus: 2-liter round-bottom flask.
condenser to hang in neck of flask (Fig. 25.)
8-inch porcelain dish.
250° thermometer.
125-cc. casserole.
2-ounce glass-stoppered bottle.
tripod.
burette clamp.
wood ring.
Bunsen burner.

Procedure: Place 295 cc. of $6N$ nitric acid in a 2-liter round-bottom flask; connect the condenser with the cold water tap, and hang it in the neck of the flask to condense acid vapors and allow them to drip back into the reacting mixture. Add about one-fifth of the phosphorus and warm the flask very cautiously until red vapors begin to appear; then stand the flask in a wooden ring and allow the reaction to proceed, keeping a pan of cold water at hand, in which to immerse the flask if the reaction gets too violent. After the foaming has abated somewhat add a little more of the phosphorus, and again wait until action has abated, and so on, until all the phosphorus is used. Then add 20 cc. of $16 N$ HNO_3; boil the mixture gently in the flask with the condenser in place until no more red vapor is evolved and until the last specks of phosphorus have dissolved. If any black residue does persistently remain filter it off at this point. Transfer the solution to an 8-inch porcelain dish and boil it under the hood until a rather violent reaction begins to take place. Remove the flame and let the reaction proceed; it grows very violent and then suddenly ceases altogether.

The solution should now be clear and almost colorless, and should contain no phosphorous acid. Test for phosphorous acid by adding a few drops of the liquid to 10 cc. of distilled water, adding 1 cc. of $0.05 N$ $AgNO_3$ and warming; a dark coloration, or black precipitate, appearing within 2 minutes indicates phosphorous acid. If it is found, follow the special procedure given in Note 1; otherwise transfer the solution to a small casserole and evaporate it over a low flame until a thermometer whose bulb is immersed in it stands at 180°. During this final evaporation one must give it constant attention, for if it is left and the temperature rises above 180°, not only does the orthophosphoric acid become changed partially into pyrophosphoric acid, but it attacks the material of the dish, and the preparation becomes contaminated. Allow the acid to cool nearly to room temperature and then pour it into a previously weighed 2-ounce glass-stoppered bottle, and stopper it tightly. When cool introduce a small crystal of phosphoric acid to induce crystallization of the mass.

Note 1. If phosphorous acid was found at the point where the test was made, it showed that the reaction had been allowed to take place too violently in the earlier part of the procedure, the heat driving nitric acid vapor out of the flask. Unless nitric acid is present in the right amount and at the right concentration when the secondary reaction takes place, the phosphorous acid is not all oxidized and it is afterwards extremely difficult to bring about conditions under which the oxidation can be completed. However, the following may be tried: Pour the solution back into the large flask, add 275 cc. of $6 N$ HNO_3 and 10 cc. of $12 N$ HCl to act as a catalyzer, insert the condenser in the neck of the flask, and boil very gently for an hour. Then proceed as before.

Note 2. In the above procedure no provision is made for removing traces of arsenic. If this is to be done, the solution, immediately after the violent secondary reaction has ceased, is poured into a flask, diluted to about a liter with water, saturated with hydrogen sulphide gas, stoppered, and allowed to stand over night. If, the next morning, the contents of the flask smell strongly of hydrogen sulphide, the precipitate of arsenic sulphide is filtered off; if not, the solution is again treated with hydrogen sulphide in the same manner as before. Evaporate the filtrate until its temperature has risen to 125°, and proceed as above.

Note 3. If no crystallized phosphoric acid is at hand for use as seed crystals the sirupy acid can be made to crystallize if it is heated to 180° and then cooled with a freezing mixture.

QUESTIONS

1. Write the reaction by which phosphoric acid can be prepared from calcium phosphate.
2. How can phosphoric anhydride, pyrophosphoric acid, and metaphosphoric acid be prepared? Give formulas. Why cannot the anhydride be prepared by heating orthophosphoric acid? For what practical purpose is phosphoric anhydride used?
3. Compare the acid strength of phosphoric acid with that of other common acids. Do all three hydrogen ions of H_3PO_4 dissociate with equal readiness?
4. Give the formulas of primary, secondary, and tertiary sodium phosphates. State how the solution of each behaves with litmus.
5. Write the reaction for the precipitation which occurs when magnesium chloride and a large excess of NH_4OH are added to a solution of phosphoric acid. This precipitate constitutes one of the most important tests for a phosphate.
6. Give an example of phosphorous acid acting as a reducing agent.

PREPARATION 53

DISODIUM PHOSPHATE, $Na_2HPO_4 \cdot 12H_2O$

The raw material from which phosphorus and its compounds are prepared is calcium phosphate, either in the form of natural "phosphate rock" or in bone ash. For laboratory preparations bone ash is preferable since it is practically free from fluorides and compounds of iron. This bone ash may be assumed to be 80 per cent

$Ca_3(PO_4)_2$, 10 per cent $CaCO_3$, and 10 per cent inert material. The following reactions with sulphuric acid may take place:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4\downarrow + CO_2 + H_2O \qquad (1)$$
$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4\downarrow + 2H_3PO_4 \text{ soluble} \qquad (2)$$
$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow 2CaSO_4\downarrow + Ca(H_2PO_4)_2 \text{ soluble} \qquad (3)$$
$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow CaSO_4\downarrow + 2CaHPO_4\downarrow \text{ insoluble} \qquad (4)$$

The inert material does not react at all with the acid.

It is obvious that if all the phosphate is to be dissolved, such an amount of sulphuric acid should be taken that after all the calcium carbonate has reacted there will be more than 2 F.W. of H_2SO_4 for each formula weight of $Ca_3(PO_4)_2$. Furthermore, an amount of acid in excess of that required for reaction (2) is to be avoided since the excess would remain in solution. A quantity is chosen, therefore, which is more than sufficient to complete reaction (3) but insufficient to complete reaction (2). All the phosphate is converted into soluble form, and all the sulphate appears as insoluble calcium sulphate.

After the removal of the insoluble calcium sulphate the filtrate is treated with sodium carbonate in sufficient amount to satisfy the equations:

$$H_3PO_4 + Na_2CO_3 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$
$$Ca(H_2PO_4)_2 + 2Na_2CO_3 \rightarrow 2Na_2HPO_4 + CaCO_3\downarrow + CO_2 + H_2O$$

An excess of sodium carbonate does not react to convert Na_2HPO_4 to $Na_3(PO_4)$. On page 100 it is seen that the acidic ionization of HCO_3^- is greater than that of HPO_4^{--}. Since a stronger acid displaces a weaker acid, the reaction $NaHCO_3 + Na_3PO_4 \rightarrow Na_2HPO_4 + Na_2CO_3$ would take place rather than the reverse reaction.

Materials: bone ash, 80 per cent $Ca_3(PO_4)_2$, 100 grams.
$36N$ H_2SO_4, 47 cc.
anhydrous sodium carbonate, Na_2CO_3.

Apparatus: 8-inch porcelain dish.
suction filter and trap bottle.
8-inch crystallizing dish.
iron ring and ring stand.
Bunsen burner.

Procedure: Put the bone ash in a porcelain evaporating dish, add 70 cc. of water, and stir the mixture until a thick paste is obtained. Stir and add 47 cc. of concentrated sulphuric acid as rapidly as possible without excessive heating. Continue to stir vigorously until the mixture begins to stiffen. This usually requires from 10 to 15 minutes. Add 500 cc. of cold water and stir until a thin paste, free from lumps, is obtained. Filter the cold mixture, using suction. Wash the solid in the funnel with 50 cc. of cold water. Combine the filtrates. Add anhydrous sodium carbonate in small portions with stirring until effervescence no longer takes place and a drop of the solution turns phenolphthalein pink. This usually takes 55–60 grams. Filter and evaporate the solution to 250 cc. Transfer the clear liquid to an 8-inch crystallizing dish and allow it to stand until a satisfactory crop of crystals is obtained. Decant the liquid from the crystals and rinse them with a little distilled water. Dry them thoroughly on paper towels (Note 9 (*b*), page 15). Disodium phosphate is efflorescent.

QUESTIONS

1. Test solutions of monosodium phosphate, NaH_2PO_4, disodium phosphate, Na_2HPO_4, and trisodium phosphate, Na_3PO_4, with litmus paper. See pages 116–117. Explain how a compound can be an acid salt and react alkaline to litmus.

2. List the solubilities of the three sodium phosphates. How would you prepare each from phosphoric acid?

3. To 5 cc. of magnesium chloride solution add $6\,N$ NH_4OH until it is alkaline. Add solid NH_4Cl in small portions until the precipitate of magnesium hydroxide is dissolved. This solution is known as "magnesia mixture" and is used in testing for phosphates. Add a little Na_2HPO_4 solution and allow the tube to stand until a white, crystalline precipitate of $MgNH_4PO_4$ is formed. Write equations for all reactions.

Preparation 54

Phosphorus Tribromide, PBr_3

Phosphorus reacts directly with bromine to form two compounds. With an excess of phosphorus the tribromide, PBr_3, is formed; the pentabromide, PBr_5, results from the use of an excess of bromine. In both cases the reaction is very vigorous, and considerable caution must be exercised in the following preparation. Phosphorus tribromide is a colorless liquid which freezes at $-40°$ and boils at 173°. The pentabromide is a yellow crystalline solid which, when heated, decomposes into the tribromide and bromine. Since both bromides hydrolyze completely, perfectly dry materials and apparatus must be employed.

Materials: bromine 12.5 cc. = 40 grams = 0.25 F.W. Br_2.
red phosphorus, 7 grams.

Apparatus: special Pyrex test tube 1 inch in diameter and 24 inches long.
2.5-inch funnel.
125 cc. distilling flask.
small beaker.
2-ounce glass-stoppered bottle.
250° thermometer.
Bunsen burner.

Procedure: Clamp the long test tube in a vertical position, covering the clamp jaws with folded paper instead of rubber. Under the hood pour the bromine into the test tube. Take about 0.05 gram of the red phosphorus on a spatula and drop it into the bromine. When the heat from the reaction has dissipated add another portion of phosphorus. Continue the addition of the phosphorus until all is used, being careful to avoid driving red bromine vapors out of the top of the tube. About 20 minutes is required. The tube now has a yellow deposit of PBr_5 along the sides, red bromine vapor and liquid and excess phosphorus in the bottom. Apply a small flame held by the hand to the bottom of the tube, and boil the liquid. The level of the top of the vapor column can be clearly seen. Boil the liquid until this level has risen to within half an inch of the top of the tube. The hot vapor decomposes the PBr_5. The condensed PBr_3 dissolves the bromine and carries it back to the bottom of the tube to react with the excess phosphorus. Continue this " refluxing " until the red color of free bromine has disappeared from the tube. After partial cooling, pour the liquid PBr_3 with the aid of a dry funnel into the distilling flask. Close the neck of the flask with a cork stopper carrying a thermometer. Insert the side arm 1 inch into the small bottle, and distil the PBr_3 slowly into the bottle. The side arm of the flask and the sides of the bottle offer sufficient cooling surface to condense all the vapor if the distillation is not too rapid. Cover the mouth of the bottle with an inverted beaker until it has cooled; then insert the glass stopper.

QUESTIONS

1. *Experiment.* **Caution** at the hood. Place 0.5 cc. of PBr_3 in each of two dry test tubes. To one tube add 0.5 cc. of water and note that it forms a layer above the heavier PBr_3. Agitate gently to mix the layers and increase the surface of contact. The mixture warms up, and rather suddenly the two liquids become homogeneous and a gas is evolved. Blow the breath across the mouth of the tube while this gas is issuing and note the effect. What is the gas? What is left in the residual solution? To the other tube add suddenly 15 cc. of cold water and let the tube stand until the two layers become homogeneous. Explain the difference in the observed effect in the two tubes.
2. Write the equations for the hydrolysis of PBr_3 and PBr_5 respectively.
3. What are the specific gravity, melting point, and boiling point of phosphorus trichloride — of phosphorus pentachloride? How would you arrange an apparatus to prepare each of these compounds?

PREPARATION 55

CRYSTALLIZED ARSENIC ACID, $(H_3AsO_4)_2 \cdot H_2O$

Arsenic acid in its properties shows a striking similarity to phosphoric acid; and even the method of its preparation is similar, in that use is made of the oxidizing action of nitric acid. Instead of starting with uncombined arsenic, however, use is made of arsenious oxide, As_2O_3, a product which condenses in the flues wherever ores which contain arsenic are roasted. This is oxidized by the nitric acid to the higher oxide, As_2O_5, which, with water, yields arsenic acid, H_3AsO_4. By evaporating its solution for a long time on the water bath, crystals of ortho-arsenic acid having the composition H_3AsO_4 can be obtained. By prolonged evaporation at higher temperatures crystals of the composition $H_4As_2O_7$ and $HAsO_3$, respectively, can be obtained. When a solution of arsenic acid is concentrated according to the following directions, a liquid is obtained of almost exactly the composition given by the formula $(H_3AsO_4)_2 \cdot H_2O$. This liquid when cooled to 35.5°, or below, can be crystallized to a solid product of the same composition, and this is the most satisfactory form in which to crystallize arsenic acid. It is interesting to note that this liquid can be much supercooled below 35.5°, but when once crystallization is induced the temperature immediately rises to this point and remains there until solidification is complete. Likewise when the solid is being melted the temperature will not rise above the melting point, 35.5°, until the whole mass is liquefied.

Materials:	arsenious oxide, As_2O_3, 50 grams = 0.25 F.W.
	$16N$ HNO_3, 75 cc.
	seed crystal of $(H_3AsO_4)_2 \cdot H_2O$.
Apparatus:	750-cc. casserole.
	150-cc. casserole.
	250° thermometer.
	2-ounce glass-stoppered bottle.
	iron ring and ring stand.
	Bunsen burner.

Procedure: Place 50 grams of arsenious oxide in a 750-cc. casserole; add 20 cc. of water, and then at the hood add 75 cc. of $16N$ HNO_3, warm occasionally, just enough to keep up an action, but do not allow the reaction to become violent, because the heat would drive off nitric acid. When red vapors cease to be given off, all the original white powder should have dissolved, and a clear colorless or very pale yellow solution should be obtained. It will sometimes happen, however, for no very apparent reason that the reaction stops with a considerable amount of white powder still undissolved although a plentiful excess of nitric acid may be present. When this happens the addition of 5 cc. of $6N$ HCl will make the reaction start up vigorously again and run to completion. Arsenious chloride is volatile and very poisonous; if HCl is added keep the dish under the hood during the reaction and the subsequent evaporation. Since HCl is not an oxidizing agent its action must be essentially that of a catalyzer. Finally evaporate the solution, holding the casserole with the hand and rotating it to spread the liquid up on the sides, until the residue is just dry. This residue should be arsenic pentoxide, and it should dissolve completely, although somewhat slowly, when treated with 60 cc. of water (see Note 1). Evaporate the solution by boiling it gently in a small casserole until the temperature has risen to 115°. Then transfer the liquid to a very narrow beaker or a test tube, and boil it carefully with a small flame until the temperature shown by a thermometer inserted in the liquid has just risen to 160°. Cool the product to below 35.5°, place it in a weighed sample bottle, and seed it with a small crystal of $(H_3AsO_4)_2 \cdot H_2O$, whereupon the whole will slowly crystallize to a solid mass. Stopper the bottle tightly, since arsenic acid takes moisture rapidly from the atmosphere.

Note 1. If the residue on evaporation does not redissolve after warming it 10 minutes with 60 cc. of water, it contains arsenious oxide either from incomplete oxidation by nitric acid, or from a decomposition of arsenic pentoxide by overheating. Test 1 cc. of the suspension containing the undissolved substance by adding 10 cc. of water, then solid sodium bicarbonate until no more effervescence occurs, and then a considerable quantity in excess. Add to this a solution of iodine, drop by drop. The amount of the latter which is decolorized (if any) corresponds to the amount of arsenious acid (As_2O_3), which was in the sample.

If arsenious acid is present it must be oxidized by further treatment with $16N$ HNO_3 and a little HCl.

QUESTIONS

1. Compare the strength of arsenic and arsenious acids. Of what general rule is this comparison an example?

2. To a solution of arsenic acid (0.1 gram in 10 cc. of water) add magnesium chloride and then NH_4OH until strongly alkaline. Compare with Question 5 under Phosphoric Acid.

3. Add a little potassium iodide solution to some arsenic acid solution, and warm gently. Is iodine set free? Write equation.

Prepare a faintly alkaline solution of arsenious acid as follows: Dissolve a minute quantity of arsenious oxide in not more than 2 or 3 drops of hydrochloric acid; dilute to 10 cc. and add, without heating, a considerable amount of sodium bicarbonate in excess of what is necessary to neutralize the acid. To this solution add, drop by drop, a solution of iodine, and determine whether any free iodine disappears. Write the equation. So far as the state of oxidation of the arsenic is concerned, the reaction is exactly the reverse of the one preceding. Recall a previous instance in which the direction of a reaction of oxidation and reduction is changed on passing from an acid to an alkaline solution.

Preparation 56

Antimony Trichloride from Stibnite, $SbCl_3$

(by-product: antimony oxychloride)

Native antimony sulphide (stibnite) dissolves quite readily in hydrochloric acid, yielding antimony trichloride,

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

If the solution so obtained is distilled, steam and hydrochloric acid pass off at first, later a mixture of hydrochloric acid and antimony trichloride, and finally pure antimony trichloride.

Antimony trichloride hydrolyzes with a moderate amount of water, giving a precipitate according to the reactions

$$SbCl_3 + 2H_2O = Sb(OH)_2Cl \downarrow + 2HCl$$
$$\underline{Sb(OH)_2Cl} = \underline{SbOCl} + H_2O$$

with more water a further hydrolysis takes place:

$$\underline{4SbOCl} + H_2O = \underline{Sb_4O_5Cl_2} + 2HCl$$

The product obtained in this preparation by mixing the next to the last distillates with a considerable amount of water has the latter composition. This compound, however, if repeatedly boiled with fresh portions of water may be made to undergo complete hydrolysis, leaving finally only Sb_2O_3.

Pure antimony trichloride melts at 73° and boils at 223°.

Materials: stibnite, Sb_2S_3, 168 grams = 0.5 F.W.
12 *N* commercial concentrated HCl, 840 cc.
shredded asbestos suspended in water.
unglazed porcelain.

Apparatus: 8-inch porcelain dish.
suction filter and trap bottle.
wide 6-inch test tube.
350-cc. retort or distilling flask.
6-inch sand bath.
asbestos paper.
1-liter flask.
2-liter common bottle.
5-inch watch glass.
Bunsen burner.

Procedure: Treat the powdered stibnite in an 8-inch dish at the hood with the commercial hydrochloric acid; warm the mixture slightly and keep it at 50–70°, with frequent stirring, for 20 minutes. Finally, boil the solution for 5 minutes. Then add 15 cc. more of concentrated hydrochloric acid; filter the solution through asbestos felt (Note 4 (*d*), page 8) which has previously been moistened with hydrochloric acid, and rinse the residue on to the filter with an additional 15 cc. of hydrochloric acid. Evaporate the filtrate in an open dish to 200 cc.; then transfer it to a retort, in the bottom of which are placed a few small pieces of unglazed porcelain to prevent bumping. Place the retort on a sand bath and distil, after first covering the bulb of the retort with an asbestos mantle to prevent loss of heat. At first insert the neck of the retort into a liter flask half filled with cold water (to absorb the hydrochloric acid). When a little of the distillate begins to give a precipitate on dropping into a tube of cold water, exchange the receiving flask for a smaller dry one and continue the distillation until a drop of the distillate will solidify when cooled on a watch glass. Save the portion thus obtained for later use and continue distilling, using a wide 6-inch test tube, which has previously been weighed, as a receiving vessel, until all the liquid is driven out of the retort. Stopper the test tube tightly and preserve the preparation in it. If the product thus obtained is not white it should be dissolved in concentrated hydrochloric acid and redistilled.

Note. If the stibnite contains a considerable quantity of silicates soluble in acids, there will be left in the retort as the distillation progresses a quantity of gelatinous silicic acid which is likely to interfere with obtaining distinct fractions of the distillate. In such a case distil until the residue in the retort is left dry, but without making the final change in receiving vessels. Then pour all the distillate containing any of the antimony salt into a fresh retort and distil again, this time separating the fractions.

Antimony Oxychloride. Pour the first portion of the distillate saved from the above procedure into 2 liters of water. Stir, allow to settle, and draw off the clear liquid. Stir up with water once more, let settle, draw off as much of the water as possible, and drain the precipitate on a suction filter. Dry it on paper towels and put it up in a cork-stoppered test tube.

QUESTIONS

1. Treat a fragment of antimony trichloride with water. Why does it not give a clear solution? Add HCl. Why does this cause a clear solution to be formed?

2. Pass hydrogen sulphide into the solution of antimony trichloride. What is the color of the precipitate? How could it be converted into a product like stibnite?

3. Compare the reactions of phosphorus, arsenic, and antimony trichlorides with water. Is hydrolysis more complete or less complete in the case in which a precipitate forms?

PREPARATION 57

SODIUM SULPHANTIMONATE, $Na_3SbS_4 \cdot 9H_2O$

The oxides of arsenic and antimony, and more particularly the higher oxides, are acidic in nature, and form salts with basic oxides.

$$3Na_2O + As_2O_3 = 2Na_3AsO_3$$
$$3Na_2O + As_2O_5 = 2Na_3AsO_4$$

Sulphur, in accord with its similarity to oxygen, can be substituted for it in many of its compounds without essentially altering their chemical nature, and the compounds thus obtained have the same nomenclature as the corresponding oxygen compounds, except that the prefix *thio* or *sulpho* is used. Thus sulpho-salts are produced in the same manner as the oxy-salts above:

$$3Na_2S + As_2S_3 = 2Na_3AsS_3$$
$$3Na_2S + As_2S_5 = 2Na_3AsS_4$$

The sulpho-salts of arsenic, antimony, and stannic tin are particularly characteristic of these metals. (See Preparation 43 and Experiment 11, page 294.) They are easily produced, and all are soluble. They are stable in neutral or basic solutions, but are decomposed by acids, because the anions of the salts combine with hydrogen ions to produce the very weak sulpho-acids, which, being unstable, decompose at once into the sulphides of the metals and hydrogen sulphide:

$$6H^+ + 2AsS_3^{---} \rightarrow 2H_3AsS_3 \rightarrow 3H_2S + As_2S_3 \downarrow$$
$$6H^+ + 2AsS_4^{---} \rightarrow 2H_3AsS_4 \rightarrow 3H_2S + As_2S_5 \downarrow$$

Sodium sulphantimonate can be prepared from stibnite by the combined action of a solution of sodium sulphide and sulphur,

$$2S + Sb_2S_3 \rightarrow Sb_2S_5$$
$$3Na_2S + Sb_2S_5 \rightarrow 2Na_3SbS_4$$

it crystallizes well with nine molecules of water.

The hydrolysis of this salt, which produces a dirty appearing reddish brown precipitate consisting of an indefinite mixture of Sb_2S_5 and Sb_2O_5, may be prevented by an excess of sodium sulphide or by the presence of sodium hydroxide.

Materials: powdered stibnite, Sb_2S_3, 67 grams = 0.2 F.W.
sodium sulphide, $Na_2S \cdot 9H_2O$, 140 grams, or use 47 grams of anhydrous sodium sulphide and an additional 93 cc. of water.
powdered sulphur, 13 grams.

Apparatus: 750-cc. casserole.
suction filter and trap bottle.
8-inch crystallizing dish with glass plate.
iron ring and ring stand.
Bunsen burner.

Procedure: To the finely powdered stibnite, sodium sulphide, and powdered sulphur in a casserole add 150 cc. of water, bring to a boil, and keep at the boiling temperature for 15 minutes. Filter with suction and rinse the residue in the dish and on the filter with hot water containing a little NaOH, bringing up the volume of the solution to 250 cc. While still hot put it away in a covered dish, with a towel placed over it, to crystallize. Drain the crystals; evaporate the mother liquor somewhat to obtain a second crop of crystals. If there is any tendency for a muddy brownish precipitate to form in the solution, or for the same substance to form as a scum on the crystals, add a little 6 *N* NaOH to the solution and rinse the crystals in it. Spread the crystals on paper towels, and as soon as they are dry, stopper them tightly in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. What is the acid of which Na_3SbS_4 is the salt? Add HCl to a solution of this salt. Is the acid set free? Is it a stable acid?
2. What is the primary reaction in the hydrolysis of Na_3SbS_4?

What secondary reaction accounts for the formation of the precipitate if its formula is Sb_2S_5?

3. Actually the precipitate is a mixture of Sb_2S_5 and Sb_2O_5 or an oxysulphide. Write an equation for the change of Sb_2S_5 to Sb_2O_5 in the presence of NaOH solution, and show that Na_2S ought to repress the change to the oxide.

4. What general principle is illustrated in the fact that Sb_2S_3 dissolves much less readily than Sb_2S_5 in Na_2S solution?

PREPARATION 58

ANTIMONY PENTASULPHIDE, Sb_2S_5

This compound cannot be prepared directly from the trisulphide and sulphur, because it is decomposed at a temperature below that at which the latter substances would react. As has just been seen, however, the higher sulpho-salt of antimony can be readily prepared in the wet way; and this, on decomposition with a dilute acid, yields antimony pentasulphide. This substance is used in vulcanizing rubber and produces a red colored product.

Materials: sodium sulphantimonate, $Na_3SbS_4 \cdot 9H_2O$, from preceding preparation, 48 grams = 0.1 F.W.
$6N$ H_2SO_4, 108 cc.

Apparatus: 2-liter common bottle.
5-inch funnel.

Procedure: Dissolve the sodium sulphantimonate obtained in the last preparation, and dilute with 1 liter of cold water. Add the sulphuric acid and 350 cc. of water to the large common bottle. To this add slowly, and with constant stirring, the solution prepared above. Fill the bottle with water and stir thoroughly. Let the precipitate settle, draw off the liquid, and wash by decantation until the wash water no longer gives the test for a sulphate with barium chloride. After the last washing let the solid settle for some time, draw off as much as possible of the clear liquid, and transfer the sludge to a large plain filter (Note 4 (*c*), page 7; do not omit to reënforce the point of the filter) to drain for 12 hours or longer. Without removing the pasty antimony sulphide, open out the filter on paper towels, and leave it on a shelf above the steam table where the temperature does not rise above 50°. When the product is completely dry, detach the hardened lumps from the paper and pulverize them in a mortar. Put up the product in a cork-stoppered bottle.

QUESTIONS

1. Write equations for all reactions involved in the preparation of antimony pentasulphide from stibnite.

PREPARATION 59

METALLIC ANTIMONY, Sb

This metal is obtained on a commercial scale both by reducing antimony oxide with carbon and by reducing antimony sulphide by means of metallic iron. The second method possesses the advantage that antimony sulphide, a natural product, is used directly and does not need to be first converted into the oxide. The iron sulphide formed by this method is fusible and forms an immiscible layer which floats on top of the molten antimony. The addition of borax facilitates the separation of the liquid layers, and thus the globules of melted antimony are allowed to sink more easily to the bottom of the crucible and form a metallic regulus. The upper layer furthermore covers the surface of the metal and hinders its oxidation and the escape of the volatile Sb_2O_3.

Materials: stibnite, Sb_2S_3, 112 grams = 0.33 F.W.
iron filings, 48 grams.
borax, $Na_2B_4O_7$, 30 grams.

Apparatus: clay crucible 30 grams, with cover.
gas furnace.
iron stirrer.

Procedure: Mix thoroughly 112 grams of stibnite, 48 grams of iron filings, and 30 grams of borax. Pack the mixture into a clay crucible. Cover the crucible and heat it strongly in a gas furnace. After half an hour remove the cover and stir gently with an iron rod to determine if the flux is completely melted. If it is not, replace the cover and heat for 10 minutes and again examine the contents of the crucible. (Antimony boils at 1,380°, and prolonged heating diminishes the yield.) When the reaction is complete, remove the crucible from the furnace and let it cool with the cover on. Break the crucible with a hammer and separate the regulus of antimony. Crack the regulus so as to show the crystalline structure of the metal.

QUESTIONS

1. Warm a piece of metallic antimony with hydrochloric acid. Where does antimony stand in the electromotive series?

2. Boil 0.5 gram of powdered antimony in a small flask with 6 *N* HNO_3. Describe the result and write equations remembering that Sb_2O_3 is basic and gives a soluble nitrate with HNO_3, but that Sb_2O_5 (H_3SbO_4) is an acidic oxide.

PREPARATION 60

BISMUTH BASIC NITRATE (BISMUTH SUBNITRATE), $Bi(OH)_2NO_3$ OR $BiONO_3$

Bismuth is the most strongly metallic element of the fifth group, yet its salts in aqueous solution undergo partial hydrolysis very readily. In presence of a considerable amount of free acid, the Bi^{+++} ion is capable of existence in solution; but with decreasing quantities of acid the tendency to hydrolyze increases, and the basic salt of bismuth, which is only slightly soluble, separates:

$$Bi(NO_3)_3 + 2H_2O \rightleftharpoons Bi(OH)_2NO_3 \downarrow + 2HNO_3$$

On pouring a solution of bismuth nitrate into a considerable quantity of cold water the basic nitrate is precipitated, according to the above formula. This salt, however, is not stable in contact with a solution which does not contain nitric acid of a concentration of at least 0.5 molal, but slowly changes over into some other more basic nitrate, and if washed repeatedly with pure water will finally go over completely into the hydroxide:

$$\underline{Bi(OH)_2NO_3} + H_2O \rightleftharpoons Bi(OH)_3 \downarrow + HNO_3$$

Under the conditions in the following procedure, this production of a more basic salt will occur if the precipitate is allowed to stand in contact with the solution for a considerable time; hence the directions to filter at once.

The basic nitrate is by no means completely insoluble in water, and the filtrate contains considerable quantities of bismuth, which can be conveniently saved as oxide by precipitating with sodium carbonate.

Materials: crystallized bismuth nitrate, $Bi(NO_3)_3, 5H_2O$, 42 grams = 0.1 F.W.
$6N$ HNO_3, 10 cc.
Na_2CO_3 solution.

Apparatus: 250-cc. beaker.
2-liter common bottle.
suction filter and trap bottle.

Procedure: Dissolve without heating the crystallized bismuth nitrate, in 10 cc. of $6N$ HNO_3 and 20 cc. of water. Pour this into 2 liters of cold water and stir thoroughly for a few minutes. Let the precipitate settle completely, and as soon as this has occurred draw off and save the supernatant liquor; drain the precipitate on a suction filter, and wash it quickly with about 20 cc. of water. Dry the precipitate on the steam table, and preserve it as a powder in a cork-stoppered bottle.

Bismuth Oxide. Combine all the liquors from the foregoing; add sodium carbonate until alkaline to litmus; let settle, and draw off the supernatant liquor; boil the remaining suspension after adding to it about 20 grams more of sodium carbonate. Then wash the precipitate twice by decantation, drain on a suction filter, and wash with two or three portions of water. Dry and preserve this product in a cork-stoppered bottle.

QUESTIONS

1. In accordance with the above directions, sodium carbonate is used to precipitate bismuth hydroxide. Why should not the precipitate be bismuth carbonate?

2. If this precipitate is not finally boiled with an excess of sodium carbonate, it is likely to contain a certain amount of basic nitrate. Explain why this should be so and why the boiling will convert it completely into the hydroxide.

Experiments

Review in Chapter III the section on the ionization of polybasic acids, page 116; in Chapter IV, Preparations 8 and 14, and Experiments 15 and 25; in Chapter VIII, Experiments 11 and 12.

1. Oxidation Products of the Elements of Group V. Treat 0.5 gram each of (*a*) red phosphorus, (*b*) powdered arsenic, (*c*) powdered antimony, and (*d*) powdered bismuth with excess of 6*N* HNO_3 (10–15 cc.) and note that red gases are evolved in each case.

(*a*) A clear solution results. Evaporate this until excess of volatile nitric acid is expelled, but do not exceed a temperature of 180°. A sirupy liquid is left which dissolves in water to give an acid solution.

(*b*) A clear solution is left. Evaporate this carefully to dryness. A white solid is left which dissolves in water to give an acid solution.

(*c*) The metal disappears and a white powdery solid remains in the liquid. This solid is insoluble in nitric acid or water.

(*d*) A clear solution results out of which, after concentrating and cooling, clear crystals of a salt separate. These crystals dissolve in a little water acidified with HNO_3 to give a clear solution, but a white precipitate is formed if the solution is diluted with a large amount of water.

Phosphorus, arsenic, and antimony are oxidized by nitric acid to hydrated forms of the pentoxides, giving respectively: phosphoric acid, H_3PO_4, which is very soluble in water and a fairly strong acid; arsenic acid, H_3AsO_4, which can be dehydrated to the oxide As_2O_5 which will dissolve in water again to form the acid; meta-antimonic acid, which is a very weak and insoluble acid. Bismuth is oxidized only to the trivalent condition; Bi_2O_3 is basic and forms the salt $Bi(NO_3)_3$ with the excess of HNO_3. This salt hydrolyzes very easily to an insoluble salt, and with a large amount of water it hydrolyzes completely to $Bi(OH)_3$.

2. Sulphides and Thio-Salts. Pass hydrogen sulphide into hot dilute solutions of arsenic, antimony, and bismuth trichlorides in separate test tubes. Note that yellow, orange, and black precipitates respectively are formed. Let the precipitates settle to the bottom of the tubes, pour off the liquid, and treat the solid with sodium polysulphide (Na_2S solution in which sulphur is dissolved) in each case. The yellow and orange precipitates dissolve; the black one does not. To the two solutions add 6*N* HCl in excess and note that yellow and orange precipitates respectively are again thrown out.

Review the discussion of thio- or sulpho-salts under Preparation 57. The trisulphides As_2S_3 and Sb_2S_3 are oxidized by the free sulphur to the pentasulphides, As_2S_5 and Sb_2S_5, which react with the Na_2S to form the soluble thio-salts, Na_3AsS_4 and Na_3SbS_4. The addition of HCl displaces the weak thio-acids, H_3AsS_4 and H_3SbS_4, which are too unstable to exist alone and decompose into H_2S and the respective pentasulphides. The color of the pentasulphides seems to be identical with that of the trisulphides. Bismuth shows no tendency to form a thio-salt.

3. Reducing Action of Phosphorous Acid; Non-Oxidizing Property of Phosphoric Acid. Review the discussion of Preparation 52, and the test employed for phosphorous acid. Phosphorous acid reduces silver nitrate to metallic silver, it itself being oxidized to phosphoric acid.

Recall that in Experiment 15, page 169, phosphoric acid did not oxidize hydrogen bromide or hydrogen iodide, which are exceptionally strong reducing agents.

4. Arsenious and Arsenic Acids. Review Note 1 and Experiment 3 under Preparation 55. Arsenious acid reduces iodine to hydriodic acid in a solution containing sodium bicarbonate, the latter neutralizing the acid produced:

$$H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2HI$$

but in an acid solution the reaction goes in the opposite direction, the hydrogen iodide being oxidized.

The reaction progressing to the right according to the equation produces H^+ ions. It is natural that the removal of H^+ ions favors the reaction and their presence reverses it.

5. Reduction of Bismuth Salts. (*a*) Suspend about 2 milligrams of bimuth subnitrate in 10 cc. water, add 5 cc. 6*N* NaOH, boil, and note that the white suspension does not change color. Add a few drops of dextrose solution, continue to boil, and note that the white suspension turns black.

(*b*) Again suspend about 2 milligrams of bismuth subnitrate in 10 cc. boiling water. Pour through a filter leaving the white $Bi(OH)_3$, to which the salt is hydrolyzed, on the paper. Make a sodium stannite solution by adding drop by drop 6*N* NaOH to 2 cc. of $SnCl_2$ solution with constant shak-

> ing and cooling until the precipitate formed at first is redissolved. Pour this solution over the filter paper, and note the intense black color.

Bismuth stands low in the electromotive series, and its salts are easily reduced to the metal which in the finely divided state is intensely black.

$$2Bi(OH)_3 + 3Na_2SnO_2 \rightarrow 2Bi \downarrow + 3Na_2SnO_3 + 3H_2O$$

6. Bismuth in a Higher State of Oxidation. Fusion of bismuth salts with sodium hydroxide and an oxidizing agent yields a material which has been called sodium bismuthate, from the hypothetical oxide Bi_2O_5. Such a compound has never been obtained pure. If the melt is extracted with water, the salt hydrolyzes completely and analysis of the brown residue gives a composition approximating the formula BiO_2, rather than Bi_2O_5.

> Add 1 drop of $Mn(NO_3)_2$ or $MnSO_4$ solution (but not $MnCl_2$) to 5 cc. of cold $6N$ HNO_3. Add about 0.1 gram solid bismuth dioxide, agitate, let the brown solid settle, and note the deep red permanganate color of the solution.

Bismuth in a higher state of oxidation than that corresponding to the oxide Bi_2O_3 must be a very strong oxidizing agent if it can oxidize a manganese compound to permanganic acid.

$$Mn(NO_3)_2 + 13HNO_3 + 5BiO_2 \rightarrow 5Bi(NO_3)_3 + HMnO_4 + 6H_2O$$

GENERAL QUESTIONS X

ELEMENTS OF GROUP V

1. State in each case whether the nitrate or sulphate of trivalent phosphorus, arsenic, antimony, or bismuth can be prepared, and if so whether it can be dissolved in water without suffering complete hydrolysis. How does the basic nature of the trioxide change in the series phosphorus to bismuth? Can nitrates or sulphates of any of these elements in their pentavalent condition be prepared? For any one of the elements, which is the more strongly basic in nature, the trioxide or the pentoxide? Which is the more strongly acidic? Give the formula of the most common acid, if one exists, which is derived from the pentoxide of each of these elements. How does the acidic nature of the pentoxide change in passing from nitrogen to bismuth?

2. Name the simplest hydrogen compounds of nitrogen, phosphorus, arsenic, and antimony. Compare the stability of these hydrides when heated. Compare any ability they may possess to unite with water to form bases, and with acids to form salts.

3. Write the equations for the reaction of nitric acid with phosphorus, arsenic, antimony, and bismuth, respectively. Describe the properties of the product in each case.

4. How do the trisulphides of arsenic and antimony behave when treated with a solution of Na_2S? With a solution of $Na_2S \cdot S_x$? How does the solution obtained with sodium polysulphide behave when it is acidified? Give equations for all the reactions.

What is the relation between sulpho- and oxy-acids? Show, for example, how sodium sulpharsenate is derived from two simple sulphides, and sodium arsenate from the corresponding oxides.

CHAPTER XI

HEAVY METALS OF GROUPS VI, VII, AND VIII OF THE PERIODIC SYSTEM

An inspection of the Periodic Table of the elements shows that chromium, manganese, iron, cobalt, and nickel, and following these copper and zinc, come in the middle portion of the long period that begins with potassium and ends with bromine. The seven elements mentioned possess high specific gravities, and all come under the classification of *heavy metals*. In certain of their compounds they are similar to one another; in other of their properties they are very dissimilar and exhibit the chemical characteristics of the respective groups to which they belong.

The heavy metals occupying a corresponding position in the middle of the next long period are molybdenum, an element which should come below manganese, ruthenium, rhodium, palladium, silver, and cadmium. In the middle of the next long period come tungsten, rhenium, osmium, iridium, platinum, gold, and mercury. In the last long period, of which there is at best only a fragmentary indication, the only representative of this class of heavy metals is uranium.

In the sixth group, chromium, molybdenum, tungsten, and uranium constitute Family A. In their trioxides they show the characteristic valence of the sixth group and resemble in properties the non-metals of Family B, of which sulphur is the type. In their lower oxides they possess none of the characteristics of Group VI but show the general base-forming properties of the heavy metals.

In Group VII, manganese, the best-known representative of Family A, resembles the halogens in its heptoxide, Mn_2O_7; in its lower oxides it shows no resemblance to the halogens, but does show properties similar to those of other heavy metals when they are in the same state of oxidation; in its lowest oxide, MnO, it is distinctly a base-forming element. The most characteristic compound of rhenium which justifies its position in Group VII is potassium perrhenate, $KReO_4$, which corresponds to potassium permanganate, $KMnO_4$, and is derived from the oxide Re_2O_7.

In Group VIII, each position instead of being filled by a single element is occupied by a group of three elements. Thus there appear in triads: iron, cobalt, and nickel; ruthenium, rhodium, and palladium; and osmium, iridium, and platinum. In this group there is no subdivision into families, but all the members are heavy metals.

Of the heavy metals discussed above, the ones that are of most frequent occurrence and that are to receive detailed treatment in this chapter are chromium, manganese, and iron.

PREPARATION 61

POTASSIUM CHROMATE AND DICHROMATE, K_2CrO_4 AND $K_2Cr_2O_7$

The most important source of chromium is the mineral chromite, $FeO \cdot Cr_2O_3$ or $Fe(CrO_2)_2$. This substance, as indicated by the formula, may be regarded as a compound of ferrous oxide and chromic oxide, in which ferrous oxide is the basic constituent and chromic oxide the acidic. Chromite is a difficult material to decompose, and the ordinary method by which this is done is treatment at a high temperature with an alkali and an oxidizing agent. The iron is thereby converted to the ferric condition (Fe_2O_3), and the chromium is oxidized to the sexivalent condition (CrO_3), at the same time combining with the alkali to form a chromate.

In the commercial method for manufacturing chromates, atmospheric oxygen is the oxidizing agent. The chromite is mixed with sodium carbonate and calcium carbonate, the latter to give porosity, and then heated for a considerable time in a furnace with free access of air. Treatment of the cooled furnace product with water causes a metathesis between the $CaCrO_4$ and Na_2CO_3, and Na_2CrO_4 is obtained in the aqueous extract. The exact amount of H_2SO_4 is added: $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$. By a carefully regulated procedure the Na_2SO_4 is crystallized from the solution of the very soluble $Na_2Cr_2O_7$, and lastly the latter salt itself separates on cooling. Chromates and dichromates bear the same relation to each other as sulphates and acid sulphates, Na_2SO_4 and $NaHSO_4$; acid chromate and acid sulphate differ by the ease with which the former loses water,

$$2NaHCrO_4 \rightleftharpoons Na_2Cr_2O_7 + H_2O$$

On account of the difficulty of carrying out the industrial process on a laboratory scale, the following less economical procedure is recommended: The raw material, chromic oxide, Cr_2O_3, is first treated with fused KOH. The oxidizing agent, KNO_3, is then added and it works more effectively than if it had been added at the outset. The aqueous extract of this fusion is allowed to crystallize to obtain a preparation of potassium chromate. The mother liquor from these crystals is acidified with acetic acid to obtain a preparation of potassium dichromate. Potassium compounds are prepared because they are less soluble and crystallize better than the corresponding sodium compounds.

$$5Cr_2O_3 + 14KOH + 6KNO_3 = 10K_2CrO_4 + 7H_2O + 3N_2$$
$$2K_2CrO_4 + 2HC_2H_3O_2 = K_2Cr_2O_7 + 2KC_2H_3O_2 + H_2O$$

A saturated solution contains for each 100 grams of water the given number of grams of the anhydrous salt.

Temperature	0°	10°	20°	30°	40°	50°	70°	100°
K_2CrO_4	59	61	63	65	67	69	73	79
$K_2Cr_2O_7$	5	7	12	20	26	35	55	88

Materials: chromic oxide, Cr_2O_3, 50 grams = 0.33 F.W.
potassium hydroxide, 65 grams
potassium nitrate, 50 grams.
glacial acetic acid.

Apparatus: 4-inch sheet iron crucible with cover.
8-inch porcelain dish.
suction filter and trap bottle.
4-inch iron ring and ring stand.

Procedure: Set the iron crucible in a 4-inch iron ring and support it on a ring stand. Put 65 grams of solid KOH into the crucible and heat it until the hydroxide is completely melted. Remove the flame and add 50 grams of chromic oxide, Cr_2O_3, free from lumps. Stir the mixture with an iron spatula or the wire end of a test-tube brush. Add 50 grams of finely powdered KNO_3 and stir the mixture until a thin paste is formed. Partially cover the crucible (leave a ¼-inch space at one side), and heat the mixture with a flame not more than an inch high. Remove the cover at frequent intervals to prevent boiling over. After about 15 minutes' heating the mixture becomes quite thick and is likely to froth over. To prevent this, remove the cover and stir, protecting the hand against spattering. When the mass becomes solid, heat it again until it froths very little. Finally heat this solid for 20 minutes with the full flame of one burner and with the cover on. Stir at frequent intervals and scrape any solid from the sides of the crucible into the hot mass. When the heating is finished and the solid has partially cooled, stir it and, while still hot, scrape it into an 8-inch porcelain evaporating dish. When the crucible has cooled to room temperature, heat in it 300 cc. of water to boiling and add the hot water, with what it has extracted from the crucible, to the solid in the evaporating dish. Heat this until all the lumps have disintegrated. Allow any sediment to settle and decant the yellow solution through a gravity filter. Boil an additional 50 cc. of water with the sediment in the dish, and pour this extract through the same gravity filter. Transfer the entire yellow filtrate to the porcelain evaporating dish, and evaporate it over a flame until crystals of potassium chromate begin to separate on the surface of the liquid. (If a small amount of dark-colored solid separates during the evaporation, the solution should be filtered a second time.) Add 50 cc. of water to the hot solution and allow it to stand until a satisfactory crop of crystals has separated. Remove the crystals from the solution, using suction filtration. Press the solid on the filter plate to remove as much of the mother liquor as possible. Spread the yellow crystals of K_2CrO_4 on a white paper towel and allow them to dry at room temperature. Pour the filtrate into the evaporating dish and add 30 cc. of glacial acetic acid. Stir the mixture, and if it is not orange-red add small portions of glacial acetic acid until it is. Cool the mixture in a pan of ice water. Filter off the meal of potassium dichromate on a suction filter and press it as dry as possible. Dissolve the crystal meal in boiling water, adding small portions of water until solution is complete. If a clear solution is not obtained, filter hot, using suction. Allow the $K_2Cr_2O_7$ to crystallize from the solution.

Dry the potassium dichromate on a white paper towel at room temperature. Put the potassium chromate and dichromate into separate 2-ounce cork-stoppered bottles. Calculate the theoretical yield of potassium chromate from 50 grams of chromic oxide. Deduct your yield of chromate from this result, and calculate the theoretical yield of potassium dichromate.

QUESTIONS

1. Name at least three oxidizing agents which might have been used instead of potassium nitrate in this preparation, and write equations.

2. To 5 cc. of a chromic sulphate solution add NaOH in excess; cool, add about 1 gram of sodium peroxide, agitate for a few minutes, and then boil until effervescence ceases. Describe observations and write equations.

3. To a solution of potassium dichromate add K_2CO_3 until no more effervescence takes place. Explain the effervescence and the change in color. Write equation.

4. To the solution from Experiment 3 add $6N$ H_2SO_4; observe and explain as before. Explain fully the difference between chromates and dichromates.

5. Show that potassium acid sulphate, $KHSO_4$, and potassium dichromate, are very similar, differing mainly in the degree of hydration.

PREPARATION 62

CHROMIC ANHYDRIDE, CrO_3

The addition of sulphuric acid to a solution of either a chromate or a dichromate liberates chromic acid which is very soluble and can exist in solution in the different forms, H_2CrO_4, $H_2Cr_2O_7$ and CrO_3, in equilibrium with each other. With the addition of a large excess of concentrated H_2SO_4, water is withdrawn from the hydrated forms and the anhydride separates in the shape of red needles.

Materials: sodium dichromate, $Na_2Cr_2O_7{\cdot}2H_2O$, 100 grams = 0.33 F.W.
$36N$ H_2SO_4, 400 cc

Apparatus: 8-inch porcelain dish.
glass plate to cover the 8-inch dish.
suction filter with glass marble.
glass-stoppered sample bottle.
tripod.
Bunsen burner.

Procedure: Dissolve the 100 grams of sodium dichromate in 250 cc. of water and filter from any sediment. Add rather slowly with constant stirring about half of the concentrated sulphuric acid until a slight permanent precipitate of CrO_3 is formed. Let the mixture cool for half an hour or longer, then add slowly, while stirring, the rest of the sulphuric acid. Let the mixture stand over night covered with a glass plate in order that the crystal meal may become somewhat coarser. In such a crystal meal standing in its saturated solution, the smaller grains dissolve and their material deposits out on the larger crystals. But even now the crystal meal will be rather fine and it will at first run through the filter; if, however, while waiting, the mixture is heated with stirring to 100° and allowed to cool slowly, and this process is repeated once or twice, a more satisfactory product will be obtained. To collect the crystals, use a suction filter, but place a small glass marble in the funnel instead of the usual plate and paper. If the red crystals at first run past the sides of the marble, pour the liquid in the bottle repeatedly back on to the filter until finally the filtrate runs clear (see last sentence of Note 3 on page 5). After draining the crystals completely and pressing the surface with the round end of a test tube, stop the suction and pour 15 cc. of $16\,N$ HNO_3 so as to wash down the sides of the funnel and cover the surface of the product. Stir up the product with this washing fluid for a depth of about $\frac{1}{2}$ inch. Suck dry and repeat the operation twice with 10 cc. of nitric acid each time. Finally drain the red crystals as free of liquid as possible, transfer the crystals to a dry 8-inch evaporating dish and place this on a hot plate to let the nitric acid evaporate. When the product is dry and no longer gives off vapors of nitric acid place it in the glass-stoppered sample bottle.

QUESTIONS

1. Dissolve 0.5 gram of chromic anhydride in a few drops of water. What is the color of the solution? Dilute with 200 cc. water. What is the color? Write ionic equations showing the equilibrium condition among the different acids of chromium and their ions in the solution. Show that according to the law of molecular concentration the proportion of the yellow to the red components should increase as the solution is diluted with water.

2. Heat a little chromic anhydride strongly on a bit of porcelain. Pulverize the residue in a white mortar so as better to observe its color. What is the residue? Is it soluble in water?

3. Without the recrystallization the weight of the product of this preparation is often greater than that calculated. To what impurity is this excess weight due?

RECRYSTALLIZATION OF CHROMIC ANHYDRIDE

Dissolve about 300 grams of the student's preparation in 0.6 its weight of water. Decant carefully from any undissolved residue and add very slowly with stirring such an amount of concentrated sulphuric acid as will make 100 cc. for every 100 grams of the crude chromic anhydride. When the suspension has cooled to room temperature, collect and wash crystals in the same manner as in the original preparation using 60 cc. of 16 N HNO_3 for the first washing and 40 cc. each for the second and third washings. Drain the crystals very thoroughly with suction, transfer them to an 8-inch porcelain dish and place it on the hot plate. Break up and turn over the mass of crystals frequently with a spatula. After several hours, when nitric acid vapors cease to come off, weigh and bottle the product.

PREPARATION 63

AMMONIUM CHROMATE AND AMMONIUM DICHROMATE, $(NH_4)_2CrO_4$ AND $(NH_4)_2Cr_2O_7$

The raw material for this preparation is the chromic anhydride from the preceding preparation, which contains at least a small amount of sodium acid sulphate. This dissolves with the chromic anhydride, and it should remain in the mother liquor (as neutral sulphate) from which the ammonium chromate is crystallized. The second and third crop of crystals of the latter, however, are likely to be contaminated with sodium sulphate. An excess of ammonium hydroxide is used to insure the formation of the neutral chromate.

Materials: chromic anhydride, CrO_3, 100 grams = 1 F.W.
15 N ammonium hydroxide, 160 cc.
6 N acetic acid.

Apparatus: 500-cc. flask.
5-inch funnel.
suction filter and trap bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Place the chromic anhydride in a 500-cc. flask and add 70 cc. of water. Shake the mixture until solution is complete and then cool the flask in a pan of water. Add the ammonium hydroxide in 5-cc. portions. Cool after each addition and shake the mixture to prevent the formation of a solid cake. After 100 cc. of the hydroxide have been added, break up any lumps with a glass rod and add the remaining 60 cc. in four portions. Shake the mixture thoroughly; cool the flask in a pan of ice water and shake for 10 minutes. Break up the solid cake by shaking and transfer the material to a suction filter. Use the filtrate to rinse out the flask and transfer all the solid to the filter. Remove the liquor as completely as possible by pressing the solid on the filter. Cover the crystals with 10 cc. of $15N$ ammonium hydroxide, and after it has stood a few minutes, apply suction again. Evaporate the filtrate, under the hood, to half the original volume. Place the flask in a pan of ice water, and when the liquid has cooled to about 60°, add 10 cc. of $15N$ NH_4OH and shake for 10 minutes. Filter off the second crop of crystals and treat them as before. If the two crops are the same color, combine them and dry them together. If, however, the second crop is much darker than the first, it should be kept separate. Dry the crystals at room temperature and weigh them. One half of the preparation should be preserved in a 4-ounce cork-stoppered bottle, and the other half used to prepare ammonium dichromate.

To convert the ammonium chromate to dichromate it is dissolved in acetic acid. Calculate the volume of $6N$ acetic acid required to convert the weight taken of dry ammonium chromate according to the equation:

$$2(NH_4)_2CrO_4 + 2HC_2H_3O_2 = (NH_4)_2Cr_2O_7 + 2NH_4C_2H_3O_2 + H_2O$$

Actually use 100 cc. of $6N$ acetic acid for each 45 grams of ammonium chromate. Pour this volume of $6N$ acetic acid into a 500-cc. flask and add the solid ammonium chromate. Insert a funnel in the neck of the flask and heat the mixture until it just boils. Keep it below the boiling temperature until solution is complete. If solution is not complete in 10 minutes, add a little more $6N$ acetic acid through the funnel. When solution is complete, place the flask containing the solution in a pan of ice water and shake for 10 minutes. Filter off the ammonium dichromate, using suction. Remove the liquor as completely as possible by pressing the solid on the filter. Wash the crystals with 10 cc. of ice water and drain again. Dry the product in a warm place until it does not smell of acetic acid. Preserve the preparation in a 4-ounce cork-stoppered bottle.

QUESTIONS

1. Heap up 10 grams of ammonium dichromate in a small mound on a porcelain plate, and apply the flame to the top of the mound until a reaction starts. Write the equation. What element is oxidized and what one reduced? Show that the algebraic sum of the valence changes is zero.
2. Note the color of the dry crystals of ammonium chromate and ammonium dichromate. Do either have the odor of ammonia? Dissolve 1 gram of the chromate in as little water as possible. Note whether the solution has an odor of ammonia. What is its color (yellow like K_2CrO_4 or orange like $K_2Cr_2O_7$)? Write equation for the hydrolysis of $(NH_4)_2CrO_4$ and explain why it should hydrolyze more than K_2CrO_4.
3. Heat 10 grams of ammonium chromate and compare its action with that of ammonium dichromate and with that of chromic anhydride when heated.

PREPARATION 64

CHROMIC ALUM, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

The preparation of potassium dichromate (Preparation 61) illustrated how chromic oxide, Cr_2O_3, can be oxidized to a chromate in which chromium exists as CrO_3. For the preparation of chromic alum, it might seem as if chromic oxide or the natural chromite should yield chromic sulphate directly on treatment with sulphuric acid. This is impossible, however, because both of these substances are very resistant to the action of acids. Practically, they yield only to the action of alkaline oxidizing agents, which convert them into a chromate. Therefore potassium, or sodium, dichromates are always the products made directly from the mineral, and these serve as the materials from which other compounds of chromium are prepared. To make chromic alum from potassium dichromate it is necessary to reduce the chromium to the state of oxidation in which it originally existed in the mineral, and to add sufficient sulphuric acid to form the sulphates of potassium and chromium. Alcohol may be used as the reducing agent, it being itself oxidized to acetaldehyde, C_2H_4O, a substance whose presence is made very evident by its penetrating odor.

Chromic alum is isomorphous with common alum and can easily be obtained in large and beautiful deep purple crystals. Chromic salts present a phenomenon which complicates the task of crystallizing out definite salts. In cold solution the simple chromic ion probably has the composition $[Cr{\cdot}6H_2O]^{+++}$. At higher temperatures this ion becomes altered, through loss of H_2O and substitution of OH^- ions or of the anions of the salt. For example, $[Cr{\cdot}4H_2O{\cdot}SO_4]^+$ is a possible composition of the chromium ion in a hot solution of chromic sulphate. The ion $[Cr{\cdot}6H_2O]^{+++}$ is purple, and with the SO_4^{--} ion the crystallizable purple chromic sulphate, or the chromic alum, can be obtained. The altered ion in the hot solution is of a very deep green color, and it does not give crystallizable compounds.

Probably similar conditions hold in the solutions of the salts of most heavy metals, but in most cases the change back and forth is so rapid that the crystallizable form of the salt is at once obtained when the solution is cooled. With chromium, however, once the green form is obtained when the solution is heated, the change back to the purple form, which is the stable form at lower temperature, is very slow. In this preparation we have the option of carrying out the reduction at a low temperature and obtaining the crystallizable chromic alum at once, or of letting the temperature rise and then leaving the green non-crystallizable form to change very slowly back to the purple form and crystallize slowly as it does so. We shall choose the latter option particularly as it offers the advantage of a very slow crystallization which of course favors the formation of large, perfectly formed crystals.

At 25°, 24 grams of $K_2SO_4{\cdot}Cr_2(SO_4)_3{\cdot}24H_2O$ will dissolve in 100 grams of water, and the solubility increases very rapidly with the temperature.

Materials: potassium dichromate, $K_2Cr_2O_7$, 98 grams = 0.33 F.W.
$36\,N$ H_2SO_4, 76 cc.
95 per cent ethyl alcohol, 63 cc.

Apparatus: 8-inch porcelain dish.
8-inch glass plate.

Procedure: Pulverize 98 grams of potassium dichromate, and cover it in an 8-inch porcelain dish with 400 cc. of water. Add 76 cc. of concentrated sulphuric acid, and stir until all the salt is dissolved. Adding the sulphuric acid should produce enough heat to dissolve the dichromate, but, if it is necessary, heat the mixture a little more. After all the salt has dissolved, filter the solution if it is not absolutely clear. Add the alcohol rather cautiously, stirring after each addition. Allow the heat of the reaction to raise the temperature of the solution to the boiling point. Cover the hot solution with a glass plate and set it away in a cupboard for a week or longer. Remove the crystals from the liquid, and if possible get a further crop of crystals. Dry the crystals by leaving them wrapped in paper towels over night (Note 9 (*b*), page 15), and then stopper them at once in a bottle, since they are efflorescent.

QUESTIONS

1. Write equations for the following steps in the reaction of potassium dichromate in acid solution with alcohol. (*a*) Resolve the salt into its basic and acidic anhydrides. (*b*) Let the acid anhydride, which is the higher oxide of chromium, be reduced by the alcohol to the lower oxide, Cr_2O_3. (*c*) Let the sulphuric acid form salts with the basic anhydride and the lower oxide of chromium, which is also a basic oxide. Add the steps together to give the complete equation.

2. Sulphur dioxide might serve as the reducing agent. Write equations for the reaction in steps and add the equations.

3. Describe the effect observed when hydrogen sulphide is passed into a hot acidified solution of $K_2Cr_2O_7$. Write the equation in one line marking the valences of sulphur and chromium and showing that the algebraic sum of the valence changes is zero.

PREPARATION 65

BASIC LEAD CHROMATE, $PbCrO_4 \cdot PbO$

Basic salts may be considered as bases partially neutralized by acids, or as compounds of a base and a salt of that base.

$$Bi(OH)_3 + HCl \rightarrow Bi(OH)_2Cl$$
$$Pb(OH)_2 + PbCrO_4 \rightarrow Pb(OH)_2 \cdot PbCrO_4$$

Such basic salts lose water very readily, but are still considered as basic salts in the dehydrated condition, *e.g.*, $BiOCl$, $PbO \cdot PbCrO_4$.

It is often true that a basic salt is less soluble than either the base itself or the salt, and in such cases the basic salt is especially easy to prepare. In general, basic salts do not have definite composition but are indefinite mixtures of base and salt. This is true of basic lead chromate in which the ratio of PbO to $PbCrO_4$ varies with the method of preparation. Lead chromate, $PbCrO_4$, is used as a yellow pigment for paints. Basic lead chromate is bright red and is also used as a pigment.

Materials: lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, 38 grams = 0.1 F.W.
sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$, 8 grams.
sodium hydroxide, NaOH, 12 grams.

Apparatus: 8-inch porcelain dish.
5-inch funnel.
2-liter common bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Dissolve 38 grams of lead acetate in 400 cc. of water in an 8-inch porcelain dish. (The solution will not be clear.) Dissolve 8 grams of sodium dichromate in 50 cc. of water, and add the solution to the lead acetate. Yellow lead chromate will precipitate. Dissolve 12 grams of sodium hydroxide in 50 cc. of water and add this solution while stirring. Heat the mixture to boiling. The color of the solid will slowly change to a reddish orange. Boil the mixture gently until no further change in color takes place. Pour the mixture into a liter of cold water in a large bottle. Allow the precipitate to settle and wash it three times by decantation. Transfer the basic lead chromate to a filter and let it drain without suction. When the cake is dry enough to hold its shape, unfold the filter paper from it, spread it on a watch glass, and dry it on the hot plate. Pulverize the dry product and preserve it in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Treat about 0.5 gram of your product with 5 cc. of 6 *N* acetic acid. Warm the mixture until it boils. Note the change in color. Filter and add a few drops of sodium sulphide solution to the

filtrate. (*a*) Write equation. (*b*) Explain the change in color. (*c*) Compare the reactions of normal lead chromate and basic lead chromate with acetic acid.

PREPARATION 66

CHROMIUM METAL BY THE GOLDSCHMIDT PROCESS

The readiest method of obtaining the metal chromium from its oxide, and one which yields it in a high state of purity, is the so-called Goldschmidt, or alumino-thermic, process, in which use is made of metallic aluminum as the reducing agent according to the reaction

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr$$

The heat produced by the oxidation of aluminum is so great that it is sufficient to effect the decomposition of the chromic oxide with still enough surplus heat to melt the metallic chromium and the slag of Al_2O_3. It is evident that before this reaction can be made to progress spontaneously a sufficient temperature must be developed to decompose the chromium oxide. This necessary temperature is a good deal higher than that of a flame or of a common furnace, but can be obtained by use of the fuse powder described below. When once started in this way the reaction itself produces a temperature high enough to insure its continuance.

When the reaction is carried out on the small scale of a laboratory preparation, the heat produced is not quite sufficient to melt the metal and slag so thoroughly that the metal can settle out to form a compact regulus at the bottom of the crucible. By adding a small amount of potassium dichromate to the charge, however, the reaction becomes more energetic, owing to the more available supply of oxygen.

Materials: chromic oxide, Cr_2O_3, 210 grams.
potassium dichromate, 60 grams.
granulated aluminum, 96 grams.
barium peroxide, 20 grams.
magnesium ribbon.
mortar and pestle.

Apparatus: clay crucible of 600-cc. capacity.
gas furnace.
6-inch iron sand bath.
pail of sand.
hammer.

Procedure: Heat the chromic oxide in the crucible in the gas furnace for 40 minutes or longer. Melt the potassium dichromate in a clean iron pan, and pulverize it in a mortar after it has solidified. Mix the chromic oxide, potassium dichromate, and granulated aluminum thoroughly in a mortar. Make a fuse powder with 2 grams of granulated aluminum and 20 grams of barium peroxide. Take half of the fuse powder and mix it with twice its bulk of the main charge. Hold a rather wide test tube in the middle of the crucible, pack the charge around it, and withdraw it carefully, leaving a deep hole in the middle. Carefully pour the mixture of fuse powder and charge into the bottom of the hole; pour the fuse powder on top of it in the hole; and insert a strip of magnesium ribbon into the fuse powder. Imbed the crucible in a pail of dry sand and place the pail under the hood in the furnace room at a distance from any woodwork. Start the reaction by igniting the end of the magnesium ribbon with a gas flame. It is advisable not to look directly at the reaction because of the intense light, and to keep at a little distance to be out of the way of flying sparks. When the crucible has cooled, break it with a hammer and separate the regulus of metallic chromium from the slag of fused aluminum oxide.

QUESTIONS

1. What is approximately the position of chromium in the electromotive series? What bearing does this have upon the question of reducing chromic oxide?
2. What metals can be used in place of aluminum in the aluminothermic process?
3. What other metals than chromium can be advantageously prepared by this process, and why?

PREPARATION 67

CALCIUM MOLYBDATE, $CaMoO_4$

Molybdenum trioxide, MoO_3, is, like sulphur trioxide, an acid oxide. It is a white, solid substance, sparingly soluble, but capable of combining with bases to form molybdates which are analogous to sulphates. The alkali metal and ammonium salts of molybdic acid are soluble. The calcium salt is sparingly soluble.

Materials: molybdenum trioxide, MoO_3, 5 grams.
6 *N* NaOH, 12 cc.
6 *N* HNO_3.
calcium chloride, anhydrous, 3.8 grams.
litmus paper.

Apparatus: 250-cc. beaker.
2.5-inch funnel.

Procedure: Dissolve 5 grams of MoO_3 in 12 cc. of 6 *N* NaOH. Barely neutralize with 6 *N* HNO_3, using litmus as indicator. The neutral point must not be overstepped if a precipitate of molybdic acid is to be avoided. Dissolve 3.8 grams of anhydrous calcium chloride in 9 cc. of water and stir this into the sodium molybdate solution. Collect the precipitate, wash it with cold water, and dry it on the steam table (80–100°) over night.

PREPARATION 68

AMMONIUM TUNGSTATE, $(NH_4)_2WO_4$

Tungsten like chromium and molybdenum is acidic in its highest valence, WO_3, and forms salts known as tungstates.

Materials: tungstic oxide, WO_3, 23.2 grams = 0.1 F.W.
15 *N* NH_4OH, 50 cc.

Apparatus: 250-cc. beaker.
4-inch evaporating dish.
4-inch iron ring and ring stand.
2.5-inch funnel.

Procedure: Digest the tungstic oxide with 40 cc. of 15 *N* NH_4OH for 10 minutes at 50°. Pour off the clear solution, and if a solid residue is left digest it repeatedly with 5-cc. portions of the NH_4OH, adding the extract to the main solution. Filter, if necessary, directly into the evaporating dish. Let stand at about 80° until dry. Save the needle shaped crystals in a 2-ounce, cork-stoppered bottle.

QUESTIONS

1. Heat 1 gram of the product in a dry test tube. Smell cautiously. Observations? Equations?
2. Heat a few crystals with 5 cc. of hydrochloric acid. How do you explain the results?

PREPARATION 69

SELENIOUS ACID, H_2SeO_3

Elementary selenium constitutes a large part of the " anode mud " obtained during the electrolytic refining of copper. Like many non-metals, selenium is converted to an acid (H_2SeO_3) when dissolved in nitric acid. Selenious acid, H_2SeO_3, so formed, is a solid, soluble in water, whose solubility increases rapidly with rise in temperature. Selenious acid may be oxidized to selenic acid, H_2SeO_4, by $KMnO_4$. Selenic acid is very similar to sulphuric acid. Selenious acid is easily reduced to selenium by reducing agents, for example, by sulphurous acid.

The element selenium exists in several allotropic forms.

Materials: selenium, 39 grams = 0.5 F.W.
$16N$ HNO_3, 113 cc.

Apparatus: 500-cc. flask.
250-cc. beaker.
suction filter.
spatula, iron or glass.
iron ring and ring stand.
Bunsen burner.

Procedure: Warm the nitric acid in the flask gently until the acid is almost boiling. Using a spatula, add a small amount of selenium; when this has been dissolved, add a little more. Continue this intermittent addition until all the selenium has been added. Regulate the addition and the heating so that the contents of the flask will not boil over. After all the selenium has been added, boil for 5 minutes after red fumes cease to be evolved. Cool, filter if necessary, and let the filtrate stand in a previously weighed beaker until it has evaporated to dryness. (Do not heat, as SeO_2 is volatilized by heat!) Dissolve in one-fifth its weight of boiling water, cool to room temperature, add a small seed crystal. Let stand undisturbed to aid formation of large crystals. Drain the crystals, and leave them on a large previously weighed watch glass to dry. Put the product in a 2-ounce, cork-stoppered bottle.

QUESTIONS

1. Dissolve 1–2 grams of the crystals in 15 cc. water. Dilute 1 cc. stannous chloride solution with 5 cc. hydrochloric acid; add 1 cc. of this to one-third of the solution of selenious acid. Observations? Equations? How do you account for the color?
2. To another third of the solution of selenious acid, add 5 cc. saturated solution of sulphurous acid. Let stand 5 to 10 minutes. Observations? Equations?
3. To the remainder of the solution add 5 cc. potassium permanganate solution. Observations? Equations? Filter; to the colorless filtrate add 5 cc. barium chloride solution. Let settle, pour off the supernatent liquid, add 5 cc. 12*N* hydrochloric acid to the residue and boil for 2 minutes. Dilute to 25 cc. Add 1 to 2 cc. of sulphurous acid. Observations? Equations?
4. How would you show the presence of a small amount of selenic acid in a large amount of sulphuric acid?

PREPARATION 70

MANGANESE CHLORIDE FROM WASTE MANGANESE LIQUORS

The waste liquors left after the generation of chlorine from manganese dioxide and hydrochloric acid contain principally manganous chloride. Besides this, however, there is always some free acid and almost always a considerable amount of ferric chloride present. The greater part of the free acid can be removed by evaporating the solution until a pasty mass is left which will solidify on cooling. The iron can be removed from the solution of this residue by virtue of the ease with which ferric salts hydrolyze. The nearly neutral solution is treated with suspended manganous carbonate (obtained by treating a part of the solution itself with a soluble carbonate). Ferric chloride hydrolyzes according to the reversible reaction, $FeCl_3 + 3H_2O \rightleftharpoons 3HCl + Fe(OH)_3$. In the presence of manganous carbonate the small amount of free acid thus formed is continuously used up according to the reaction $MnCO_3 + 2HCl \rightarrow MnCl_2 + H_2O + CO_2$. Thus the reaction of hydrolysis is enabled to run to completion. The remaining solution, which is neutral and entirely free from iron salts, yields crystallized manganous chloride, $MnCl_2 \cdot 4H_2O$, upon evaporation.

Materials: waste liquor from chlorine generator, 250 cc.
anhydrous sodium carbonate.

Apparatus: 8-inch porcelain dish.
5-inch funnel and filter.
2-liter common bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Boil 250 cc. of waste manganese liquor in an 8-inch porcelain dish under the hood until the residue becomes pasty. After a scum begins to form on the surface of the liquid, there is danger of spattering and the mixture should be stirred with a glass rod until it becomes semi-solid. Heat the residue to boiling with 750 cc. of water; without filtering the solution, take one-tenth of it, dilute this portion to 1,000 cc. in a 2-liter bottle, and add a solution of sodium carbonate to it until all the manganese is precipitated as carbonate (test for complete precipitation). Allow the solid to settle and wash it by decantation at least four times. Add the solid manganous carbonate to the remaining nine-tenths of the manganous chloride solution, and boil the mixture in an 8-inch dish until a few drops of the filtered liquid give no red color when tested with KSCN. Filter the solution and evaporate it until a crystal scum forms on blowing across the surface. Then allow the solution to cool slowly and crystallize, leaving it for at least 12 hours uncovered in a place protected from dust. Collect the crystals and evaporate the mother liquor to obtain further crops of crystals until practically all the salt has crystallized. Spread the light pink crystals on paper towels to dry, and preserve the product in an 8-ounce, cork-stoppered bottle.

Note. The crystals of manganous chloride are deliquescent when the temperature is low and the atmosphere charged with moisture. If the product cannot be obtained satisfactorily by the above directions, carry out the crystallization and drying in a place at a slightly elevated temperature, 25° to 30°; or cool the saturated hot solution rapidly by stirring or shaking, and dry the crystal meal so obtained by rinsing it with alcohol and then letting the latter evaporate rapidly.

QUESTIONS

1. Explain the action of manganese dioxide in the generation of chlorine gas from hydrochloric acid. In what state of oxidation does manganese exist in the salt manganous chloride?

2. If iron were in the ferrous condition, it would not be removed from the solution by the above procedure. Explain why iron is necessarily in the ferric condition in the liquors used.

3. Dissolve a small grain of manganous chloride in a half test tube of water. Test the solution with hydrogen sulphide; then add a few drops of ammonia, and if necessary add a little more hydrogen sulphide. Then add acetic acid (a weak acid) until the solution is again faintly acid. Does the manganous sulphide dissolve? Compare the solubility of manganous sulphide with that of copper sulphide; of zinc sulphide.

4. Explain how facts involved in the foregoing preparation show that $Mn(OH)_2$ is more strongly basic than $Fe(OH)_3$.

PREPARATION 71

POTASSIUM PERMANGANATE, $KMnO_4$

Although manganese dioxide is a powerful oxidizing agent, it is nevertheless capable of being itself oxidized when it is fused with a basic flux. The trioxide of manganese is acidic in nature and combines with the base to form a salt. Thus it is evident that the presence of a base favors the oxidation.

The dioxide of manganese is neither strongly basic nor acidic in nature and shows no marked tendency to form salts. The monoxide is distinctly basic and the trioxide is distinctly acidic, so that the former forms salts with acids and the latter with bases. It follows, therefore, that in the presence of acids the dioxide has a tendency to produce salts of manganous oxide whereby an atom of oxygen is set free, and that in the presence of bases manganese dioxide has a tendency to take on another atom of oxygen in order to produce a salt of the trioxide.

Thus, when manganese dioxide is fused with potassium hydroxide and an oxidizing agent, the salt potassium manganate is formed. This salt is soluble in water and is fairly stable as long as a considerable excess of potassium hydroxide is present; but in presence of an acid — even as weak a one as carbonic acid — the manganate decomposes spontaneously, two-thirds being oxidized to permanganate at the expense of the other one-third, which is reduced again to manganese dioxide:

$$3K_2MnO_4 + 4H_2CO_3 \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KHCO_3$$

The permanganate (or permanganic acid) corresponds to the heptoxide of manganese, Mn_2O_7, which is the most strongly acid-forming of the oxides of manganese. Permanganic acid is a strong and very soluble acid, being of approximately the same acid strength as nitric or hydrochloric acids. It is in addition a very powerful oxidizing agent.

Materials: powdered pyrolusite, MnO_2, 50 grams.
potassium hydroxide, 60 grams.
potassium chlorate, 25 grams.
carbon dioxide.
shredded asbestos for filter.

Apparatus: 4-inch sheet-iron crucible.
tongs.
8-inch porcelain dish.
4-inch porcelain dish.
5-inch watch glass.
porous plate.
suction filter and glass marble.
2-liter common bottle.
iron ring and ring stand.
Bunsen burner.

Procedure: Grind 50 grams of pyrolusite to as fine a powder as possible (the finer it is ground, the more successful the preparation). Place 60 grams of potassium hydroxide and 25 grams of potassium chlorate in a 4-inch sheet-iron crucible. Heat the mixture carefully until it is just melted. Remove the flame from under the crucible and add the pyrolusite, a little at a time, stirring vigorously all the while. Since the charge in the crucible effervesces and spatters particles of melted salt, great care should be taken to keep the eyes at a safe distance. The hand holding the stirrer should be protected, and with the other hand the crucible should be held firmly by means of iron tongs. After all the pyrolusite is added, place a small flame below the crucible, and keep stirring the charge. Gradually increase the strength of the flame, and stir continuously until the mass stiffens completely. Then cover the crucible and heat it 5 minutes longer at a dull red heat. When the mass has cooled, place crucible and all in 1 liter of water in an 8-inch porcelain dish. After the solid has entirely disintegrated, remove the crucible and rinse it off with a little water from the wash bottle. Transfer the mixture to a 2-liter bottle and pass carbon dioxide into the cold solution until the green color of the manganate has entirely changed to the violet red of the permanganate. Test the color by touching a drop of the solution to a piece of filter paper. Examine the spot on the reverse side. If it is purple with no trace of green the change to permanganate is complete. Let the sludge of manganese dioxide settle in the bottle for 10 minutes; then *syphon* the liquid on to an asbestos filter. Lastly, with the aid of a jet of water from the wash bottle, transfer all the sludge to the filter and drain it free from liquid. Evaporate the solution in a clean dish to a volume of 300 cc. Let it settle a moment and filter it through asbestos as before. Pour the filtrate into the 8-inch porcelain dish, and allow it to cool slowly in a place protected from dust. When cold, collect the crystals of potassium permanganate in a filter funnel in which a marble is placed. Evaporate the mother liquor to 100 cc., filter it hot through asbestos, and obtain a second crop of crystals on cooling the filtrate. Discard the remaining liquid, since it cannot contain more than about 6 grams of potassium permanganate and to evaporate it further would cause potassium chloride also to crystallize out. Weigh all the crystals, dissolve them in eight times their weight of water (to give a saturated solution at about 40°), filter the solution through asbestos at near the boiling temperature, and let it cool slowly and crystallize in a small porcelain dish covered with a watch glass. Recover another crop of crystals in the same way from the mother liquor, after evaporating it to a volume of 60 cc. Allow the crystals to dry on a clean unglazed plate, and preserve them in a 2-ounce, cork-stoppered bottle.

QUESTIONS

1. Name and give the formulas of all the oxides of manganese.
2. From which oxide is K_2MnO_4 derived? $KMnO_4$?
3. Write the reactions involved in the above preparation.
4. How could $KMnO_4$ be converted back into K_2MnO_4? Equation?

PREPARATION 72

MANGANESE METAL BY THE GOLDSCHMIDT PROCESS

The principle of the production of manganese by this process is exactly the same as that of the production of chromium in Preparation 66. On account of the violence of the reaction between the oxide of manganese and aluminum it is not advisable to ignite the whole charge at once in the crucible; yet on account of the high melting point of manganese a considerable quantity of charge must be used in order to produce heat enough to obtain the metal melted together in a uniform lump, instead of distributed in small globules throughout the mass of the slag. Before mixing up the charge, the pyrolusite which is used must be first heated by itself in order to drive off any water which it may contain and to convert it at least partially to the lower oxide, Mn_3O_4.

Materials: powdered pyrolusite, MnO_2, 900 grams.
granulated aluminum, 250 grams.
barium peroxide, 10 grams.
magnesium ribbon, 5 inches.

Apparatus: clay crucible of 600-cc. capacity.
gas furnace.
pail of dry sand.
long-handled iron spoon.
furnace glove.
hammer.

Procedure: Place the pyrolusite in a crucible and heat it to a bright heat in a gas furnace. To prepare the charge, mix 750 grams of this material, when it is cooled sufficiently, with 250 grams of granulated aluminum. Heat the empty crucible again in the furnace, and while still hot imbed it in a pail of sand. Place about 20 grams of the charge in the bottom of the hot crucible. Put on colored glasses and a heavy glove, and start the reaction with a fuse powder made of 10 grams of barium peroxide and 1 gram of aluminum, and a magnesium ribbon (see Preparation 66). When this reaction has just passed its maximum intensity add about 20 grams more of the charge with the long-handled spoon; continue in this way to add the charge in small portions following each other rapidly. It is important not to let the reaction cool so that it cannot ignite the next addition instantly. On the other hand, if another portion is added before the previous one has acted, both may start together with explosive effect. When the crucible has cooled, break it, and separate the regulus of metallic manganese from the slag of fused aluminum oxide.

QUESTIONS

1. If pyrolusite containing water were used without previous heating, what disadvantage would result during the process?
2. What economy of materials is effected by converting the manganese dioxide into the lower oxide?

PREPARATION 73

FERROUS AMMONIUM SULPHATE, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, AND FERRIC AMMONIUM ALUM, $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, FROM IRON

Corresponding to the two most important oxides of iron, FeO and Fe_2O_3, the two sulphates, $FeSO_4$ and $Fe_2(SO_4)_3$, can be prepared. By dissolving iron in sulphuric acid a solution of ferrous sulphate is obtained. This, however, is readily oxidizable, slowly even by the oxygen of the air, to the higher sulphate, and ferrous sulphate can be preserved free from ferric salt only when all oxygen is excluded, or when it is kept in contact with an excess of metallic iron in an acidified solution. Dry, crystallized ferrous sulphate, or green vitriol, $FeSO_4 \cdot 7H_2O$, can be preserved fairly well without becoming oxidized; but the double salt, ferrous ammonium sulphate, not only is more easily prepared on account of the readiness with which it crystallizes, but also is less easily oxidized by contact with the air.

Materials: $6N$ H_2SO_4, 222 cc. + 61 cc.
iron filings, 40 grams.
ferrous carbonate, 10 grams.
ammonium sulphate, 45 grams + 25 grams.
$16N$ HNO_3, 14 cc.

Apparatus: 500-cc. flask.
500-cc. graduated cylinder.
two 8-inch crystallizing dishes.
8-inch porcelain dish.

Procedure: Measure 222 cc. of 6 N H_2SO_4 into a 500-cc. flask, and add 40 grams of iron filings in small portions. Shake the mixture after each addition, and do not add a second portion until the vigorous effervescence has begun to slacken. When all the iron has been added, set the flask on the hot plate and let it stand until no further reaction takes place. Allow the solution to cool, and add cautiously 5 grams of ferrous carbonate. Shake the mixture, and after 5 minutes again add 5 grams of ferrous carbonate. Heat the mixture to boiling. The free acid should be completely exhausted, and the solution should contain 2/3 F.W. $FeSO_4$. Filter the hot solution and divide it into two equal portions. Use one for preparing ferrous ammonium sulphate, and the other for preparing ferric ammonium alum.

Ferrous Ammonium Sulphate

To one portion of the ferrous sulphate solution add 45 grams of ammonium sulphate and 5 cc. of 6 N H_2SO_4. From the solubility data given below determine the volume of solution required to crystallize ferrous ammonium sulphate. (Note that the data are for anhydrous salts.) After your instructor has checked your result, adjust the volume to the proper value. Filter the solution if it is not clear, and allow it to stand in a crystallizing dish until a satisfactory yield of the double salt has formed. Decant the mother liquor from the crystals, and wash them with a little distilled water. Dry them thoroughly at room temperature with white paper towels.

Test the finished product for ferric iron, by dissolving a little in water, adding a drop of 6 N H_2SO_4 and a few drops of KSCN. A red color indicates ferric iron.

A saturated solution contains for each 100 grams of water the given number of grams of the anhydrous salt.

Temperature	0°	10°	20°	30°	40°	50°	70°	90°
$FeSO_4$	16	21	26	33	44	48	56	43
$(NH_4)_2SO_4$	71	73	75	78	81	84	92	99
$FeSO_4 \cdot (NH_4)_2SO_4$	12	17	22	28	33	40	52	..

QUESTIONS

1. What tests can be applied to show whether this preparation dissociates in solution into the ions of the two simple salts?
2. Recall instances in which complex salts of heavy metals do not give the simple ions of the heavy metals.

FERRIC AMMONIUM ALUM

Ferrous sulphate in solution can be oxidized by nitric acid to a ferric compound, but to obtain the full yield of ferric sulphate the presence of sulphuric acid is necessary according to the equation

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

After adding $(NH_4)_2SO_4$ to the solution so obtained, the double salt, ammonium ferric sulphate, or ferric alum, may be crystallized out. In order to obtain a satisfactory product it is very important to adjust the amount of acid very precisely. Too little acid will allow a brown basic salt to form ($m\text{Fe(OH)}_3 \cdot n\text{Fe}_2(\text{SO}_4)_3$), which will discolor the preparation. Too much acid has the obvious disadvantage that it will cling to the crystals of the product from which it cannot be removed by evaporation or by washing (because of the great solubility of the product).

Procedure: Transfer the second portion of the ferrous sulphate solution to an 8-inch porcelain evaporating dish, and add 61 cc. of $6N$ H_2SO_4. The volume of the mixture should be not less than 165 cc. or more than 185 cc. Carry the dish to the hood, add 14 cc. of $16N$ HNO_3, and heat the mixture slowly to the boiling point. Continue heating, and stir until a very vigorous reaction begins to take place with the evolution of oxides of nitrogen. Remove the flame, and let the reaction proceed. This reaction may take place when the nitric acid is added but usually it is necessary to heat the solution for several minutes. When the reaction is complete the color of the solution will change from black to light brown. The solution may be tested for ferrous iron at this point with potassium ferricyanide. When the oxidation is complete heat the mixture for a few minutes, and then add 25 grams of ammonium sulphate. Cool to room temperature, and add enough distilled water to make the total volume 250 cc. Allow it to stand in the evaporating dish until the alum has crystallized. Decant the mother liquor from the crystals, and wash them with a little distilled water. Dry them thoroughly at room temperature with white paper towels. Do not expose the crystals to direct sunlight or to temperatures higher than that of the room. Discolored crystals may be washed with a little distilled water and dried as before.

QUESTIONS

1. If an unacidified solution of ferrous sulphate is oxidized by the oxygen of the air, what products are formed? Equation? Compare the equation for the oxidation of ferrous sulphate as carried out in this preparation.

2. *Experiment:* Prepare a solution of a ferrous salt by dissolving 2 grams of ferrous ammonium sulphate in 20 cc. of water, adding a little dilute sulphuric acid and a piece of iron wire. Test both this solution and a solution of a ferric salt (nitrate or chloride) with potassium ferrocyanide, potassium ferricyanide, and potassium sulphocyanate. Tabulate the results. These constitute the standard tests for ferrous and ferric salts. Write equation.

Experiments

The elements of the alkali and alkaline earth families show a uniform valence in all their compounds. Proceeding in the order in which the elements have been taken up in this book, a constantly increasing tendency has been shown to display two or more valences. In fact, the most important chemical properties of the elements considered in the present chapter depend on their ability to change their valence. When the valence changes to a lower one the element acts as an oxidizing agent. Examples of compounds of chromium and manganese acting as oxidizing agents are shown in Experiments 10 and 23, pages 164 and 176.

1. Stability of Carbonates of Metals in Divalent State. Heat about 1 gram of dry, light green nickel carbonate in a dry test tube by shaking it a little distance above a small flame. The powder turns black, and the gas that comes off clouds a drop of lime water. Treat a second sample of nickel carbonate with dilute HCl. It dissolves with effervescence to give an apple green solution; no odor of chlorine is manifest. Treat the black residue with dilute HCl. It dissolves to give an apple green solution, and a strong odor of chlorine is manifest.

The ease with which carbon dioxide is expelled from $NiCO_3$ indicates that nickelous oxide, NiO, is a weakly basic oxide. The fact that $NiCO_3$, the salt of weak carbonic acid, exists at all shows that NiO has distinct, even if rather weak, basic properties. Since the carbonates $CrCO_3$, $MnCO_3$, $FeCO_3$, $CoCO_3$, $CuCO_3$, $ZnCO_3$, $PbCO_3$ all decompose at about the same temperature the oxides CrO, MnO, FeO, CoO, CuO, ZnO, PbO are indicated as having a basic strength of about the same order as that of NiO. The black oxide which remained after heating $NiCO_3$ dissolved in HCl to give a solution of $NiCl_2$, but the evolution of free chlorine indicated an oxidizing agent. Nickelous oxide, NiO, takes on oxygen from the air to form nickelic oxide, Ni_2O_3, and this is the oxidizing agent

$$Ni_2O_3 + 6HCl \rightarrow 2NiCl_2 + 3H_2O + Cl_2$$

2. Non-Existence of Carbonates of Trivalent Metals. Dissolve 2 grams of ferric alum in 10 cc. of water and add $2N$ Na_2CO_3 in excess. Effervescence and a reddish brown, voluminous precipitate are noted. Collect the precipitate on a filter and wash it free of Na_2CO_3 solution. Then treat the precipitate with $6N$ HCl in which it dissolves without effervescence.

The ions of ferric carbonate are brought together in the solution, but this salt evidently cannot exist. Its hydrolysis products, ferric hydroxide and carbonic acid (CO_2), are obtained. The behavior of the red precipitate when treated with HCl shows that it is ferric hydroxide and not ferric carbonate.

Chromic salts and sodium carbonate show the same behavior. Since the carbonates of trivalent iron and chromium do not exist the oxides Fe_2O_3 and Cr_2O_3 are more weakly basic than FeO and CrO.

3. Oxidation of An Oxide of a Divalent Metal. Heat 0.5 gram of cobalt carbonate in a dry porcelain dish, holding the dish in crucible tongs and rotating it gently over a small flame. Do not allow it even to approach a visible red heat. The light pink cobalt carbonate turns jet black. After it cools treat this black powder with $6N$ HCl. It dissolves, and a pronounced odor of chlorine is observed. The solution is deep blue when concentrated but light pink when diluted.

The decomposition of cobalt carbonate gives cobaltous oxide, $CoCO_3 \rightarrow CoO + CO_2$, but this is easily oxidizable in the air to a higher oxide. The higher oxide reacts as an oxidizing agent towards HCl and the chloride corresponding to CoO is obtained:

$$Co_2O_3 + 6HCl \rightarrow 2CoCl_2 + 3H_2O + Cl_2$$

The monoxides CrO, MnO, FeO, CoO, NiO are all easily oxidizable in contact with air. The higher oxides of manganese and nickel behave as the cobaltic oxide above. On the other hand, the chlorides $CrCl_3$ and $FeCl_3$ are stable, and the treatment of Fe_2O_3 and Cr_2O_3 with HCl produces no free chlorine.

Note. In Experiment 1 a higher oxide of nickel was probably formed in the same manner, although to a considerably less extent.

4. Properties of the Hydroxides. In separate test tubes take 2 cc. each of $1N$ solutions of (*a*) $CrCl_3$, (*b*) $MnCl_2$, (*c*) $FeCl_2$, (*d*) $FeCl_3$, (*e*) $CoCl_2$, (*f*) $NiCl_2$. Add 10 cc. of water to each tube and $6N$ NaOH until the solution is alkaline in each case.

(*a*) Chromic hydroxide, $Cr(OH)_3$, a light greenish gray voluminous precipitate. Soluble in excess of cold NaOH. Reprecipitated on boiling.

(*b*) Manganous hydroxide, $Mn(OH)_2$, a light buff-colored precipitate. Insoluble in excess of NaOH. Oxidizes easily, turning dark brown or black as it comes in contact with air, $Mn(OH)_3$.

(*c*) Ferrous hydroxide, $Fe(OH)_2$, a gray-green precipitate insoluble in excess NaOH. Oxidizes easily, turning reddish brown as it comes in contact with air, $(FeOH)_3$.

(*d*) Ferric hydroxide, $Fe(OH)_3$, a reddish brown voluminous precipitate insoluble in excess of NaOH.

(*e*) Cobaltous hydroxide, $Co(OH)_2$, insoluble in excess of NaOH.

(*f*) Nickelous hydroxide, $Ni(OH)_2$, an apple green precipitate insoluble in excess NaOH, not oxidized by air.

5. Action of Aqueous Alkaline Oxidizing Agents. Prepare a sodium hypochlorite solution by stirring bleaching powder and an excess Na_2CO_3 solution and filtering. Place about 2 cc. of thin suspensions of each of the hydroxides prepared in Experiment 4 in separate test tubes and treat each with excess NaOH and the sodium hypochlorite solution.

(*a*) The gray-green $Cr(OH)_3$ dissolves to give a clear yellow solution.

$$2Cr(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2CrO_4 + 3NaCl + 5H_2O$$

The basic Cr_2O_3 is oxidized to the acidic CrO_3 which forms the soluble salt with the alkali.

(*b*) The light buff $Mn(OH)_2$ is turned black

$$Mn(OH)_2 + NaOCl \rightarrow MnO_2 + H_2O + NaCl$$

MnO is oxidized to MnO_2 which is indifferent and forms salts with neither bases nor acids.

(*c*) The gray-green $Fe(OH)_2$ turns reddish brown

$$2Fe(OH)_2 + NaOCl + H_2O \rightarrow 2Fe(OH)_3 + NaCl$$

(*d*) The reddish brown $Fe(OH)_3$ is not altered.

(*e*) The light-colored $Co(OH)_2$ turns jet black

$$2Co(OH)_2 + NaOCl + H_2O \rightarrow 2Co(OH)_3 + NaCl$$

(*f*) The apple green $Ni(OH)_2$ turns jet black

$$2Ni(OH)_2 + NaOCl + H_2O \rightarrow Ni(OH)_3 + NaCl$$

6. Oxidation in Alkaline Fusion. (*a*) Melt sodium carbonate in a loop on the end of a platinum wire until a colorless bead is obtained. Dip the bead in a precipitate of MnO_2 obtained as in Experiment 5 (*b*), and melt it again, holding it in the outer edge of the flame to come under the oxidizing influence of the air. (It is better to use a blow-pipe, holding the bead in the oxidizing part of the flame.) After the bead is cold it has a green color.

(*b*) Repeat (*a*) using $Cr(OH)_3$ instead of MnO_2. A yellow bead is obtained.

(*c*) Prepare a somewhat larger amount of sodium manganate as follows: Melt a mixture of 5 grams of sodium hydroxide, 1 gram of potassium nitrate, and 0.1 gram of manganese dioxide in a small iron crucible and heat it until it ceases to foam and the crucible is dull red. Cool the crucible and treat the contents with about 200 cc. of water. A most intense green solution of sodium manganate is formed. Let the solution settle in a tall beaker, pour the clear, but intense green, liquid into another beaker, and reserve it for Experiment 7 (*a*).

In (*a*) the oxygen of the air oxidizes MnO_2 to MnO_3, an acidic oxide, in the presence of a base which will form a stable salt with the acidic oxide.

$$\begin{aligned} MnO_2 + \tfrac{1}{2}O_2 &\rightarrow MnO_3 \\ MnO_3 + Na_2CO_3 &\rightarrow Na_2MnO_4 + CO_2 \end{aligned}$$

In (*b*) the Cr_2O_3 is oxidized to the acidic CrO_3 which gives the yellow salt Na_2CrO_4.

7. Permanganate. (*a*) Add 6 *N* HNO_3, drop by drop, to the solution of Na_2MnO_4 reserved from Experiment 6 (*c*). The intense green color changes to the equally intense purplish red of permanganate. Let the solution settle and carefully pour off the red liquid; a very small dark brown precipitate is found in the bottom. Reserve the solution for (*b*).

(*b*) To the red permanganic acid solution reserved in (*a*), add 6 *N* NaOH until it is strongly alkaline. The color changes back to the intense green of the manganate.

(*c*) To 1 drop of $Mn(NO_3)_2$ solution and 10 cc. 6 *N* HNO_3 in a test tube add 1 gram of lead dioxide and boil. Let the surplus of lead dioxide settle, and note that the clear solution has the intense permanganate color.

In (*a*), nitric acid displaces manganic acid from its salt:

$$2HNO_3 + K_2MnO_4 \rightarrow H_2MnO_4 + 2KNO_3$$

The free manganic acid is very unstable and decomposes

$$3H_2MnO_4 \rightarrow 2HMnO_4 + MnO_2 + 2H_2O$$

or

$$3Mn^6 \rightarrow 2Mn^7 + Mn^4$$

In (*b*) the instability of permanganate ion in presence of OH^- ions is shown

$$2MnO_4^- + 2OH^- \rightarrow 2MnO_4^{--} + H_2O + \tfrac{1}{2}O_2$$

In (*c*) in an acid solution the very strong oxidizing agent PbO_2 oxidizes the manganous ion Mn^{++} to the permanganate ion MnO_4^-

$$\begin{aligned} 2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 &\rightarrow 2HMnO_4 \\ &+ 5Pb(NO_3)_2 + 2H_2O \end{aligned}$$

8. Chromate and Dichromate. To a yellow solution of potassium chromate add 6 *N* H_2SO_4, and note that the color changes to orange red. To an orange red solution of potassium dichromate add 6 *N* NaOH and note that the color changes to yellow.

The yellow color of the chromate solution is due to the CrO_4^{--} ion, the orange red of the dichromate to the $Cr_2O_7^{--}$ ion. The changes take place according to the reversible reaction.

$$Cr_2O_7^{--} + 2OH^- \rightleftharpoons 2CrO_4^{--} + H_2O$$

It is obvious that presence of OH^- ions must favor the formation of chromate, and presence of H^+ ions, since they remove OH^- ions, must favor the formation of dichromate.

It should be noted that the valence of chromium is 6, both in chromate and dichromate. The difference between manganate and permanganate lies in the changing valence of the manganese. The difference between chromate and dichromate lies merely in the state of hydration and can be referred back to the acids.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \text{ chromic acid}$$
$$2CrO_3 + H_2O \rightarrow H_2Cr_2O_7 \text{ dichromic acid}$$

GENERAL QUESTIONS XI

HEAVY METALS OF GROUPS VI, VII, AND VIII

1. In which groups of the periodic system do the elements chromium, manganese, iron, nickel, and cobalt fall? What is peculiar about the position of the last three? What other metals belong to the same family as chromium? In what relation do they stand to sulphur, selenium, and tellurium? In what relation does manganese stand to the halogens? What other elements occur in the eighth group in triads similar to iron, nickel, and cobalt?

2. How do the monoxides of chromium, manganese, iron, cobalt, and nickel compare in basic strength with the oxides of copper and zinc and with the oxides of the alkali and alkaline earth metals? How do the sesquioxides, R_2O_3, compare with the monoxides of this group as regards basic strength?

What is true as regards the base- or acid-forming properties of the oxides higher than the sesquioxides, *e.g.*, of CrO_3, MnO_3, Mn_2O_7?

3. Give the formulas and names of salts derived from each of the three oxides of chromium, CrO, Cr_2O_3, CrO_3. In which of its compounds does chromium most resemble sulphur? iron and aluminum? nickel, cobalt, copper, and zinc?

4. Give the formulas and names of salts derived from each of the oxides of manganese, MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7. In which of its compounds does manganese most resemble chlorine? aluminum? cobalt, nickel, copper, and zinc? sulphur? lead in the dioxide?

5. Give a definition of oxidation and reduction. Consider two examples, (*a*) the action of $KMnO_4$ with H_2SO_3, and (*b*) the action of $K_2Cr_2O_7$ with HCl. For both of these cases write equations according to the *oxide method* as outlined in Question 1, under Preparation 64, Chromic Alum. Also write the equations according to the *valence method* as outlined in Question 3 under the same preparation.

APPENDIX

CONCENTRATION OF REAGENTS

The use of a uniform concentration of 6 *N* for the acids and bases in the desk reagent bottles has proved to be very satisfactory. The more concentrated reagents, which are kept under the hood, are of the full strength supplied by the manufacturers.

Acetic acid

17 *N*, use commercial *glacial* acetic acid, about 99.5%, of sp. gr. 1.055.

6 *N*, mix 350 cc. of glacial acetic acid with 650 cc. of water.

Hydrochloric acid

12 *N*, use commercial concentrated HCl of sp. gr. 1.19.

6 *N*, mix 12 *N* HCl with an equal volume of water.

Nitric acid

16 *N*, use commercial concentrated HNO_3 of sp. gr. 1.42.

6 *N*, mix 380 cc. of 16 *N* HNO_3 with 620 cc. of water.

Sulphuric acid

36 *N*, commercial 96% H_2SO_4 of sp. gr. 1.84.

6 *N*, pour 1 volume of the 96% H_2SO_4 into 5 volumes of water.

Ammonium hydroxide

15 *N*, use commercial concentrated NH_4OH of sp. gr. 0.90.

6 *N*, mix 400 cc. of 15 *N* NH_4OH with 600 cc. of water.

Sodium hydroxide

6 *N*, add to 250 grams of $NaOH$ enough water to make the volume 1,000 cc.

Salts

1 *N*, all salt solutions on the reagent shelves unless otherwise labeled are understood to be 1 *N*.

TENSION OF SATURATED AQUEOUS VAPOR

Temp.	Pressure	Temp.	Pressure	Temp.	Pressure
0°	4.6 mm.	21°	18.5 mm.	30°	31.5 mm.
5	6.5	22	19.7	35	41.9
10	9.2	23	20.9	40	55.0
15	12.7	24	22.2	50	92.2
16	13.5	25	23.6	60	149.2
17	14.4	26	25.1	70	233.8
18	15.4	27	26.5	80	355.5
19	16.3	28	28.1	90	526.0
20	17.4	29	29.8	100	760.0

ELECTROMOTIVE SERIES

When a metal is in contact with a solution containing its ions, a difference in electrical potential arises due to the resultant effect of two tendencies: of the metal on the one hand to throw off positive ions and thus charge the solution positively, and of the metal ions on the other hand to deposit on the metal and impart their charges to it.

The figures given in the table are for the potential of a solution, normal in the ions of the given metal, measured against the metal itself which dips in the solution. The potential of a normal solution of hydrogen ions measured against a hydrogen electrode (platinum electrode saturated with hydrogen gas under atmospheric pressure) is taken as zero, and the other potentials are measured from this arbitrary zero point.

The elements for which no figures are given are placed in approximately their correct position in the series.

METALS

K	+2.9	Fe(Fe^{++})	+0.44	As	—
Na	+2.7	Cd	+0.40	Bi	—
Ba	+2.7	Co	+0.23	Sb	—
Ca	+2.7	Ni	+0.23	Hg(Hg^{+})	−0.74
Mg	+1.8	Sn(Sn^{++})	+0.13	Ag	−0.80
Al	+1.3	Pb	+0.12	Pd	—
Mn	+1.1	H_2	+0.00	Pt	—
Zn	+0.8	Cu(Cu^{++})	−0.34	Au	−1.3
Cr	+0.5				

NON-METALS

F_2	—	I_2	−0.53
Cl_2	−1.36	O_2 (in 1 N OH^- solution)	−0.40
O_2 (in 1 N H^+ solution)	−1.24	S	—
Br_2	−1.06		

PERIODIC CLASSIFICATION OF THE ELEMENTS ACCORDING TO THEIR ATOMIC NUMBERS AND THE ARRANGEMENT OF THEIR ELECTRONS

The periodic recurrence of similar properties in passing through the series of chemical elements suggests a recurrence of similar structural units within the atom, the properties of the element being dependent on the extent to which each of the units in turn has been developed. Modern knowledge of the structure of the atom, although still very inadequate, indicates very clearly certain principles which render the periodicity of the elements more comprehensible.

Atoms of Electricity. Atoms of matter are believed to be built entirely of electrical atoms, of which there are two kinds: the electron, or atom of negative electricity, with a charge of 4.774×10^{-10} electrostatic unit and a mass $\frac{1}{1840}$ that of the hydrogen atom; and the proton, or atom of positive electricity, with a charge equal in magnitude to that of the electron but opposite in sign, and a mass equal that of the hydrogen atom. In fact, the proton is identical with the hydrogen ion — the neutral hydrogen atom consisting of one proton and one electron.

Atoms of Matter. Electrically neutral atoms consist of two parts: the nucleus, and the planetary electrons. There is a certain analogy between the atom and the solar system, the nucleus corresponding to the sun and the planetary electrons to the planets, and an atom is mostly space just as our solar system is.

The Nucleus. The nucleus of hydrogen consists of a single proton with unit positive charge; the nucleus of helium consists of an aggregate of four protons and two electrons with mass four and two units of net positive charge. The nuclei of all the elements consist of closely packed aggregates of protons and electrons, with protons always in excess, so that the net charge is always positive. The atomic number of an element is equal to the number of net positive charges of the nucleus; the atomic weight is approximately equal to the number of protons of the nucleus. Elements are now known representing practically all the atomic numbers from hydrogen 1 to uranium 92.

Variation of Mass in Close Packing of Nucleus. The atomic weight of hydrogen is 1.008, that is to say, 6.06×10^{23} (Avogadro's number) hydrogen atoms weigh 1.008 grams. The atomic weight

THE PERIODIC ARRANGEMENT ACCORDING TO ELECTRON GROUPINGS

		O	1 H						1 H	2 He								
He	2	2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne								
Ne	2-8	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 A								
A	2-8-8	18 A	19 K	20 Ca	21 Sc	*22* *Ti*	*23* *V*	*24* *Cr*	*25* *Mn*	**26** **Fe**	**27** **Co**	**28** **Ni**						
Niβ	2-8-18	28 Niβ	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr								
Kr	2-8-18-8	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	*41* *Cb*	*42* *Mo*	*43* *Ma*	*44* *Ru*	**45** **Rh**	**46** **Pd**						
Pdβ	2-8-18-18	46 Pdβ	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe								
Xe	2-8-18-18-8	54 Xe	55 Cs	56 Ba	57 La	*58* *Ce*	**59** **Pr**	**60** **Nd**	**61** **Il**	**62** **Sa**	**63** **Eu**	**64** **Gd**	**65** **Tb**	**66** **Dy**	**67** **Ho**	**68** **Er**	**69** **Tm**	**70** **Yb**
Erβ	2-8-18-32-8	68 Erβ			71 Lu	72 Hf	73 Ta	*74* *W*	*75* *Re*	*76* *Os*	**77** **Ir**	**78** **Pt**						
Ptβ	2-8-18-32-18	78 Ptβ	*79* *Au*	*80* *Hg*	*81* *Tl*	*82* *Pb*	*83* *Bi*	*84* *RaF*	*85*	86 Nt								
Nt	2-8-18-32-18-8	86 Nt	87	88 Ra	89 Ac	90 Th	91 Pa	92 U										

Symbol printed in heavy type — the kernel never acquires the structure of an inert gas or a beta kernel
Symbol printed in italics — the kernel sometimes acquires the structure of an inert gas or a beta kernel
Symbol printed in ordinary type — the kernel usually or invariably has the structure of an inert gas or a beta kernel

Elements 43, Masurium; 61, Illinium; 84, Polonium or Radium F; 89, Actinium; 91, Uranium X_2 do not appear in the atomic weight tables. Although their existence has been indicated by means of X-rays or radioactive properties, they have not been isolated in amounts to allow of atomic weight determination.

of helium is exactly 4, that is to say, 6.06×10^{23} helium atoms weigh 4.00 grams. If it is true, as we believe, that the helium nucleus contains four protons, which apart have a mass of 4.032 units, they must, in the process of packing together with two electrons into the minute space of the nucleus, have lost 0.032 unit of mass. When we consider the incredibly great forces that must exist within the nucleus, such a loss of mass cannot be considered as surprising. In the building up of all the other atoms the protons always suffer about the same diminution of mass as in the formation of helium nuclei. Thus the masses of all atoms except hydrogen are very nearly even multiples of the same unit, that is, one-fourth the mass of the helium atom, or one-sixteenth the mass of the oxygen atom.

Isotopes. Elements which like chlorine have uneven atomic weight really consist of a mixture of atoms of different masses but of the same atomic number. Ordinary chlorine, for example, of atomic weight 35.45 consists of a mixture of atoms of masses 35 and 37 of which there are about three times as many of the former as of the latter. These two atomic species are called *isotopes.* It is the atomic number, or the charge of the nucleus, which determines the chemical properties of the element; so the different isotopes are identical in chemical properties and cannot be separated by any chemical processes. Thus the uniformity of the atomic weight of chlorine wherever found. The isotopes must have been uniformly mixed at the creation of our earth and no process since has ever sorted them out into separate fractions.

Permanency of Nucleus. The force which must be overcome in forcing protons together against their enormous electrostatic repulsion into the narrow confines of the nucleus is beyond our comprehension. No adequate theory has been devised to explain the stability of the nucleus; yet the fact of the permanency of the nucleus exists. The identity of the element depends on the permanency of the nucleus, and our well-known law of the conservation of the elements expresses the almost absolute permanency of the nuclei of the common elements. Only with the radioactive elements is the nucleus subject to change, and this change is in most ways entirely unaffected by any physical or chemical forces which scientists are able to bring to bear.

Radioactive Disintegration. In radioactive disintegration a nucleus suddenly explodes ejecting either an electron (beta particle) or a helium nucleus (alpha particle) and leaving as a residue the nucleus of a simpler element. The beta or alpha particles are ejected with enormous velocity, and streams of these particles constitute the so-called beta and alpha rays. For each radio element there is a definite probability as to the length of time an atom will maintain its identity before the radioactive disintegration occurs. The radioactivity of uranium, for example, is very weak, and if we start with a definite mass today it will take eight billion years (8×10^9) before one-half of its atoms have disintegrated. On the other hand, the much more strongly radioactive radium disintegrates more rapidly, and it takes but two thousand years before one-half of its atoms have changed.

Without doubt somewhere in the universe nuclei of all elements are being both built up and disintegrated. Such processes are perhaps going on in the interior of the sun and the hot stars where temperatures of 40,000,000 degrees prevail, perhaps also out in infinite space, but such ideas are highly speculative.

Law of Electrostatic Attraction and Repulsion. This law, which is known as Coulomb's law, has the same mathematical form as Newton's law of gravitation: The force repelling two like charges is equal to the product of the charges divided by the square of the distance between. The force attracting unlike charges is of the same magnitude. If the charges are of 1 electrostatic unit each and the distance is 1 cm. the force is 1 dyne. The total net charge on one electrochemical equivalent of ions,* say on 35.45 grams of chlorine ions, is $6.06 \times 10^{23} \times 4.774 \times 10^{-10}$ or 29×10^{13} electrostatic units. Therefore, if this charge is concentrated at a point and the total net charge on 23 grams of sodium ions is concentrated at a point 1 cm. away, the attraction between these charges will be 84×10^{27} dynes, or 10^{20} metric tons.

If these charges are a meter apart the attraction will be 10^{16} metric tons. If they are as far apart as the north and south poles of our earth the attraction will still be 60 metric tons.

Structural Forces within the Atom. Coulomb's law holds accurately for all distances outside of atomic dimensions (10^{-8} cm.),

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* The total charge on one gram equivalent of ions, expressed in the common unit, is 96,500 coulombs. This quantity of electricity is known as the *faraday*, and it is constantly used by electrochemists. One coulomb consists of 3×10^9 electrostatic units, and the faraday therefore contains 29×10^{13} electrostatic units.

and there are indications that it holds down to the dimensions of the nucleus (10^{-13} cm.). Within the atom there are other forces, which include possible magnetic and centrifugal forces, which, superimposed upon the force of Coulomb's law, give a condition of stability to electrons in certain discrete positions within the atom. If Coulomb's law alone were operative all electrons would sink into the nucleus. The forces which prevent this and hold the planetary electrons out at relatively great distances from the nucleus are an expression of the nature of the electrons themselves, but about this we know very little and have in the main to content ourselves with the fact that there are certain discrete levels of shells around the nucleus which can be occupied by electrons, and the number of electrons in a shell cannot exceed a certain maximum. Within the limitations of these discrete shells the electrons appear to be subject to the electrostatic attraction of the positive nucleus and the mutual repulsion of the electrons, and to take such positions within atoms and molecules as are in conformity with the requirements of Coulomb's law.

Electron Shells. A very theoretical study of the spectrum lines of the light emitted by the elements, combined with a study of the chemical properties of the elements, seems to establish the general rule that the maximum number of electrons which can occupy the succeeding shells* around the nucleus progresses as twice the square of succeeding whole numbers, or as 2, 8, 18, 32 . . . . . . The mutual repulsion of the electrons for each other, however, tends to prevent the larger numbers collecting in a shell, and electrons may stay in outer shells rather than enter into an inner one up to the maximum number. The configuration produced by these numbers, however, seems to impart stability to a shell, and whenever the shell is not filled to the maximum there seems to be a strong tendency to acquire the number eight, and, next to that, eighteen.

Stability of Inert Gases. The key to the method of building up the electronic structure of atoms in layers was found through a consideration of the inert gases. Their inertness points to the great stability of their atomic structure. Since they never form

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* Although spectroscopic study indicates the existence of subgroups within the shells here discussed, the subgrouping does not seem to exhibit itself strongly in determining chemical properties. For the sake of simplicity it is omitted entirely in this discussion.

compounds their atoms are always electrically neutral and the number of planetary electrons is the same as the nuclear charge. The atomic numbers give the sequence 2, 18, 36, 54, 86, and it is obvious that these numbers of electrons must fall into layers of great stability. The numbers in the succeeding shells are probably as follows:

He_2	2					
Ne_{10}	2	8				
A_{18}	2	8	8			
Kr_{36}	2	8	18	8		
Xe_{54}	2	8	18	18	8	
Nt_{86}	2	8	18	32	18	8

To take for example the atom of xenon, the first three shells are filled to the maximum numbers of 2, 8, and 18. There remain 26 electrons, but when the number 18 in the fourth shell is reached, it is more difficult for the remaining electrons to enter this shell than to begin building a new shell. The 8 electrons left are just enough to give the stable configuration of 8 in the fifth shell.

The neutral atom of cesium has one more electron than xenon, and this extra electron stays in the sixth shell rather than forcing itself into either the fourth or fifth shells and disturbing the stable arrangements of 18 and 8 in these.

Positive Polar Valence. This single electron in the outer layer has very little stability in its isolated position and is easily removed altogether from the atom, leaving the atom with a net positive charge of one unit. Thus the ease with which cesium changes to cesium ion Cs^+ is accounted for. Similarly, the formation of barium ion Ba^{++} and lanthanum ion La^{+++} is accounted for.

Negative Polar Valence. There still exists the usual electrostatic attraction between the electron and the kernel of the cesium atom. The *kernel* consists of the nucleus and all the electron layers except the outer layer, or *valence layer*. In fact, the electron would ordinarily be held in the outer layer unless some other atom were ready to take it up. Neutral atoms with nearly complete outer shells show a strong tendency to take on enough electrons to complete the shell. This tendency is strong enough to overcome the electrostatic repulsion of the other electrons and impart to the atom a net negative charge. Thus the chlorine atom Cl_{17} 2–8–7 will take up the electron lost by the cesium atom and become the chlorine ion, Cl_{17} 2–8–8.

Major Periods. The major periods of the periodic classification embrace all the elements between two succeeding inert gases.

The first period comprises but two elements, hydrogen and helium.

The next two periods comprise eight elements each.

The next two periods comprise eighteen elements each.

The next period comprises thirty-two elements.

Only a fragment of the next period is known. Obviously nuclei of elements of a higher atomic number than 92 are unable to exist. In fact, all the known elements of this period, and RaF (or polonium) in the preceding period, are radioactive.

In the eight element periods the chemical properties of the elements are dependent on the tendency for the atoms to gain or lose electrons to acquire the structure of the atoms of the inert gases at either end.

The electrostatic strain of acquiring a large charge (either positive or negative) is great and distinctly polar valences of more than 3 are very unusual. Yet sulphur in H_2SO_4 is considered to have a positive valence of 6 due to its tendency to revert to the structure of neon; and chlorine in $HClO_4$ is considered to have a positive valence of 7 due to the same cause. Yet these high valences are not altogether of a polar nature, although they are obviously dependent on the distance of the element beyond the preceding inert gas.

In the longer periods (of 18 and 32 elements) the elements near the beginning and end obviously derive their properties from their proximity to the inert gases.

In the middle parts of the longer periods the electrons to be gained or lost to acquire the structure of the nearest inert gas would impart too great an electrostatic strain. The usually encountered positive valences of two or three of such elements is attributed to a shifting of electrons into the kernel layers, thus leaving but two or three electrons in the valence layer (or sheath) of the neutral atom. Take, for example, the period beginning with Xe_{54}: The elements Cs_{55}, Ba_{56}, La_{57} display the expected valences of 1, 2, and 3, respectively. Cerium, Ce_{58}, sometimes displays a valence of 4 which is derived from the structure of xenon, Ce_{58} 2–8–18–18–8–4, but cerium shows an even stronger inclination to display the valence of 3 which is explained by the transfer of one electron from the sheath to the fourth kernel layer giving the structure Ce_{58} 2–8–18–19–8–3.

Praseodymium Pr_{59} never displays the valence of 5, but it and the succeeding elements up through lutecium Lu_{71} display almost without exception the valence of 3. Each additional electron in this so-called transition series, La_{57} to Lu_{71}, sinks into the fourth kernel layer until in lutecium this layer is filled to a maximum of 32. Lu_{71} 2–8–18–32–8–3. The next element, hafnium, should retain four electrons in its valence layer and display an invariable valence of 4.

It is one of the great triumphs of theory that Bohr's predictions concerning element 72 were proved to be accurate. Bohr concluded from reasonings along the lines we have indicated that the element of atomic number 72 should have a valence of 4 and resemble zirconium and thorium in chemical properties, instead of having a valence 3 and resembling the rare earth elements as had previously been supposed. He instigated a search in his laboratories at Copenhagen for this element, and very shortly it was found in some of the minerals that were tested and it proved to be present in the earth in fair abundance. It proved to have the properties predicted, and it was named hafnium in honor of the country in which it was discovered.

The shorter transition series in the eighteen element periods are indicated in the table by printing the symbols of the elements in heavy type or italics.

Subordinate Periods. Within the long periods are clearly recognizable subordinate periods, which were already indicated in the older Mendelejeff and Lothar Meyer charts of the periodic system (see back cover page). Closer study seems to indicate that the elements of the subordinate periods are related to the elements Ni, Pd, Er, Pt in the same way that the elements of the two short periods are related to He and Ne. The number of electrons in these apparently key elements is such as might give the following structures.

Ni_{28}	2	8	18		
Pd_{46}	2	8	18	18	
Er_{68}	2	8	18	32	8
Pt_{78}	2	8	18	32	18

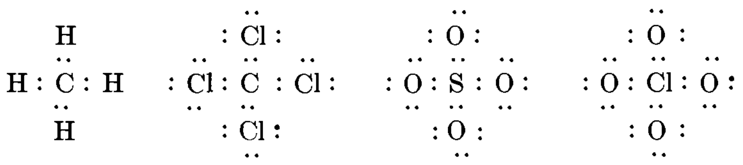
These structures possess layers of inherent stability, but the nuclear charge is not great enough to hold the large outer layer of 18 or the next to the last of 32 against the repulsive forces.

Given the greater nuclear charge of the succeeding elements, however, and these structures become stable. (In the case of erbium the three additional nuclear charges of lutecium are necessary before this particular erbium kernel structure becomes stable.) Thus the following elements derive their properties from the tendency to revert to the stable forms of the key elements. These are called the beta forms, or Niβ, Pdβ, Erβ, Ptβ, and the subordinate periods are based on these forms, as is apparent in the table, in the same way that the major periods are based on the inert gases.

Non-Polar Valence. Inorganic chemists very generally ascribe a polarity to valence even in compounds which show little or no ionization. In the carbon compounds of organic chemistry there is almost absolutely no evidence of polarity, and the organic chemist has been in the habit of regarding valence merely as the number of non-polar chemical bonds holding atoms together in molecules. These two ideas of valence formerly led to much misunderstanding. But this misunderstanding is obviated by an hypothesis first suggested by G. N. Lewis in 1916 and extended by Langmuir in 1919, which allows both polar and non-polar valence to be referred back to the same common cause. This cause is the tendency of atoms to acquire outer layers containing stable numbers, (most often 8, but 2 for the period ending with He and 18 in the periods based on Niβ, Pdβ, and Ptβ). The specific hypothesis is that in the case of non-polar valence certain electrons may simultaneously occupy places in the completed sheaths of two atoms. Thus in forming the chlorine molecule from two neutral chlorine atoms Cl_{17} 2–8–7, the two sheaths are completed if two electrons are held jointly in both sheaths. The kernel charge of chlorine is 7. The following formula, in which the sheath electrons are represented by dots and the symbol Cl stands for the chlorine kernel with its 7 net positive charge, represents the arrangement in the chlorine molecule:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

The pair of electrons held jointly constitutes the chemical bond, for it exerts an electrostatic attraction for both kernels and thus holds them together. The formulas of methane, carbon tetrachloride, sulphate ion, perchlorate ion, are shown as follows, it being remembered that the kernel charges are: 1 for hydrogen, 4 for carbon, 6 for oxygen, and 7 for chlorine; and that the completed sheath of hydrogen contains but two electrons.



$$\begin{array}{ccc} & \mathrm{H} & \\ & \cdot\cdot & \\ \mathrm{H}: & \mathrm{C} & :\mathrm{H} \\ & \cdot\cdot & \\ & \mathrm{H} & \end{array} \qquad \begin{array}{ccc} & \cdot\cdot & \\ & :\mathrm{Cl}: & \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ :\mathrm{Cl}: & \mathrm{C} & :\mathrm{Cl}: \\ \cdot\cdot & \cdot\cdot & \\ & :\mathrm{Cl}: & \\ & \cdot\cdot & \end{array} \qquad \begin{array}{ccc} & \cdot\cdot & \\ & :\mathrm{O}: & \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ :\mathrm{O}: & \mathrm{S} & :\mathrm{O}: \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ & :\mathrm{O}: & \\ & \cdot\cdot & \end{array} \qquad \begin{array}{ccc} & \cdot\cdot & \\ & :\mathrm{O}: & \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ :\mathrm{O}: & \mathrm{Cl} & :\mathrm{O}: \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ & :\mathrm{O}: & \\ & \cdot\cdot & \end{array}$$

If one counts the positive and negative charges of these formulas it is noted that CH_4 and CCl_4 are electrically neutral, but that the sulphate ion has a net of 2 negative charges, SO_4^{--}, and the perchlorate ion has a net of one negative charge, ClO_4^{-}.

SOLUBILITIES

A substance is classified as soluble if as much as 2 parts by weight dissolves in 100 parts of water. There is no sharp dividing line between soluble and insoluble, but in general a substance is classified as insoluble if less than 1 part by weight dissolves in 100 parts of water. It is advisable to learn the following general statements of solubilities.

SOLUBLE IN WATER

1. All simple salts of sodium, potassium, and ammonium.
2. Acetates and nitrates, except some basic acetates and nitrates.
3. Chlorides, except AgCl, HgCl, CuCl, $PbCl_2$.
4. Sulphates, except $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$.

INSOLUBLE IN WATER

1. Oxides and hydroxides
2. Carbonates
3. Phosphates
4. Sulphides

} except those of sodium, potassium, and ammonium.

TABLE OF SOLUBILITIES[1]

The tables on the following pages give more exact data which should be useful in connection with the preparations and questions in this book.

The formulas are those of the crystallized compounds which most readily separate from aqueous solution at the laboratory temperature, but it should be remembered that many salts have several hydrates.

In the second column the behavior of the crystallized salt when it is exposed to the air of the laboratory is indicated: s = stable, i.e. unchanged by exposure to atmosphere; e = efflorescent; d = deliquescent; d, e = deliquescent or efflorescent, according as to whether the humidity is above or below the average; CO_2 = absorbs carbon dioxide and falls to a white powder; Ox = compound is oxidized, especially in presence of moisture; Hyd = hydrolyzed, even by the water vapor of the air.

In the third column are given the figures for the solubility at 0°, 25°, and 100°, except in the cases in which other temperatures are indicated in parenthesis. Fractions have, as a rule, been dropped in giving the solubilities.

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[1] Much of the data in this table has been obtained from Seidell, Solubilities of Inorganic and Organic Substances.

Salt Formula of crystallized salt. Color (White unless otherwise specified)	Behavior when exposed to atmosphere.	Solubility in Water			
		Grams anhydrous salt per 100 grams water in a saturated solution at			F W per liter of solution at laboratory temperature.
		0°	25°	100°	
Aluminum:					
chloride, $AlCl_3\ 6H_2O$	d	(15°) 70			4
nitrate, $Al(NO_3)_3\ 9H_2O$	d	very soluble			
sulphate, $Al_2(SO_4)_3.18H_2O$	s	31	38	89	0.8
sulphide, Al_2S_3	Hyd	hydrolyzes completely			
Ammonium·					
acetate, $NH_4C_2H_3O_2$	d	very soluble			
bromide NH_4Br	s	61	79	146	6
(bi) carbonate, NH_4HCO_3	s	12	24		2 7
chloride, NH_4Cl	s	29	39	77	5
chromate, $(NH_4)_2CrO_4$, yellow	s	(30°) 40			2.3
dichromate, $(NH_4)_2Cr_2O_7$, orange	s	(30°) 47			1.4
iodide, NH_4I	d	154	177	250	6
nitrate, NH_4NO_3	d	118	214	871	11
oxalate, $(NH_4)_2C_2O_4$	s	2 1	4 8		0 4
sulphate, $(NH_4)_2SO_4$	s	71	77	103	4.5
Antimony:					
chloride, $SbCl_3$.	d	hydrolyzes with water to insoluble basic salt. very soluble in acids			
sulphate, $Sb_2(SO_4)_3$	d				
sulphide, Sb_2S_3, black, orange	s	insoluble. soluble in concentrated acids			
Arsenic·					
sulphide, As_2S_3, yellow.	s	insoluble in water or acids. soluble in alkalies			
Barium:					
acetate, $Ba(C_2H_3O_2)_2\ H_2O$	s	58	77	75	2
bromide, $BaBr_2\ 2H_2O$	s	98	106	149	2 5
carbonate, $BaCO_3$	s	0 0023			0 000,11
chloride, $BaCl_2\ 2H_2O$	s	32	37	59	1 7
chromate, $BaCrO_4$, yellow	s	0 0004			0 000,015
hydroxide, $Ba(OH)_2.8H_2O$	CO_2	1 7	4 7	(80°) 101	0 2
iodate, $Ba(IO_3)_2\ H_2O$ ...	s	0 008	0 03	0 2	0 001
iodide, $BaI_2\ 6H_2O$ ...	d	170	213	272	3
nitrate, $Ba(NO_3)_2$	s, d	5	10	34	0 3
peroxide, $BaO_2\ 8H_2O$. . . .	e	0 15			0 01
sulphate, $BaSO_4$	s	0 00023			0 000,010
sulphide, BaS	Ox	hydrolyzes to $Ba(SH)_2$ (soluble) and $Ba(OH)_2$			
sulphite, $BaSO_3$..........	s	(20°) 0 020		(80°) 0 002	0 001
Bismuth:					
chloride, $BiCl_3$	d	hydrolyzes with water to insoluble basic salt. very soluble in acids			
nitrate, $Bi(NO_3)_3\ 5H_2O$	d				
sulphate, $Bi_2(SO_4)_3$	d				
sulphide, Bi_2S_3, black	s	insoluble in acids or alkalies			

Salt. Formula of crystallized salt Color (White unless otherwise specified)	Behavior when exposed to atmosphere	Solubility in Water: Grams anhydrous salt per 100 grams water in a saturated solution at 0°	25°	100°	Solubility in Water: F W per liter of solution at laboratory temperature
Cadmium:					
carbonate, $CdCO_3$ . .	s	insoluble. soluble in acids			
chloride, $CdCl_2\ 2\frac{1}{2}H_2O$	e	90	(18°) 110	147	5
nitrate, $Cd(NO_3)_2\ 4H_2O$	d	110	(18°) 127	326	4 3
sulphate, $CdSO_4\ 2\frac{2}{3}H_2O$	e	76	(40°) 79	61	2
sulphide, CdS, yellow	s	insoluble. soluble in concentrated acids			
Calcium:					
acetate, $Ca(C_2H_3O_2)_2\ 2H_2O$	e	37	34	30	1 9
bromide, $CaBr_2\ 6H_2O$	d	125	153	295	5
carbonate, $CaCO_3$	s		0 0013		0 00013
chlorate, $Ca(ClO_3)_2\ 2H_2O$	d		(18°) 178		5 3
chloride, $CaCl_2\ 6H_2O$.	d	60	88	159	5 2
chromate, $CaCrO_4\ 2H_2O$, yellow	e	11	12	3	0 8
fluoride, CaF_2 .	s		0 0016		0 0002
hydroxide, $Ca(OH)_2$	CO_2	0 19	0 16	0 08	0 02
nitrate, $Ca(NO_3)_2\ 4H_2O$	d		(18°) 122		5 2
oxalate, $CaC_2O_4\ H_2O$	s		0 0007		0 00004
sulphate, $CaSO_4\ 2H_2O$.	s	0 18	0 21	0 16	0 015
sulphide, CaS . .	Ox	hydrolyzes to $Ca(SH)_2$ (soluble) and $Ca(OH)_2$			
sulphite, $CaSO_3$.			0 004		0 0003
Chromium:					
chloride, $CrCl_3\ 6H_2O$, purple	d		130		8
nitrate, $Cr(NO_3)_3\ 9H_2O$, purple		very soluble melts 36 5°			
sulphate, $Cr_2(SO_4)_3\ 18H_2O$, purple .	s, e		120		4
Cobalt:					
carbonate, $CoCO_3$, pink	s	insoluble. soluble in acids			
chloride, $CoCl_2\ 6H_2O$, pink	s	42	53	104	3
nitrate, $Co(NO_3)_2\ 6H_2O$, pink	d	(0°) 84		(91°) 340	4 3
sulphate, $CoSO_4\ 7H_2O$, pink	s	26	39	83	2
sulphide, CoS, black. .	s	insoluble in water or dilute acids			
Copper:					
carbonate, mCu(OH)$_2$ nCuCO$_3$, green	s	insoluble, soluble in acids			
chloride, $CuCl_2\ 2H_2O$, blue	s, d	71	79	108	5 0
nitrate, $Cu(NO_3)_2\ 6H_2O$, blue	e	82	150	275	4 8
sulphate, $CuSO_4\ 5H_2O$, blue	s, e	14	23	75	1 2
sulphide, CuS, black	s	insoluble in water or acids			

Salt Formula of crystallized salt. Color (White unless otherwise specified)	Behavior when exposed to atmosphere	Solubility in Water: Grams anhydrous salt per 100 grams water in a saturated solution at 0°	25°	100°	F W per liter of solution at laboratory temperature.
Hydrogen:					
arsenic acid, H_3AsO_4 $\frac{1}{2}H_2O$	d	very soluble melts 35 5°			
benzoic acid, $HC_7H_5O_2$	s	0 17	0 35	5 9	0 03
boric acid, H_3BO_3	s	2 0	4 7	27 5	0 6
iodic acid, HIO_3	d, s		300		
oxalic acid, $H_2C_2O_4$ $2H_2O$	s	3 5	11 4	(70°) 64	0 9
phosphoric acid, H_3PO_4	d	very soluble. melts 37°			
Iron:					
carbonate (ous), $FeCO_3$.	s	insoluble soluble in acids			
chloride (ous), $FeCl_2$ $4H_2O$, pale green	d	(15°) 67		(80°) 100	
chloride (ic). $FeCl_3$ $6H_2O$, yellow	d	very soluble. melts 31°			
nitrate (ous), $Fe(NO_3)_2$ $6H_2O$	Ox		(18°) 82		
(ic), $Fe(NO_3)_3$ $9H_2O$	d	very soluble melts 47°			
sulphate (ous), $FeSO_4$ $7H_2O$, pale green	e, Ox	(0°) 16	(30°) 33	(90°) 43	2
sulphate (ic), $Fe_2(SO_4)_3$ $9H_2O$	d	very soluble			
sulphide, FeS, black	s	insoluble, soluble in acids			
Lead					
acetate, $Pb(C_2H_3O_2)_2$ $3H_2O$	s		50	200	1 5
bromide, $PbBr_2$	s	0 5	1 0	4 8	0 02
carbonate, $PbCO_3$	s		0 0001		0 000,003
chloride, $PbCl_2$	s	0 7	1 1	3 3	0 05
chromate, $PbCrO_4$, yellow	s		0001		000,000,3
hydroxide, $Pb(OH)_2$	s		0 01		0 000,4
iodide, PbI_2, yellow	s	0 04	0 08	0 44	0 002
nitrate, $Pb(NO_3)_2$	s	38	61	139	1 4
sulphate, $PbSO_4$	s		0 004		0 000,13
sulphide, PbS, black	s	insoluble soluble in concentrated strong acids			
Lithium					
carbonate, Li_2CO_3	s	1 5	1 3	0 7	0 17
(bi) carbonate, $LiHCO_3$	s		(13°) 5 5		0 8
chloride, LiCl	d	67	82	128	13 3
hydroxide, LiOH H_2O	CO_2	12 7	12 9	17 5	5 0
nitrate, $LiNO_3$ $3H_2O$	d	(0°) 54	(30°) 138	(70°) 176	7 3
sulphate, Li_2SO_4	s	35	34	30	2 8
Magnesium					
bromide, $MgBr_2$ $6H_2O$	d	92	98	120	4 6
carbonate, $MgCO_3$ $3H_2O$	s		0 2		0 01
chloride, $MgCl_2$ $6H_2O$	d	53	57	73	5 1
hydroxide, $Mg(OH)_2$	CO_2		0 001		0 000,2
nitrate, $Mg(NO_3)_2$ $6H_2O$	d	(0°) 67		(40°) 85	4 0
sulphate, $MgSO_4$ $7H_2O$	e	27	39	74	2 8

Salt. Formula of crystallized salt Color (White unless otherwise specified)	Behavior when exposed to atmosphere	SOLUBILITY IN WATER			
		Grams anhydrous salt per 100 grams water in a saturated solution at			F W per liter of solution at laboratory temperature.
		0°	25°	100°	
Manganese:					
carbonate, $MnCO_3$, pale pink.	s	insoluble. soluble in acids			
chloride, $MnCl_2.4H_2O$, rose	e, d	63	77	115	5
nitrate, $Mn(NO_3)_2.6H_2O$, rose	d	102	166 (35.5°)	331	5
sulphate, $MnSO_4.5H_2O$, rose	s, e	53	65	32	4
sulphide, MnS, pink .	Ox	insoluble soluble in dilute acids			
Mercury:					
chloride (ous), HgCl	s		0.0002		0.000,01
(ic), $HgCl_2$	s	3.7	7.4	61	0.2
iodide (ic), HgI_2, red	s		0.005		0.000,1
nitrate (ous), $HgNO_3.H_2O$	s, e	very soluble in a little water much water ppts basic salt very soluble in HNO_3			
(ic), $Hg(NO_3)_2.\frac{1}{2}H_2O$	d				
sulphate (ous), Hg_2SO_4	s		0.06		0.001
(ic), $HgSO_4$.	s	hydrolyzes. moderately soluble in acids			
sulphide (ic), HgS, black..	s	insoluble insoluble in concentrated acids			
Nickel:					
carbonate, $NiCO_3$, green .	s	insoluble, soluble in acids			
chloride, $NiCl_2.6H_2O$, green	s, d	54	67	88	4
nitrate, $NiNO_3.6H_2O$, green	s, d	(0°) 80	(20°) 96	(95°) 233	6
sulphate, $NiSO_4.7H_2O$, green	e	(0°) 27	(30°) 43	(99°) 77	2
sulphide, NiS, black .	s	insoluble in water or dilute acids			
Potassium:					
acetate, $KC_2H_3O_2$	d	(5°) 188	(14°) 230	(62°) 492	25
bromate, $KBrO_3$.. ...	s	3.1	8.0	50	0.38
bromide, KBr	s	54	68	104	4.6
carbonate, $K_2CO_3.1\frac{1}{2}H_2O$	d	89	113	156	5.9
(bi) carbonate, $KHCO_3$	s	22	36	(60°) 60	2.8
chlorate, $KClO_3$ ..	s	3.1	8.2	56	0.52
chloride, KCl	s	28	36	57	3.9
chromate, K_2CrO_4, yellow	s	59	64	79	2.7
(di) chromate, $K_2Cr_2O_7$, orange	s	5	16	89	0.4
ferricyanide, $K_3Fe(CN)_6$, red	s	31	46	82	1.2
ferrocyanide, $K_4Fe(CN)_6.3H_2O$, yellow	s	13	28	76	0.6
fluoride, $KF.2H_2O$.	d		(18°) 92		12.4
hydroxide, $KOH.2H_2O$ ..	d	97	119	178	18
iodate, KIO_3 . .	s	4.7	9.9	32	0.35
iodide, KI . .	s	128	148	208	6.0
manganate, K_2MnO_4, intense green . .	d		very soluble		
nitrate, KNO_3..	s	13	37	246	2.6

Salt. Formula of crystallized salt Color (White unless otherwise specified)	Behavior when exposed to atmosphere.	Solubility in Water			
		Grams anhydrous salt per 100 grams water in a saturated solution at 0°	25°	100°	F W per liter of solution at laboratory temperature.
Potassium:					
oxalate, $K_2C_2O_4\ H_2O$	s		38		1 6
perchlorate, $KClO_4$	s		1 9	20	0 11
permanganate, $KMnO_4$, intense purple	s	2 8	8 0	(65°) 25	0 33
sulphate, K_2SO_4	s	7	12	24	0 62
(bi) sulphate, $KHSO_4$		36	(20°) 51	122	3 5
sulphide, $K_2S\ 5H_2O$	d		very soluble		
sulphite, $K_2SO_3\ 2H_2O$	d		very soluble		
thiocyanate, KSCN	d	177	(20°) 217		11
Silver:					
acetate, $AgC_2H_3O_2$	s	0 7	1 1	(80°) 2 5	0 06
bromate, $AgBrO_3$	s		0 19		0 008
bromide, AgBr	s		0 000,01		0 000,000,6
carbonate, Ag_2CO_3	s		0 003		0 000,1
chlorate, $AgClO_3$	s		15		0 6
chloride, AgCl	s		0 000,2		0 000,01
chromate, Ag_2CrO_4, red	s		0 002		0 000,15
fluoride, AgF . .	d		(16°) 182		13 5
iodate, $AgIO_3$.	s		0 005		0 000,2
iodide, AgI, yellow	s		0 000,000,3		0 000,000,01
nitrate, $AgNO_3$	s	122	257	952	8 4
nitrite, $AgNO_2$	s	0 16	0 4	1 36(60°)	0 03
oxide, Ag_2O, brown, dissolves as AgOH	s		0 0025		0 000,2
perchlorate, $AgClO_4$	d		very soluble		
sulphate, Ag_2SO_4	s	(18°) 0 73		(100°) 1 5	0 024
sulphide, Ag_2S, black	s		insoluble in water or acids		
Sodium:					
acetate, $NaC_2H_3O_2.3H_2O$	s, e	36	50	170	6
(tetra) borate, $Na_2B_4O_7\ 10H_2O$.	s	1 3	3 3	53	0 15
bromate, $NaBrO_3$	s	28	38	91	1 7
bromide, $NaBr\ 2H_2O$	s	73	87	118	6 9
carbonate, $Na_2CO_3\ 10H_2O$	e	7 0	28	46	1 8
(bi) carbonate, $NaHCO_3$	s	6 9	10		1 1
chlorate, $NaClO_3$. . .	s	82	105	233	6 4
chloride, NaCl .	s	36	36	40	5 4
chromate, $Na_2CrO_4.10H_2O$, yellow	e	32	86	127	3 3
(di)chromate, $Na_2Cr_2O_7\ 2H_2O$ orange	d	(0°) 163		(98°) 433	5 0
fluoride, NaF	s		(21°) 4 2		1 1
hydroxide, $NaOH\ H_2O$	d	42	114	348	21
iodate, $NaIO_3$	s	2 5	11	34	0 5
iodide, $NaI.2H_2O$	e, d	159	184	302	8 1

Salt. Formula of crystallized salt Color (White unless otherwise specified)	Behavior when exposed to atmosphere	Solubility in Water			
		Grams anhydrous salt per 100 grams water in a saturated solution at			F W per liter of solution at laboratory temperature.
		0°	25°	100°	
Sodium:					
nitrate, $NaNO_3$	s	73	92	178	7 4
nitrite, $NaNO_2$	d	72	88	162	10
oxalate, $Na_2C_2O_4$	s		3 6		0 3
permanganate, $NaMnO_4$ $3H_2O$, intense purple	d	very soluble			
phosphate, Na_3PO_4 $12H_2O$	e	1	15	108	0 85
Na_2HPO_4 $12H_2O$	e	1	12	102	0 81
NaH_2PO_4 H_2O	s	58	95	247	6 0
sulphate, $Na_2SO_4.10H_2O$	e	5	28	43	1 8
(bi) sulphate, $NaHSO_4$ H_2O	d		29	50	2
sulphide, Na_2S $9H_2O$	Ox d, e		17		2
sulphite, Na_2SO_3 $10H_2O$	e	(0°) 14	(20°) 27	(40°) 50	2
(bi) sulphite, $NaHSO_3$	e	very soluble			
thiosulphate, $Na_2S_2O_3.5H_2O$	s, e	(10°) 60	(25°) 76	(45°) 124	5
Strontium:					
carbonate, $SrCO_3$	s		0 001		0 000,07
chloride, $SrCl_2$ $6H_2O$	e	44	56	101	3 0
hydroxide, $Sr(OH)_2$ $8H_2O$	CO_2	0 4	1 0	32	0 06
nitrate, $Sr(NO_3)_2$ $4H_2O$	e	40	79	101	2 7
sulphate, $SrSO_4$	s		0 01		0 000,6
Tin:					
chloride (ous), $SnCl_2$ $2H_2O$	s Ox	(0°) 84		(15°) 270	7
sulphide (ous), SnS, black	s	insoluble	soluble in Na_2S_x		
(ic), SnS_2, yellow	s	insoluble	soluble in Na_2S		
Zinc:					
carbonate, $ZnCO_3$	s	insoluble	soluble in acids		
chloride, $ZnCl_2$ $3H_2O$	d	208	432	615	9 2
nitrate, $Zn(NO_3)_2$ $6H_2O$	d	95	127		4 7
sulphate, $ZnSO_4$ $7H_2O$	e	42	58	81	3 1
sulphide, ZnS	s	insoluble	soluble in acids		

DENSITIES OF HYDROCHLORIC ACID SOLUTIONS

Per cent HCl by weight	Density 20°/4°
1	1 0032
2	1 0082
4	1 0181
6	1 0279
8	1 0376
10	1 0474
12	1 0574
14	1 0675
16	1 0776
18	1 0878
20	1 0980
22	1 1083
24	1 1187
26	1 1290
28	1 1392
30	1 1493
32	1 1593
34	1 1691
36	1 1789
38	1 1885
40	1 1980

DENSITIES OF HYDROBROMIC ACID SOLUTIONS

Per cent HBr by weight	Density 20°/4°
1	1 0053
2	1 0124
4	1 0269
6	1 0417
8	1 0568
10	1 0723
12	1 0883
14	1 1048
16	1 1219
18	1 1396
20	1 1579
22	1 1767
24	1 1961
26	1 2161
28	1 2367
30	1 2580
35	1 3150
40	1 3772
45	1 4446
50	1 5173
55	1 5953
60	1 6787
65	1 7675

LIST OF APPARATUS

Articles which have a limited use are indicated by the experiment (E) or preparation (P) number for which they are required. Articles in the desk equipment are indicated by *. Roman numerals refer to chapters.

Anvil and hammer P. 59, 66, 72
Asbestos paper P. 13, 35
Balance, analytical, sensitive to 0.01 gram E. 1, 2, 3, 4, 5, 6, P. 17
Balance, Trip
Bath, sand, iron 6-inch P. 27, 43, 49, 66
*Beaker, 150 cc.
*Beaker, 250 cc.
*Beaker, 400 cc.
*Beaker, 600 cc.
*Block, test tube
Boat, porcelain, 88 mm. E. 4
Bottle, tincture, common, 1-pint E. 6, P. 16
Bottle, wide mouth, common 2 oz.
Bottle, wide mouth, common 4 oz.
*Bottle, wide mouth, common 8 oz.
*Bottle, wide mouth, common ½ gallon
Bottle, tincture, glass stopper 8 oz. E. 6, P. 7
Bottle, wide mouth, glass stopper, 2 oz. P. 52, 53
Bottle, wide mouth, glass stopper, 4 oz. P. 62
Bottle, Woulff, 3 neck, 500 cc. P. 7, 18
*Brush, test tube
Bulb, Dumas, 250 cc. E. 5 (Note 1)
Burette, plain 50 cc. E. 6, P. 16, 17
Burner, furnace P. 10, 11, 20, 22, 59, 66, 72
*Burner, Bunsen
Burner, ring P. 48
*Burner, wingtop
Casserole, 150 cc. P. 48, 52, 55
Casserole, 750 cc. P. 1, 55
*Clamp, burette, small
*Clamp, test tube holder
Condenser, Liebig, 36-inch P. 44
Condenser, phosphoric acid P. 52
Conductivity apparatus Chapter III
Connector, brass P. 17
Cork borers, sizes 1–3
Crucible, clay, with cover, 30 gram, 3½ × 3¾-inch, P. 10, 11, 20, 22, 59
Crucible, clay, with cover, size I, 4½ × 5¾-inch, P. 66, 72
Crucible, porcelain, with cover, 15 cc.
Crucible, porcelain, with cover, 100 cc. P. 39
Crucible, iron, with cover, 400 cc. P. 61, 71
*Cylinder, graduated 50 cc.
Cylinder, graduated 500 cc. E. 6, P. 62, 73
Desiccator 6-inch P. 25
Dish, crystallizing, 4-inch
Dish, crystallizing, 8-inch
*Dish, evaporating, porcelain, 4-inch
*Dish, evaporating, porcelain, 8-inch
Electrode, carbon, ¼ × 6-inch, P. 17
Electrode, copper, spiral, about 13 gauge wire, P. 17
Electrode, iron, spiral, about 18 gauge wire, P. 17
File, round
*File, triangular
Flask, distilling, 125 cc. P. 26, 45, 54
Flask, distilling, 250 cc. P. 44
*Flask, Erlenmeyer, 300 cc. E. 6, P. 16, 17, 19
*Flask, filtering, 500 cc.
Flask, flat bottom, 300 cc.
*Flask, flat bottom, 500 cc.
Flask, flat bottom, 1000 cc. P. 56
Flask, round bottom, 2000 cc. P. 7, 15, 18, 24, 51
*Forceps, iron

*Funnel, $2\frac{1}{2}$-inch
*Funnel, 5-inch
Funnel, short stem, $2\frac{1}{2}$-inch P. 28, 38
Funnel, separatory, 125 cc. P. 8, 14, 19, 26, 30, 45
*Funnel, support
Furnace, gas, P. 10, 11, 20, 22, 59, 66, 72
*Gauze, iron wire
Hydrometer, sp. gr. 1.00–1.20 P. 7, 8
Jar, hydrometer, 6-inch, P. 7, 8
Labels, bottle
Marble, glass P. 25, 62
*Mortar and pestle, $3\frac{1}{2}$-inch
Mortar and pestle, 8-inch P. 12, 13
*Paper, filter, 5.5-cm.
*Paper, filter, 11-cm.
*Paper, filter, 24-cm.
Pinchcock, spring E. 2, 3
Pipette, volumetric, 10 cc. E. 6, P. 16
*Plate, filter, porcelain, $1\frac{1}{2}$-inch
Plate, glass, 8-inch
Plate, iron 2–4 mm. thick P. 13, 48
Plate, porous, 6-inch P. 71
Retort, 350 cc. Pyrex P. 44, 56
*Ring, iron, 4-inch
*Ring, iron, 6-inch (Note 2)
Ring, wood, 4-inch hole P. 15, 52
Rod, glass, 5 mm.
Shears, 6-inch
Specific gravity apparatus, P. 7, 8
Spatula, glass P. 12
*Spatula, stainless iron, 4-inch blade
*Sponge
Spoon, deflagrating IV, VIII
Spoon, iron, 18-inch P. 72
Stirrer, iron (Note 3) P. 59
Stopper, cork, numbers 7, 9, 12, 15, 26
Stopper, rubber, numbers 00 solid, 00 1-hole, 0 solid, 0 1-hole, 1 solid, 1 1-hole, 2 solid, 2 1-hole, 3 solid, 3 1-hole, 3 2-hole, 4 solid, 4 1-hole, 4 2-hole, 5 solid, 5 1-hole, 5 2-hole, 6 solid, 6 1-hole, 6 2-hole, $6\frac{1}{2}$ 2-hole, 7 1-hole, 7 2-hole, 8 2-hole
Support, ring stand
*Test tube, 6-inch
Test tube, 6-inch Pyrex E. 2, P. 45
Test tube, 8-inch Pyrex P. 43
Thermometer, 250° P. 1, 45, 52, 54, 55, 56
Thermometer, 360° P. 26
Tongs, crucible
Tongs, furnace P. 10, 11, 20, 22, 59, 66, 72
Towel, cotton
Towel, white paper (Note 4)
Triangle, nichrome wire 2-inch
Tripod, iron, 6-inch
Trough, water
Tubing, glass, 6–7 mm.
Tubing, rubber, $\frac{3}{16}$-inch
Tubing, rubber, $\frac{1}{4}$-inch
Tubing, rubber, $\frac{1}{4}$-inch medium wall
Tube, combustion E. 4
Tube, Pyrex, $\frac{5}{8}$" × 18" P. 26
*Tube, drying, 4-inch
*Tube, thistle
U-tube, 3-inch Chapter III
U-tube, 8-inch P. 8, 14, 17
U-tube, side arm, 4-inch E. 4, P. 8
*Vial, 1 × 3-inch E. 4, Chapter III
*Watch glass, 5-inch
Wire, platinum Q. 23, V, IX, XI

Note 1. Dumas bulb made from a 250 cc. Pyrex flat bottomed flask. The neck replaced by a 12 mm. tube drawn down to a capillary at the end. See Figure 13, p. 35.

Note 2. Iron ring, 6-inch, should have an extra long shank to permit its use to support an 8-inch evaporating dish without tilting the dish. Otherwise tripods are required.

Note 3. An iron rod $\frac{1}{4}$ inch diameter and 24 inches long with a 4-inch right angle bend at one end.

Note 4. Paper towels are generally used for drying crystals.

Note 5. Made of Pyrex glass with side arms of unequal length.

LIST OF RAW MATERIALS

Preparations are indicated by P and number and Quantitative Experiments by E and number.

Aluminum, granular 10–20 mesh P. 10, 66, 72
Aluminum powder ("aluminum bronze") P. 13
Aluminum turnings P. 25, 26
Ammonium chloride P. 43
Ammonium sulphate P. 3, 73
Antimony sulphide (stibnite) P. 56, 57, 59
Arsenic acid (seed crystals) P. 55
Arsenic trioxide P. 55
Barium carbonate P. 9, 22
Barium hydroxide P. 6
Barium nitrate P. 38
Barium peroxide P. 6, 9, 66, 72
Bismuth nitrate P. 60
Bleaching powder or calcium hypochlorite P. 31, 47
Bone ash P. 53
Bromine P. 8, 19, 26, 35, 45, 54
Calcium carbonate P. 15, 71
Calcium chloride, anhydrous E. 4, P. 67
Calcium hydroxide P. 16
Calcium hypochlorite or bleaching powder P. 31, 47
Calcium sulphate (plaster of Paris) P. 11
Calcium sulphate (gypsum) page 63
Carbon (charcoal powder) P. 11, 20, 22, 35
Carbon (lampblack) P. 13
Carbon dioxide (cylinder or generator) P. 15, 71
Carbon tetrachloride E. 5
Cerium dioxide P. 50, 51
Cerium oxalate P. 49
Chlorine (cylinder or generator) P. 36, 44
Chromic anhydride P. 63
Chromic oxide P. 61, 66
Copper ribbon P. 28
Copper turnings P. 5, 27
Copper wire, 16 gauge, E. 3
Copper chloride P. 28
Copper oxide, powder P. 20
Copper oxide, wire E. 4
Copper sulphate P. 3, 4, 29, 30
Copper sulphate, saturated solution P. 17
Dextrose E. 29
Hydrogen peroxide 3% P. 24
Hydrogen sulphide (cylinder or generator) P. 43
Iodine P. 37
Iron filings, 20 mesh P. 59
Iron filings (" Amco ") P. 73
Ferrous carbonate (siderite) P. 73
Ferrous sulphide (for H_2S) P. 43
Lead acetate P. 47
Lead dioxide P. 48
Lead monoxide (litharge) P. 46, 48
Lead monoxide (massicot) P. 48
Lead sulphide (galena) P. 10
Magnesium, powder P. 14
Magnesium, ribbon P. 13, 66, 72
Manganese chloride (waste liquor from chlorine generator) P. 70
Manganese dioxide, granular for chlorine generator P. 36, 44
Manganese dioxide, fine powder P. 71, 72
Mercury P. 12, 32, 33
Molybdenum trioxide P. 67
Oxalic acid P. 50
Phosphorus, red P. 8, 52, 54
Phosphoric acid, ortho, seed crystals P. 52
Potassium chlorate P. 37, 39, 71
Potassium chlorate, dry powder E. 2
Potassium dichromate P. 64, 66
Potassium hydroxide P. 35, 36, 61, 71

Potassium iodate P. 38
Potassium nitrate (crude) P. 1
Potassium nitrate P. 61
Potassium sulphate P. 4
Potassium sulphocyanate P. 34
Rosin P. 22
Selenium P. 69
Sodium borate (borax) P. 23, 24, 59
Sodium carbonate, anhydrous E. 6, P. 5, 16, 21, 31, 40, 60, 70
Sodium carbonate, crude P. 2
Sodium chloride (fine crystal) P. 15
Sodium chloride (rock salt) P. 7, 18, 25
Sodium chloride, saturated solution P. 17
Sodium dichromate P. 62
Sodium hydroxide P. 25, 36, 47
Sodium nitrate (crude) P. 1
Sodium potassium tartrate P. 29
Sodium silicate P. 41
Sodium sulphantimonate P. 58
Sodium sulphide P. 57
Strontium sulphate (celestite) P. 20, 21
Sulphur (flowers) P. 12, 40, 43, 57
Sulphur dioxide P. 40
Tin, feathered metal P. 42, 44, 45
Tin, foil P. 42
Stannous chloride P. 43
Tungsten trioxide P. 68
Zinc, feathered metal E. 4
Zinc C.P. granular metal 20 mesh E. 1
Zinc C.P. rod E. 3
Zinc sulphate P. 31

REAGENTS

Roman numerals indicate reagents required for experiments in the text of that chapter. Reagents required for experiments in questions at the end of a preparation are indicated by the letter Q and number of the preparation. Reagents used in a preparation are designated by the letter P and number of the preparation.

SOLIDS

Aluminum metal, turnings II
Aluminum carbide IX
Ammonium chloride Q. 53, V
Antimony metal, powdered X
Arsenic metal, powdered X
Arsenious oxide Q. 55
Asbestos fibre V, IX
Barium peroxide IV
Bismuth metal, powdered X
Bismuth dioxide X
Bismuth trioxide III, X
Bleaching powder VIII, IX
Calcium metal, turnings II
Calcium carbide IX
Calcium carbonate, lump V, IX
Calcium carbonate, powder III
Calcium chloride II
Calcium hydroxide V
Calcium oxide II
Cobalt carbonate XI
Carbon, decolorizing
Carbon, granulated charcoal II, IX
Copper metal, wire III
Copper metal, turnings VIII
Copper basic carbonate VII
Copper oxide, powder IV
Copper sulphate Q. 3, III, VII
Cotton wool E. 4, IV
Cotton cloth, colored VIII
Dextrose X
Glass, broken P. 8
Glass wool P. 7, 8
Iodine IV
Iron metal, wire III Q. 73
Ferric ammonium alum XI
Ferric chloride II, III
Ferric oxide XI
Ferrous ammonium sulphate Q. 73
Ferrous sulphide for H_2S generator IV, VIII, X, P. 70
Lead dioxide IV, IX
Lead monoxide IV, IX
Lead nitrate Q. 47, IX
Litmus paper, blue
Litmus paper, red
Magnesium metal, powder IV
Magnesium metal, ribbon II, IV, V, VIII
Magnesium carbonate V
Manganese carbonate P. 70
Manganese dioxide, powder IV, XI
Nickel carbonate XI
Phosphorus, red II, X
Porcelain chips, unglazed E. 5, P. 56
Potassium carbonate IX
Potassium chlorate III, VIII
Potassium dichromate IV
Potassium hydroxide II, III
Potassium iodate VIII
Potassium iodide IV, VIII
Potassium nitrate IV, XI
Potassium permanganate IV, VIII
Potassium sulphate Q. 3
Silicon dioxide, precipitated IX
Silicon dioxide, coarse sand P. 66, 67
Silicon dioxide, fine sand P. 8, 43
Sodium bicarbonate P. 55
Sodium bromide IV
Sodium carbonate, anhydrous III, IX, XI
Sodium carbonate, crystal II
Sodium chlorate III
Sodium chloride III
Sodium hydroxide II, III, IV

Sodium nitrate III
Sodium nitrite VIII
Sodium peroxide IV, Q. 61
Sodium sulphate Q. 3, II
Sodium tetraborate Q. 23
Starch, soluble IV, VII, VIII
Strontium carbonate P. 21
Sugar, cane III, VIII
Sulphur, flowers II, IV, VIII
Tartaric Acid III
Tin metal, feathered IX
Stannous chloride IX
Urea III, VIII
Vaseline
Wood splinters IV, VIII
Zinc metal, dust II
Zinc metal, feathered III, VII
Zinc chloride II, VII
Zinc sulphate II, VII

LIQUID REAGENTS AND SOLUTIONS

Acetic acid, glacial III, P. 61
Acetic acid, 6-normal VI, Q. 65
Alcohol, reagent P. 28, 30, 64, Q. 23, III
Aluminum sulphate, 1-normal VI
Ammonium chloride, 1-normal V
Ammonium hydroxide, 6-normal
Ammonium hydroxide, 15-normal
Ammonium sulphate, 2-normal V
Ammonium sulphide, 6-normal Q. 43, III, VII
Asbestos suspension for filtering
Barium chloride, 1-normal Q. 69, VIII
Barium hydroxide, 0.4-normal Q. 6, IV
Bromine Q. 19, VIII
Bromine water, saturated IV, VIII
Cadmium chloride, 1-normal VII
Calcium chloride, 1-normal III
Calcium hydroxide, saturated VII, IX, XI
Carbon disulphide P. 26, IV, VIII
Carbon tetrachloride IX
Chlorine water, saturated P. 21, II, IV, IX
Chromium chloride, 1-normal Q. 61, XI
Cobalt nitrate, 0.3-normal XI
Copper sulphate, 1-normal III, IV, VII
Ether P. 28, 30
Gasoline IX
Glycerine III
Hydrobromic acid, 0.1-normal IV
Hydrochloric acid, 6-normal
Hydrochloric acid, 12-normal
Hydrogen peroxide, 3% Q. 6, IV
Hydriodic acid, 0.1-normal IV
Iodine water, saturated P. 55, IV, VIII
Ferric chloride, 1-normal P. 34, IX, XI
Ferrous sulphate, 2-normal III, XI
Lead acetate, 1-normal IV
Litmus solution, blue III
Litmus solution, red III
Magnesium chloride, 1-normal P. 55, V
Magnesium sulphate, 1-normal XI
Manganese sulphate, 1-normal X
Mercuric chloride Q. 45, 53, IX
Mercuric nitrate, 0.2-normal VII
Mercurous nitrate, 0.2-normal VII
Mercury II
Methyl orange III, P. 23
Nickel chloride XI
Nitric acid, 6-normal
Nitric acid, 16-normal
Phenolphthalein P. 53
Phosphoric acid, ortho, 85% IV
Potassium chlorate (chloride free) III
Potassium ferricyanide III, IX, P. 73, Q. 73
Potassium ferrocyanide, 1-normal III, Q. 73
Potassium hydroxide, 6-normal III, VIII
Potassium iodide, 0.1-normal Q. 55, IV, VII
Potassium thiocyanate, 1-normal P. 70, III, IX, Q. 73

Silver nitrate, 0.1-normal P. 1, 6, 35, 47, 52, III, VII
Sodium acetate, 3-normal III, VII
Sodium bromide, 0.5-normal IV
Sodium benzoate, III
Sodium carbonate, 3-normal III, VI, IX, XI
Sodium chloride, 2-normal III, IV
Sodium hydroxide, 6-normal Q. 13, II, III, VI
Sodium (mono) phosphate, 1-normal Q. 53
Sodium (di) phosphate, 1-normal Q. 53
Sodium (tri) phosphate, 1-normal Q. 53
Sodium polysulphide Q. 45, X
Sodium silicate, Sp. Gr. 1.1 IX
Sodium sulphide, 1-normal Q. 43, 45
Stannous chloride, 1-normal Q. 33, 45, 69, IX, X
Sulphuric acid, 6-normal
Sulphuric acid, 36-normal
Titanium sulphate reagent IV
Zinc sulphate, 1-normal III, VII

INDEX

Preparations are indicated by *

p	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	p
740	1·175	1·171	1·166	1·162	1·158	1·154	1·150	1·146	1·142	1·138	1·135	1·131	1·127	1·123	1·119	1·115	740
742	1·178	1·174	1·170	1·165	1·161	1·157	1·153	1·149	1·145	1·141	1·138	1·134	1·130	1·126	1·122	1·118	742
744	1·181	1·177	1·173	1·169	1·165	1·160	1·156	1·152	1·149	1·145	1·141	1·137	1·133	1·129	1·125	1·121	744
746	1·184	1·180	1·176	1·172	1·168	1·164	1·160	1·156	1·152	1·148	1·144	1·140	1·136	1·132	1·128	1·124	746
748	1·187	1·183	1·179	1·175	1·171	1·167	1·163	1·159	1·155	1·151	1·147	1·143	1·139	1·135	1·131	1·128	748
750	1·191	1·186	1·182	1·178	1·174	1·170	1·166	1·162	1·158	1·154	1·150	1·146	1·142	1·138	1·134	1·131	750
752	1·194	1·190	1·186	1·181	1·177	1·173	1·169	1·165	1·161	1·157	1·153	1·149	1·145	1·141	1·137	1·134	752
754	1·197	1·193	1·189	1·185	1·180	1·176	1·172	1·168	1·164	1·160	1·156	1·152	1·148	1·144	1·140	1·137	754
756	1·200	1·196	1·192	1·188	1·183	1·179	1·175	1·171	1·167	1·163	1·159	1·155	1·151	1·147	1·143	1·140	756
758	1·203	1·199	1·195	1·191	1·186	1·182	1·178	1·174	1·170	1·166	1·162	1·158	1·154	1·150	1·146	1·143	758
760	1·206	1·202	1·198	1·194	1·190	1·185	1·181	1·177	1·173	1·169	1·165	1·161	1·157	1·153	1·149	1·146	760
762	1·210	1·205	1·201	1·197	1·193	1·189	1·184	1·180	1·176	1·172	1·168	1·164	1·160	1·156	1·152	1·149	762
764	1·213	1·209	1·204	1·200	1·196	1·192	1·188	1·183	1·179	1·175	1·171	1·167	1·163	1·159	1·156	1·152	764
766	1·216	1·212	1·207	1·203	1·199	1·195	1·191	1·187	1·182	1·178	1·174	1·170	1·166	1·162	1·159	1·155	766
768	1·219	1·215	1·211	1·206	1·202	1·198	1·194	1·190	1·186	1·181	1·177	1·173	1·169	1·165	1·162	1·158	768
770	1·222	1·218	1·214	1·209	1·205	1·201	1·197	1·193	1·189	1·185	1·181	1·176	1·172	1·169	1·165	1·161	770
f (mm.)	5·6	6·0	6·4	6·9	7·3	7·8	8·4	8·9	9·5	10·1	10·8	11·4	12·2	12·9	13·7	14·6	f (mm.)

If the confining liquid is 30 per cent *potassium hydroxide solution*, the pressure of water vapour over this solution at the temperature concerned (f mm., see above) must be subtracted from the observed barometric pressure after reduction to 0°.