



SYNTHETIC INORGANIC CHEMISTRY

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

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PREFACE TO THIRD EDITION

Since the adoption of an entrance requirement in chemistry at the Massachusetts Institute of Technology the problem of the instruction becomes somewhat simplified in that a certain background of chemical experience is possessed by all the students. Major experiments consisting of the preparation of inorganic substances are still believed to be the best means of training the chemical students in the laboratory, and the present edition retains the essential features of the former edition under the same title prepared by one of the authors. It has seemed very desirable to have in a single volume a comprehensive plan of laboratory work and class room study to cover a whole year's work and to this end the two authors have put together the material which they formerly published separately.

Experience has taught teachers that it is unwise to count too much upon an understanding of subjects previously studied. Therefore, although this book is presumed to outline a course continuing from a previous course in high school, it was thought best to include the essential material of the high school course. This elementary material was presented in the form of minor experiments for which the directions were written as if the experiments were to be performed, but the description of the observations and the discussion of the chemical principles were added. Thus by reading the text the pupil could quickly obtain a grasp of the review work. This treatment of the minor experiments however proved to be so excellent a method of imparting a knowledge of chemistry that it was followed to a large extent throughout the whole book. The preparations present the opportunity for original study; the minor experiments carry along the systematic instruction. The minor experiments can too at all times be performed when it seems desirable.

This volume is therefore considerably more than a laboratory manual; the authors intend to make it the text book of the full year's work in inorganic chemistry. It is to be supplemented by some one of the more comprehensive text books, which is to be

used for reference in looking up the purely descriptive parts of chemistry and the industrial and economic aspects of the subject.

If perhaps the authors may have felt at times a certain ambition to prepare a complete text book, each one of the several excellent books of this scope that have appeared within the last few years has shown them anew the entire needlessness of undertaking such a task. What they have done, namely to prepare a systematic course of study of the facts and principles of chemistry based upon the work of the laboratory, is rather different from anything that has been attempted before.

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JOSEPH W. PHELAN.

September, 1922

PREFACE TO FIRST EDITION

THIS series of notes was designed to serve as a guide for laboratory work and study in Inorganic Chemistry during the second term of the first year at the Massachusetts Institute of Technology. It had been felt for some time that Qualitative Analysis, which was previously made the basis for laboratory practice during that period, did not fully meet the requirements and that a course based upon the preparation of typical chemical substances might prove more satisfactory. In consequence, notes in essentially the form now published were prepared during the year 1906-07, they being the direct outcome of several years' previous trial of a limited amount of preparation work. The present book is a thorough revision of those notes in the light of experience in their actual application.

During the first term's study of chemistry there can be little doubt that a course of simple experiments, such as has long been in use, in the methods of formation and in the study of the properties of the non-metallic elements — oxygen, hydrogen, the halogens, sulphur, nitrogen, and carbon — and their compounds, is the most satisfactory. But when it comes to the study of the metallic elements, three options as to laboratory work present themselves: First, a continuation of experiments similar in nature to those of the first term; second, Qualitative Analysis; third, Preparation Work. The disadvantages of the first plan are that the experiments are so quickly performed and so alike in character that they fail to arouse much enthusiasm in the student or to leave very vivid impressions on his mind. Qualitative analysis is in many ways a most excellent basis for teaching the chemistry of the metallic elements; but its chief disadvantages are: First, that it is one-sided, it dealing as it does almost exclusively with the chemistry of solutions and the formation of highly insoluble substances; second, that it requires the sequence followed in the lectures to be that of the qualitative procedure instead of a more natural one based on the periodic classification; and third, that it is well-nigh impossible to keep from the student's mind the false idea that the end and aim of qualitative analysis is principally "to get the unknowns correct."

Some of the advantages which seem to be possessed by a course of preparation work such as outlined in the following pages are:

1. The sequence of the exercises may follow that of the lectures.
2. Very varied types of chemical change are illustrated, both those in the furnace and those in solution. In solution advantage is taken not only of high degrees of insolubility, but also of differences in solubility among the more soluble substances as well as of differences in the effect of temperature on solubility.
3. The danger of the work becoming a mechanical following of directions is reduced by the introduction of study questions and experiments with each exercise.
4. In its effect in awakening the student's interest this line of work has proved particularly successful, — the making of preparations is, in fact, in its very nature one of the most fascinating forms of chemical work. Since each preparation requires a good deal of time and thought, and the product when obtained is something definite and tangible, the knowledge thus gradually absorbed is more definite and less easily forgotten than when the laboratory work consists of a large number of test tube reactions.

After the completion of such a course as this, if the student commences analytical work with some conception of the sources and methods of obtaining the substances which he is to use as reagents, etc., there can be no doubt that the latter work will then have a much deeper meaning.

The plan kept in mind in preparing this course is, briefly, as follows: The greater part of the preparations selected are of industrial importance, and for the starting point of each either natural products or crude manufactured materials are used so far as is possible. The course does not aim to be an exhaustive one in chemical preparations, but a limited number of exercises are selected to illustrate the most important types of compounds of the common elements and the most important methods. Two or three times as many exercises are furnished as any one student will be able to complete in the time usually allotted; thus different students may be assigned different preparations.

The notes for each exercise are divided into three parts:
I. A discussion of the object of the exercise, with an outline of the principle of the method and the reasons for the steps involved.
II. Working directions which, if carefully followed, should re-

sult in obtaining a satisfactory product. It is believed far better to make the directions very explicit, for the reason that the inexperienced student may easily become discouraged by failures due to difficulties which he is unable to foresee. Difficulties enough are sure to arise to develop originality and resourcefulness. III. Questions for study which involve additional laboratory experiments, the consulting of text books, and original reasoning.

At the end of each group of exercises is furnished a set of general study questions, and this arrangement of the exercises in groups is such as to bring out the relationships shown in the periodic classification of the elements.

In the discussions and questions given with the various exercises it is assumed that the student has an elementary knowledge of the electrolytic dissociation theory and of the principle of mass action. In the opinion of the author a great opportunity is lost for bringing out relationships among chemical phenomena if these principles are not taught during the first term's study of college chemistry and their applications pointed out in connection with later work in inorganic preparations and in analytical chemistry. The effort has been to make the questions such as cannot be answered mechanically. Some of the questions may, in consequence, seem rather difficult and incapable of direct answers; the object of the questions is, however, not solely to bring forth correct statements of facts and theories, but is also to teach the student to use his head in seeking for the significance of facts and in reasoning from one fact to another.

Acknowledgment is due to many sources for the outline of the greater part of the methods given. The details of all of them have, however, been very carefully worked over and adapted for the purpose in view.

In conclusion the author wishes to express his sense of obligation to Professor Henry P. Talbot, head of the Department of Chemistry, at whose request the preparation of these notes was undertaken; also to other members of the instructing staff at the Massachusetts Institute of Technology for helpful criticism and suggestions, and particularly to Professor J. W. Phelan, to whose efficient management of the laboratory instruction is due any success with which this course has met at this Institute.

ARTHUR A. BLANCHARD.

March, 1908.

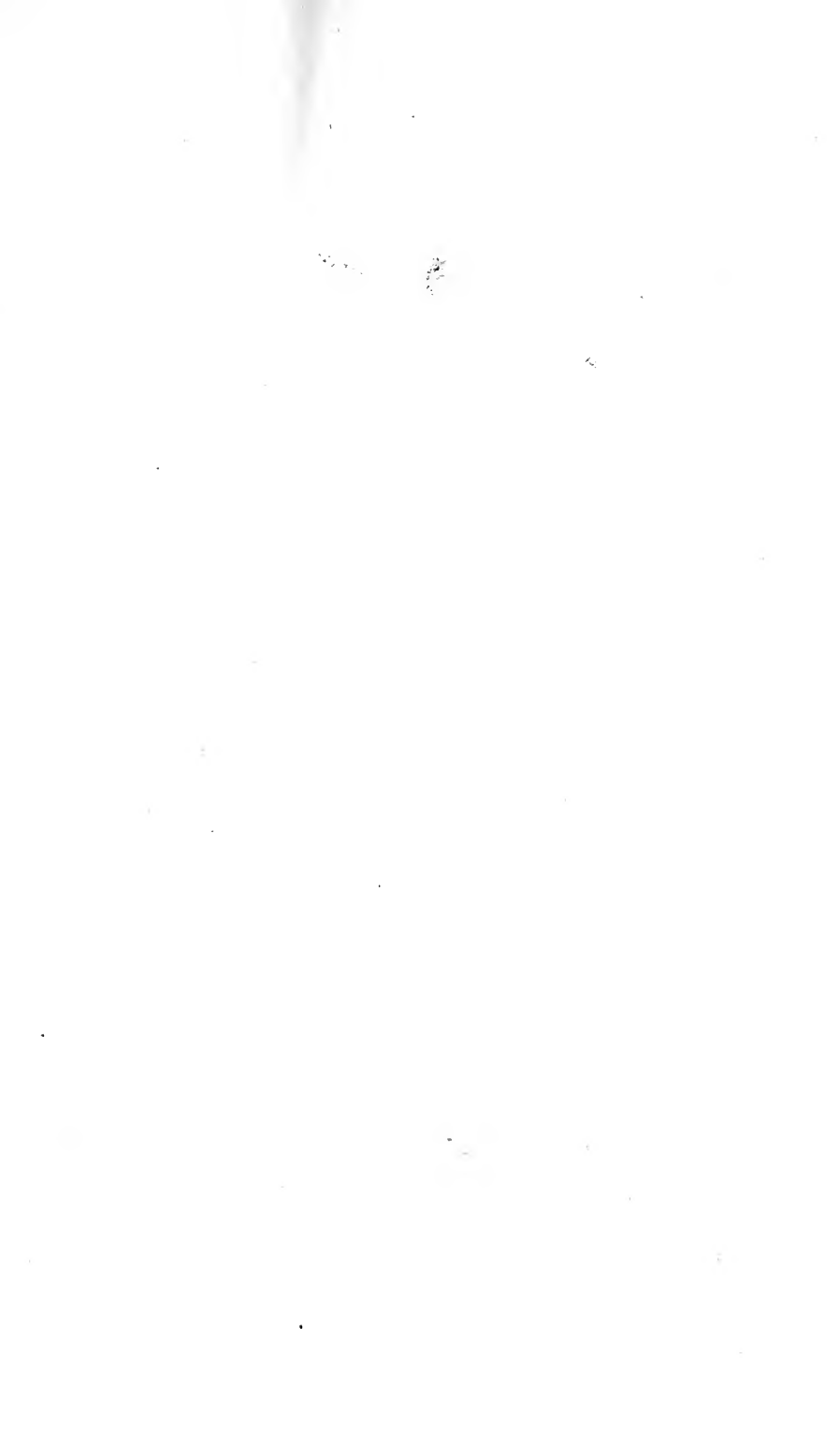


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SYNTHETIC INORGANIC CHEMISTRY

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 written 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.

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. Then write in the note book all reactions, and, 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. 4–21) 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 as, for example, 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. — The section under this title gives suggestions for study, which involves laboratory experiments, consultation of reference books, of which all that are necessary will be found upon the shelf in the laboratory, 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.

Yield of Product. — Where possible the methods employed in these preparations resemble those actually used on an industrial scale; where this is, however, 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 amounts obtained of each preparation are to be weighed 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 other ones of their own selection, — this selection of course being subject to the instructor's approval, since the laboratory may not at all times have the necessary materials and apparatus.

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. In case 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 other cases 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 nor 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



FIG. 1

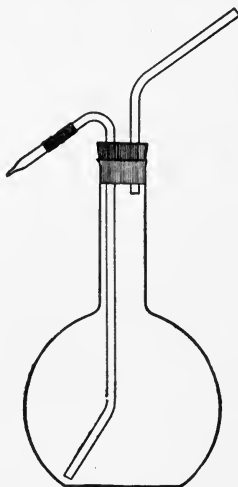


FIG. 2

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.

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).

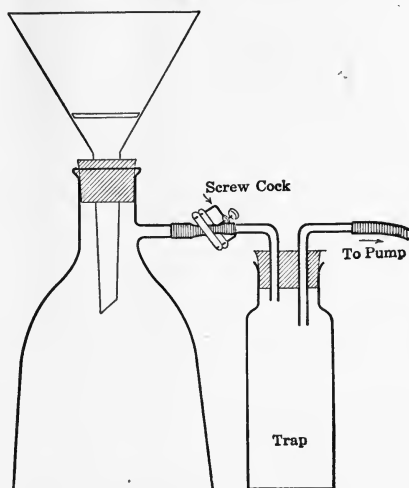


FIG. 3

Place a $1\frac{1}{2}$ -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) onto 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 bringing all of the solid 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).

The suction filter is very generally useful for the purpose of separating a solid product from a liquid. In cases that 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 it is, as explained in paragraph *c*, 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 most 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 corners of the filter should be cut off round, and the upper edge of the filter should come about one-half 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.

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

In case a considerable weight of liquid is to come on the point of the filter, this may be reinforced 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 in many cases 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 strain corrosive liquids.

(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 then 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 by no means essential in any of the following preparations.

(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.

(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.* — To remove completely the impurities contained in the mother liquor clinging to precipitates or crystals, the solid is washed. 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 other than pure water.

First, the solid should be allowed to drain as completely as possible, then the wash liquid should be 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.* — In case a precipitate is very insoluble it can be most thoroughly and quickly washed by decantation. This consists in allowing it to settle in a deep vessel and then in pouring (decanting) or siphoning off the clear liquid. 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 thrown on a filter, drained, and then dried.

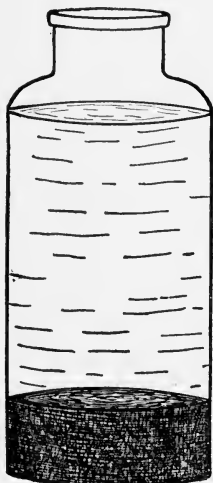


FIG. 4

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. 32), 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 $\frac{1}{5}$ 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 $\frac{4}{5}$, consisting of the clear solution, is drawn away, it follows that practically $\frac{1}{5}$ of the solution, containing $\frac{1}{5}$ 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 $\frac{4}{5}$ 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 out, 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 boiling down of a solution should always be carried out in a porcelain dish of such a size that at the outset it is well filled with the liquid. (Never evaporate in a beaker.) 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 where the dish is part cooled by liquid and part uncooled, there is great danger of breaking; 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 liquid over a flame it should be carefully

watched, for if it should be forgotten and 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 will probably 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.

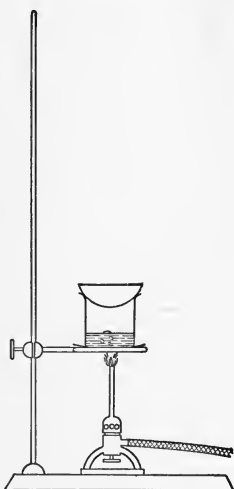


FIG. 5. Steam Bath for Evaporating to Dryness. Note 6 (b)

Each student, however, may set up a steam bath as shown in Fig. 5, at his own desk. After the water in the beaker is once boiling 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 nor of decomposing the solid product while evaporating a solution to dryness.

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 apt 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 would take the remaining coarser particles a very long time to dissolve. 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 in many cases 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; in such a case the cooling should 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 must fall 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 most generally separates in a pure condition irrespective of any other dissolved substances the solution may contain. Thus a substance can be obtained in an ap-

proximate 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 24 hours or longer. 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 in several days. With preparations that react with carbon dioxide (such as barium hydroxide) the solution which soaks into the paper retains all of the carbon dioxide which might otherwise get in to 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 of 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 thoroughly moisten it; 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 manner. 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.

Most solid raw materials for the following preparations are supplied in the powdered form, but they are rarely powdered finely enough; they should in general be further pulverized until they no longer feel gritty beneath the pestle or between the fingers.

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 is to 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 to exactly 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 save 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. In cases in which one or more of the reacting substances are melted by the heat, the

same sort of intimate contact is brought about as in the case of 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 Prepa-

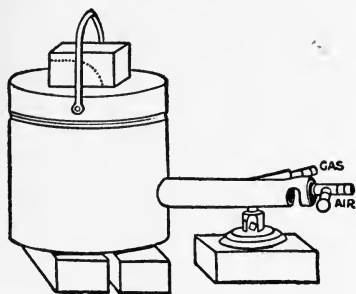


FIG. 6

ration No. 20), the process probably takes place in 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 as to which is least attacked by the reagents. For rather moderate temperatures the crucible may be heated over a flame, in other cases the requisite temperature can be obtained in a furnace.

The form of furnace to be recommended for this work is represented in Figure 6. It consists of a cylinder of fire clay, 7 inches high and $6\frac{1}{2}$ inches in external diameter, which is surrounded by a sheet iron casing. It is heated, as shown, by a gas-wind flame, introduced through an opening in the lower part of one side. If a suitable air blast is not available, a gasoline blowpipe (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 $1,350^{\circ}$ 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 is 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 6-n 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.

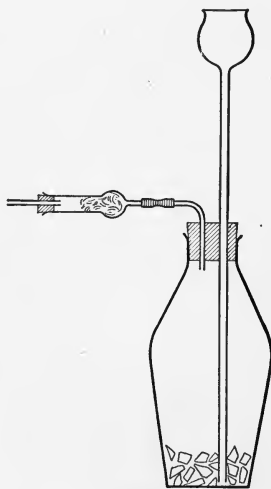


FIG. 7

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

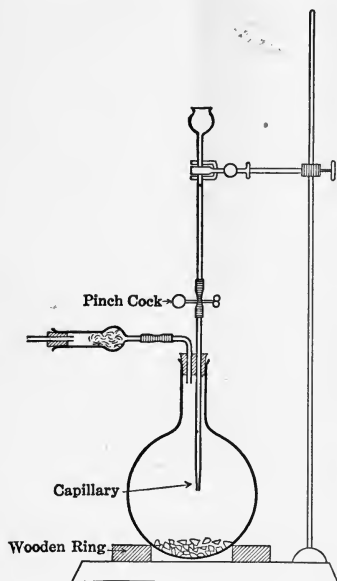


FIG. 8

(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 suited to cases in which 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.

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 $1\frac{1}{2}$ 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 auto-

matically 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

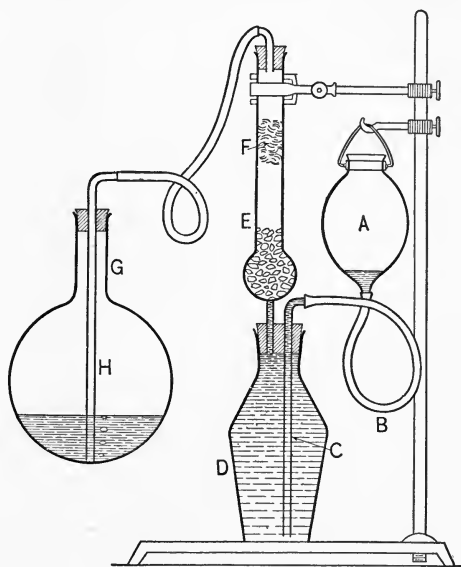


FIG. 9

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.

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 most easy 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 two volumes of hydrogen and one volume of oxygen are mixed, the gases entirely disappear after the reaction has taken place. When more than two volumes of hydrogen are taken to one of oxygen, the excess of hydrogen over the two volumes is found to remain unaffected; and likewise when more than one volume of oxygen is taken to two volumes of hydrogen, the excess of oxygen over the one volume is found to remain unchanged after the reaction. But to learn 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, when determined, is known as the combining ratio.

Similarly, exact ratios hold with respect to other chemical changes. When zinc and oxygen combine to form zinc oxide the ratio is found to be one of oxygen to 4.09 of zinc, no matter how much zinc or oxygen is used. The excess of one or the other is left over unless they are used in just this proportion.

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.

Experiments

WEIGHING

Two kinds of apparatus may be obtained for weighing:

1. **Rough balances or platform scales.** These are to be used for weighing out materials approximately for qualitative experiments and for weighing heavy objects of over 100 grams.

2. **Sensitive balances,** which will weigh accurately to a centigram. These are the balances in the 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 over 100 grams must be put on the sensitive balances. By no chance will any heavier object than this 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. If powdery, place on a piece of paper, if wet on a watch glass or in a beaker, the outside of which is clean and dry.

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

4. When altering 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.

1. THE COMBINING RATIO OF ZINC AND OXYGEN

Zinc and zinc oxide are both substances whose weight can be accurately determined, 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.

Weigh a 4-inch evaporating dish accurately. Place in it about 1 gram of turnings of chemically pure zinc and again weigh accurately. Cover the dish with a 5-inch watch glass; add 5 cc. of water and then add dilute nitric acid, a cubic centimeter at a time, until all the zinc has dissolved. Then remove the watch glass, and with the jet of the wash bottle rinse the drops clinging to it back 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 grows 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 it ceases to do so.

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

2. WEIGHT OF A LITER OF OXYGEN

The volume occupied by a given quantity of gas is influenced very appreciably by three factors: temperature, pressure, and content of aqueous vapor. The volume measured in this experiment must be reduced to what is known as standard conditions, that is, dry gas at 0° and 760 mm. pressure by means of the formula given on page 37. The oxygen used is obtained from potassium chlorate by heating, and its quantity is given by the loss in weight of that material.

For the apparatus to measure the volume of oxygen evolved (see Figure 10), clamp the wash bottle in an inverted position, re-

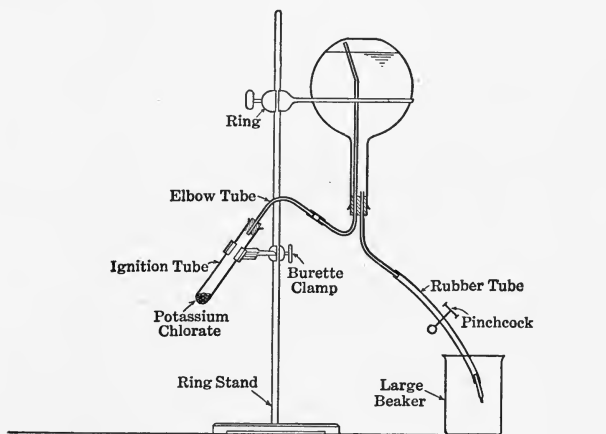


FIG. 10

move the capillary jet, and connect it to the other tube of the wash bottle by means of $1\frac{1}{2}$ feet of rubber tube, at the middle of which is placed a pinchcock. Connect the other tube of the wash bottle by means of an elbow tube with a hard glass test tube, which is to contain the potassium chlorate. Test the whole apparatus and make sure that it is tight. Fill the wash bottle with water nearly to the top of the vertical tube, allow enough to run out to fill the rubber tube and jet, and close the pinchcock.

Dry and weigh accurately the hard glass tube. Place in it about 2 grams of dry, powdered potassium chlorate and again weigh accurately. The potassium chlorate in the stock bottle is not dry and must not be used for this experiment. Use that in the

bottle marked for this purpose. Connect the tube with the apparatus. Dip the capillary jet in a beaker of water, and raise the latter 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. 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 clip and commence heating the potassium chlorate, so that a steady, but not a rapid, stream of water runs from the jet. If for any reason the heating is interrupted during the process, submerge the jet beneath the liquid, so that water, not air, shall 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. 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 scales* (be sure not to use balances at this point), 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. Calculate the weight of 1 liter of oxygen under standard conditions.

3. VOLUME OF HYDROGEN DISPLACED BY ZINC

By allowing an acid to act upon zinc a definite weight of the latter is dissolved, and the hydrogen set free can be measured and its volume corrected in a manner similar to that of the last experiment.

Experiment. (See Figure 11). Clamp a good sized 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 $1\frac{1}{2}$ feet 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 a $1\frac{1}{2}$ foot rubber tube to a trough. Over the end of this tube, which should have a right angle, 3-inch glass tube,

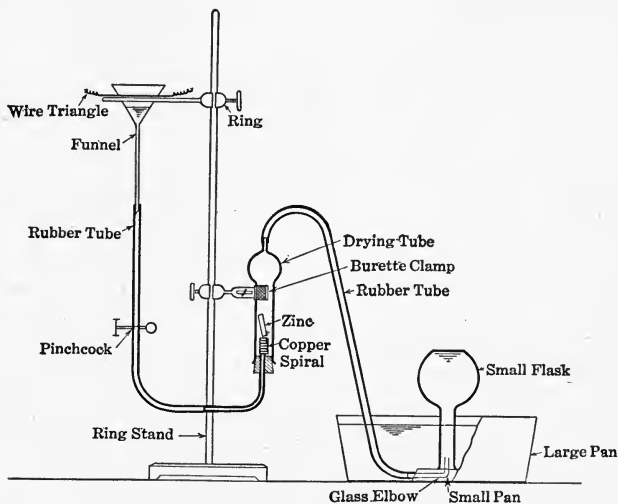


FIG. 11

invert a 250 cc. flask completely filled with water. Inside the drying tube is to be placed the zinc. Obtain a rod of it about $1\frac{1}{2}$ inches long and $\frac{1}{4}$ inch 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 pinchcock. When everything is ready pour hydrochloric acid into the funnel and allow it to pass the pinchcock until 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 through. 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 stopper it or mark the level.

Record temperature and barometric reading. Determine on the *platform scales* the weight of water required to fill the volume occupied by the hydrogen. Dry the zinc and weigh it again 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.

4. THE COMBINING RATIO OF HYDROGEN AND OXYGEN IN WATER

It is only with great care and refined apparatus that bodies of gases can be successfully weighed. It not being feasible then 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 hydrogen is led over the copper oxide, all which does not combine with the oxygen to form water will pass on unchanged. By retaining all the water formed 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 copper oxide, with the oxygen of which it combines, and then through another calcium chloride tube to absorb the water vapor formed.

Experiment. (See Figure 12.) To drive off any water which it may contain, heat 5 to 6 grams of copper oxide to redness in a porcelain boat. Place about 20 grams of feathered zinc in a generator bottle. Through a tight fitting, two-holed rubber stopper pass a thistle tube reaching to the bottom and an elbow tube just entering the top of the bottle. To the elbow tube connect a drying tube containing some loosely packed cotton; to this connect a U-tube with side arms filled with granular calcium chloride. This passes into a combustion tube about 10 inches long, which should be sloped downward at an angle of 5° to 10° . One end of the combustion tube should be drawn down in the blast lamp to fit

a rubber connector by which it is joined to the second drying tube. Do not neglect to round (with a file, or in the flame of a blast lamp) the sharp edges of the combustion tube before fitting the rubber stopper, as otherwise the latter would be cut and it would be difficult to make a tight joint. The second calcium chloride

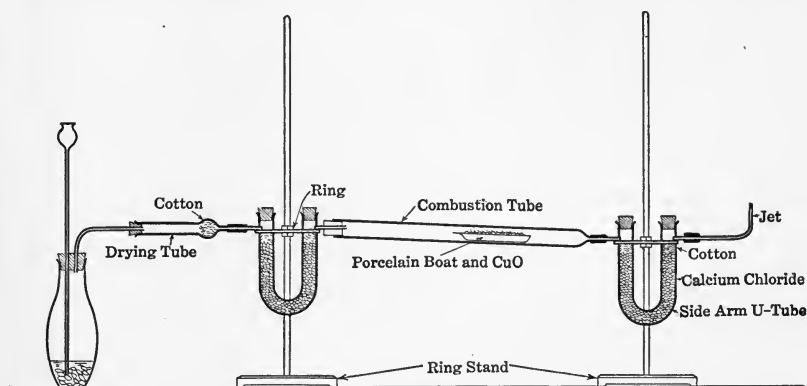


FIG. 12

tube should be prepared with especial care and be weighed 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 filling the generator bottle about $\frac{1}{2}$ inch deep with water; then holding a finger on the outer end of the apparatus and pouring more water into the thistle tube. If it sinks the apparatus is not tight. It must be made so.

Add a few cubic centimeters of hydrochloric acid to the generator bottle and then let hydrogen generate and slowly fill the apparatus while preparing the rest of the material. After it has cooled 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 collecting a 3-inch tube full by upward air displacement and carrying the tube, mouth downward, to a distant flame. If the gas does not explode, but burns

quietly, 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 may be left burning. Increase the evolution of hydrogen a little, being careful in adding acid to the generator not to allow it 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 5 minutes longer to sweep any last traces of oxygen from the apparatus, and then begin heating the copper oxide rather gently, using the flame spreader. The water vapor formed will partly condense, and great care must be exercised that it does not crack the heated tube. Before the experiment is ended this 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, disconnect between the generator and 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.

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 comes within the statement of the law of definite proportions, but it takes up the special case that two elements can form more than one definite compound. The first law holds for each of the compounds, the other states

that the definite ratios for the separate compounds are to each other in the ratio of small whole numbers. Perhaps the most easily understood statement of the law of multiple proportions is as follows: If the same weight of the first element is taken in each case, and such weights of the second element as will combine in each case with the same weight of the first element to form the different compounds are taken, these weights of the second element are to each other in the ratio of simple whole numbers.

The Atomic Theory. Dalton was impressed by the significance of these two laws 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 all of their other properties; the atoms of different elements differ in properties. When elements combine, it is the individual atoms which are concerned; they attach themselves to each other in definite and very simple groupings.

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 certain fact established by careful measurements. The theory is simply the best effort of the human mind to furnish an explanation of the facts.

It is likewise with 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 proportion 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 plain English, 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.

The atomic weight of zinc is therefore $4.09 \times 16 = 65.4$ if our assumption of the 1 : 1 ratio is correct. 65.4 grams of zinc is therefore 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. 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 all cases 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, deduce the atomic ratio by which sulphur and oxygen combine.

4. From the atomic weights printed in the table, find the combining ratio by weight in the compounds having the atomic ratio expressed by the formulas CaO , Li_2O , Fe_2O_3 , Fe_3O_4 . Also find the percent composition by weight of these compounds.

5. One oxide of chromium contains 52 percent of chromium and 48 percent of oxygen by weight; another contains 68.42 percent of chromium and 31.58 percent 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 $\text{Fe} = 72.4$; $\text{O} = 27.6$. Calculate the chemical formula of the oxide.

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

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 was 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, zero degrees Centigrade, 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

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

or

$$p_1 v_1 = p_2 v_2$$

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 degrees 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. As different gases were studied it was found that they obeyed this law pretty exactly until they got near 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, and finally helium

which was the last gas to succumb to efforts at liquefaction, follows the law with a good deal of accuracy down to within a very 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, a so-called "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

$$v = T \times k \quad (\text{pressure is constant})$$

where T stands for the absolute temperature, where k is a constant value, and where the pressure is invariable. If the volume of the gas is held constant then it is the pressure which must vary

$$p = T \times k \quad (\text{volume is constant})$$

When both pressure and volume may vary as well as the temperature we can use the equation

$$\frac{p_1 v_1}{p_2 v_2} = \frac{T_1}{T_2}$$

or

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

which embraces both Boyle's and Charles' Laws.

Dalton's Law. This law states 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.

Since the gases whose volumes we ordinarily have to measure 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. But before we can do this we must know the amount of water vapor and this can be determined at once if only one condition is met, that is that the gas is saturated with water vapor.

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 Figure 13.

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

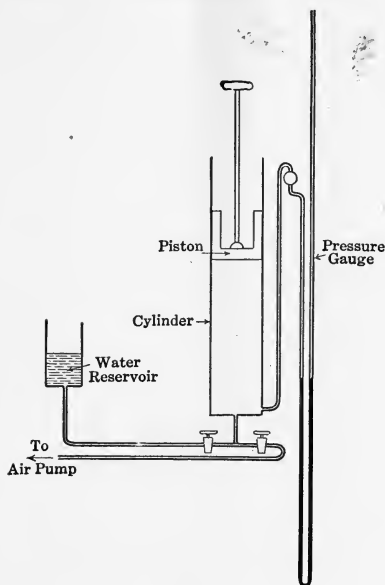


FIG. 13

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 slight flicker 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. Vapor must therefore condense to liquid water to maintain the exact state of saturation as the piston is pressed down; and when the piston is drawn up the liquid must evaporate fast enough to maintain a saturated condition of the vapor.

At 20° the concentration of saturated water vapor is such that the 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 all temperatures and the values from 0° to 100° are printed in the table on page 310 in the Appendix.

We shall now inquire as to the behavior of the water vapor if the cylinder contains also some permanent gas, for example, oxygen. Dalton's law would tell us that if the cylinder contained the same amount of water vapor its partial pressure would be exactly the same as if no oxygen were present, and that the total pressure of the gas in the piston would be the sum of the pressure of the oxygen and the pressure of the water vapor.

Experimentally we can test this deduction. Let dry oxygen 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 permanent 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 be certain 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 and this pressure 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 is 740 mm. But this pressure 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 glass is say 60 cc. Now, remembering Dalton's law, we can say that we have an amount of oxygen which at 20° and 722.6 mm. occupies a volume of 60 cc. We want to calculate its volume under standard conditions.

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

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

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

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 2275 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: When gaseous substance enter into chemical reaction with each other their volumes bear the relation to each other of small whole numbers; furthermore, if the products of

the reaction are also gases 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 offered 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 therefore not until 1860 that Avogadro's hypothesis was really taken seriously. Since then it has become one of the most important principles of Chemistry.

Demonstration that Molecules of Elementary Gases are Diatomic. Let us consider the following data which has been established by measuring combining volumes 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 one volume of oxygen contains 1 million molecules. Then the two volumes of water vapor according to Avogadro's hypothesis will contain 2 million molecules of water. But the water vapor is a homogeneous substance and, since it contains oxygen at all, every molecule of it must contain at least one 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 two atoms.

According to 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 two atoms.

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

Molecular Weights. Since the atomic weight of oxygen has been settled by convention as 16 and since there are at least two 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 at once determined if we know the weight of a measured volume of that gas under any stated conditions. Because from this, the weight of 1 liter of the gas under standard conditions can be computed, and 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 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. Since according to Avogadro's principle, the same volume would contain exactly 1 mole of any other gas under standard conditions, this volume assumes a great importance and it is named 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.

The actual number of molecules of a gas in 22.4 liters under standard conditions is 6.06×10^{23} . Although it has been only within the last two decades that this number has been ascertained, yet it is named Avogadro's number in honor of the man who reasoned out the principle on which this number rests.

Avogadro's number is the number of molecules in a mole of a substance: it is also the number of atoms in a gram atomic weight of an element.

Atomic Weights. In an earlier section we found the atomic weight of an element by multiplying 16, the atomic weight of oxygen, by the combining ratio of the element with oxygen and dividing 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 taken as 32 and first demonstrate that on this basis the atomic weight of oxygen is 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 percent by weight of oxygen in these compounds can be found by chemical analysis. This percent 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 following table a few typical examples are shown from a collection of the data for all gaseous or volatile oxygen compounds.

Substance	Weight in grams of 1 mole	Percent 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 oxy- chloride.....	153.4	10.43	16	1×16
Oxygen.....	32	100.	32	2×16

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 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 grams of mercury; furthermore when the molal volume contains a greater weight of these elements, the weight is in every case 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	Percent 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 acetic acid. 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 1.786 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 1.786 grams. 22.4 liters will weigh

$$\frac{22.4}{.6667} \times 1.786 = 60.01 \text{ grams.}$$

Thus the molecular weight is 60.01.

Chemical analysis shows that the composition of acetic acid is: C, 40 percent; H, 6.72 percent; O, 53.3 percent.

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

$$\text{C: } .40 \times 60.01 = 24.00 = 2 \times 12.01 \text{ grams}$$

$$\text{H: } .0672 \times 60.01 = 4.032 = 4 \times 1.008 \text{ grams}$$

$$\text{O: } .533 \times 60.01 = 31.99 = 2 \times 16.00 \text{ grams.}$$

Therefore the mole of acetic acid contains 2 gram atomic weights of carbon, 4 gram atomic weights of hydrogen, and 2 gram atomic weights of oxygen and the formula is $\text{C}_2\text{H}_4\text{O}_2$.

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 percent; hydrogen, 3.21 per-

cent; and bromine, 50.92 percent. Calculate the formula of the substance.

23. A certain compound of chlorine and copper is found to have the composition: copper, 64.2 percent; chlorine, 35.8 percent. 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 percent; hydrogen, 2.13 percent; bromine, 85.11 percent; 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 percent of chlorine and 61.89 percent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element so far as investigation of this one substance can give it?

26. Cyanogen contains 46.08 percent carbon and 53.92 percent nitrogen. Its density is 2.007 times that of air. Calculate its formula.

27. 0.5000 gram of a substance is burned in a current of pure oxygen in a combustion tube. 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 percent of hydrogen in the substance.

28. The products of combustion in No. 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 percent 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 Nos. 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 natural and artificial, 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 I

POTASSIUM NITRATE 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 electrified 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 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 and the latter may vary much or little with the temperature. The following table and diagram give the

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

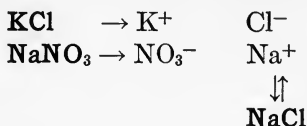
solubility at different temperatures for each salt. For example, at 10°, 21 grams of KNO₃ are soluble in 100 grams of water. This means that if an excess of solid potassium nitrate is shaken with pure water until no more will dissolve the clear solution will then contain 21 grams of KNO₃ for every 100 grams of water. On the other hand, if a solution of 42 grams of KNO₃ in 100 grams water obtained at a higher temperature is cooled to 10° and stirred for a while to bring about an equilibrium condition, 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 sodium nitrate and potassium chloride in equivalent amounts are added to 100 grams of water so that the total weight of K and NO₃ 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 equi-molal amounts of sodium nitrate and potassium chloride are taken and enough water added to dissolve at the boiling temperature all of the sodium nitrate taken or all of the potassium nitrate which could result from metathesis, but not enough to dissolve either the potassium chloride taken nor the sodium chloride which could be formed by metathesis. Nevertheless after this mixture is boiled a short time all of the solid potassium chloride disappears and the only solid salt left is sodium chloride.

The mechanism of the process may be more easily appreciated if it is represented on paper in the following fashion:



The formulas printed in bold face type stand for the substances in the solid state, — those in common type for substances in the dissolved state. Single arrows indicate that the reaction runs to completion in that direction under the conditions prevailing (the boiling temperature is supposed to be prevailing in the above representation). The double arrows indicate that an equilibrium is reached and no substance shown on either side of the arrows disappears from the sphere of action. If the conditions were to be shown at 0° solid potassium nitrate would have to be indicated in equilibrium with the dissolved salt.

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

Reagent: 1% AgNO_3 solution.

Apparatus: 500-cc. casserole.
 watch glass.
 5-inch funnel.
 perforated filter plate.
 800-cc. suction bottle and pump.
 platinum wire.

Procedure: Place the sodium nitrate and potassium chloride in a 500-cc. casserole. Add 210 cc. of water, cover with a watch glass, and place over a low flame. Keeping watch of the casserole to see that the 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 one minute, keeping the watch glass over the casserole to prevent too much evaporation of water. While it is at the boiling temperature, pour (see Figure 1, page 5) the mixture from the casserole onto the suction filter after first starting a gentle suction. Quickly scrape most of the damp salt onto the filter and suck out as much of the liquid as possible. Then return the solid salt, which is mostly NaCl ,

to the casserole. Pour the solution into a beaker and cool it to 15° or below by setting it in a pan of cold water or better ice water. Stir the crystallizing solution frequently so as to obtain a loose crystal meal which is easier to handle and drain on the filter than the larger crystals that would otherwise be obtained. Separate the crystals of KNO_3 from the cold liquor by means of the suction filter, observing last sentence of Note 3 on page 0, and pour the liquor into the casserole containing the first crop of NaCl crystals. Bring the solution to boiling point and boil gently three minutes without a watch glass over the casserole, thus allowing some of the water to escape by evaporation. Then filter at the boiling temperature exactly as in the first instance. Cool the filtrate and collect a second crop of KNO_3 crystals, adding them to the first crop and pouring the liquor into a flask labelled "Mother Liquors." Examine the two kinds of crystals, tasting them and using a microscope. Draw pictures in the note book of the crystals as seen in the microscope. Dissolve about 0.1 gram of the product in 2 cc. of water and test for chloride by adding 1 drop of AgNO_3 solution. Considerable chloride will be found and the product must be purified by recrystallization. Weigh the crystals roughly while they are still moist, add one half their weight of hot water, and warm until solution is complete. Cool to below 15° and separate the crystals from the mother liquor, adding the latter to the reserve flask. Test as above to see if this crop of crystals is free from chloride. If not repeat the recrystallization as many times as is necessary to get a perfectly pure product. A little of this when dissolved should give no turbidity with silver nitrate solution, and when held in the flame on a platinum wire should color it the violet color characteristic of potassium with none of the yellow sodium color. Spread the preparation on paper towels and allow it to dry by standing exposed to the air; then put up the salt in a 2 ounce bottle with a cork stopper and label it neatly. If the final yield of pure product is not satisfactory in amount the collected mother liquors should be boiled down to about 100 cc., and used as the starting point in a repetition of the above procedure. 50 grams may be regarded as a very satisfactory yield.

The sequence of the operations in this preparation can be followed rather more readily in the tabulated procedure shown on the following page.

TABULATED PROCEDURE

Treat 170 grams NaNO_3 and 149 grams KCl with 210 cc. water; heat to boiling and boil one minute; filter hot. Do not rinse out dish but keep it for second boiling.

<p><i>On filter:</i> NaCl, dirt, some KNO_3: transfer back to dish in which first boiling was made (1)</p>	<p><i>Filtrate: cool and filter</i></p>			
	<p><i>Crystals:</i> impure KNO_3 (2)</p>	<p><i>Filtrate</i> is saturated with KNO_3 and NaCl. Pour into dish in which original mixture was boiled and to which impure NaCl (1) was added. Bring to boil, boil 3 minutes, and filter hot.</p>		
	<p><i>On filter:</i> NaCl and dirt fairly free from KNO_3 (3)</p>	<p><i>Filtrate: cool and filter</i></p> <table border="1"> <tr> <td> <p><i>Crystals:</i> impure KNO_3 (4)</p> </td> <td> <p><i>Filtrate</i> is satu- rated with KNO_3 and NaCl. Save temporarily in flask labelled "Mother Liquors" (5)</p> </td> </tr> </table>	<p><i>Crystals:</i> impure KNO_3 (4)</p>	<p><i>Filtrate</i> is satu- rated with KNO_3 and NaCl. Save temporarily in flask labelled "Mother Liquors" (5)</p>
<p><i>Crystals:</i> impure KNO_3 (4)</p>	<p><i>Filtrate</i> is satu- rated with KNO_3 and NaCl. Save temporarily in flask labelled "Mother Liquors" (5)</p>			

RECRYSTALLIZATION

Unite impure KNO_3 (2) and (4); heat with one half their weight of water until dissolved; cool without filtering and collect the crystals that separate from the cold solution.

<p><i>Crystals:</i> Nearly pure KNO_3. Recrystallize repeatedly until en- tirely pure, adding all mother li- quors to (5) in the reserve flask.</p>	<p><i>Filtrate</i> contains nearly all of the NaCl from the impure product, and is saturated with KNO_3; add to (5) in the reserve flask.</p>
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Discard mother liquors (5) if the yield of pure KNO_3 is satisfactory.

QUESTIONS

1. Define metathesis.
2. When a metathetical reaction is carried out in the *wet way*, why is the solubility of the substances involved of importance? Explain why, according to this point of view, the reactions $\text{AgNO}_3 + \text{KCl} = \text{AgCl} + \text{KNO}_3$ and $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{NaCl}$ are much more complete than the reaction $\text{NaNO}_3 + \text{KCl} = \text{KNO}_3 + \text{NaCl}$.
3. Explain why fewer operations should be required to pre-

pare potassium nitrate from potassium sulphate and barium nitrate than by the foregoing procedure.

4. Explain why all of the solid salt should change to NaCl when the original materials are boiled with insufficient water to dissolve all of either the NaCl or the KCl.

5. In the tabulated procedure what is the advantage of adding the impure NaCl (1) to the second mother liquor instead of discarding it?

PREPARATION 2

CRYSTALLIZED SODIUM CARBONATE $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ FROM ANHYDROUS SODIUM CARBONATE

Many substances, as acids, bases, salts, oxides and even elements when they separate from solution, or crystallize, carry water with them. 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 usually known as water of crystallization. But 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. This water is held in the hydrate in chemical combination, more or less firmly, to be sure, but chemical nevertheless, because such substances always obey the law of definite proportions.

Soda ash is commercial anhydrous sodium carbonate. When a solution saturated at boiling temperature is allowed to cool to below 35° , a transparent crystalline mass separates of the formula $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, known commercially as *soda crystals* or *sal soda*.

This substance melts at about 35° but it does not yield a clear liquid; it gives rather a liquid in which is suspended a solid white substance of the formula $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The solution obtained by melting the decahydrate, is supersaturated with respect to the monohydrate, and the latter separates out leaving a solution which contains proportionately more water than the crystals of decahydrate. In the following preparation, if barely enough water were taken to form the decahydrate, a complete

solution could not be obtained because some monohydrate would separate. Enough water therefore is taken to hold all the monohydrate in solution. Besides the monohydrate and the decahydrate, there is at least one other well recognized hydrate, the heptahydrate $\text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O}$. This might, by chance, separate from the solution in the following procedure, but the decahydrate is far more likely to form. If after the solution has cooled to below 35° , the melting point of the decahydrate, a little crystal fragment known to consist of this hydrate is added, this will serve as a nucleus for the crystallization of decahydrate, and if any heptahydrate had already formed it would soon dissolve since it is more soluble than the decahydrate.

Materials: anhydrous sodium carbonate, Na_2CO_3 1 mole = 106 grams.

Apparatus: 500-cc. flask.
5-inch filter funnel.
6-inch crystallizing dish.
watch glass to cover dish.
filter plate.

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, p. 12. Fold an 8-inch paper filter, place it in the funnel, and pour the solution through the filter, collecting the clear filtrate in the crystallizing dish. Cover the latter and set it aside to cool slowly. After six 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 transfer them to some paper towels and dry them as directed in Note 9(b), page 15. When they are dry place the crystals in a 6 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 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ be prepared? (See preliminary discussion of this preparation.)

PREPARATION 3

POTASSIUM AND COPPER SULPHATE. $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6 \text{H}_2\text{O}$.

The preceding preparation illustrated the formation of a "molecular" compound. That is, starting with two substances, water and sodium carbonate, in which the ordinary chemical combining powers of the elements were seemingly satisfied, it was found that the compounds themselves would combine with each other. By this combination the character of the individual compounds was not destroyed altogether, their separate molecules apparently retaining their identity even in the combination. Hence the name molecular compound. The present preparation shows that two salts can form a molecular compound with each other and with water. Potassium sulphate ordinarily crystallizes from solution as anhydrous K_2SO_4 , copper sulphate as the hydrate $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, but when both salts are together in solution a compound hydrate separates $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6 \text{H}_2\text{O}$.

- Materials:* potassium sulphate 35 grams = $\frac{1}{5}$ mole.
 blue vitriol, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ 50 grams = $\frac{1}{5}$ mole.
- Apparatus:* 8-inch crystallizing dish.
 5-inch filter funnel and filter paper.
 thermometer.

Procedure: Grind the two salts together in a mortar until they are very finely powdered. Add the mixture to 250 cc. of water in a porcelain dish; raise the temperature to just 5° above the room temperature and keep it at that point during 10 minutes, while stirring all of the time with the stem of a thermometer. This gives a practically saturated solution of the double salt. Let the undissolved salt settle a moment and pour off the solution into another dish. With a little more water prepare in the same way a saturated solution of any residue that is left. Add a few drops of sulphuric acid to the entire solution, warm it to about 50° , and filter it, allowing the filtrate to run directly into the crystallizing dish. Set the solution away uncovered to crystallize

in a place protected from the dust; and, before it has cooled to below the saturation temperature, seed it with eight or ten small crystals of the double salt. Allow the solution to stand until a large crop of crystals has formed. Drain the crystals, wrap them in paper towels and dry them as directed in Note 9(b), page 15. If only a small amount of mother liquor is left, it may be discarded.

It is a matter of considerable difficulty to obtain clear, well-formed crystals of this salt, especially if the laboratory temperature varies a good deal. If the conditions are too unsatisfactory it is better to give up the attempt to get distinct crystals and to prepare, instead, a crystalline meal: Dissolve the same amounts of the two simple salts in 200 cc. of hot water; add a few drops of sulphuric acid; filter, and cool the solution rapidly in a flask while rotating it under the water tap. Drain the crystal meal on a suction filter and dry it as directed above.

QUESTIONS

1. Compare the color of crystals of the double salt with that of the simple salts. Likewise compare the color of the solutions. Does this indicate that the double salt exists in solution?

2. Try by experiment on a small scale whether a similar double salt containing ammonium sulphate in place of potassium sulphate can be prepared. Dissolve 1 gram of the ammonium sulphate and 2 grams of blue vitriol in 10 cc. of hot water. Pour through a filter and collect the 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). Probably the crystals will be small and a microscope will help. Notice whether in color and shape they resemble the simple salts or the double salt of the main preparation.

Repeat the same experiment with sodium sulphate (1 gram anhydrous Na_2SO_4) and copper sulphate.

Experiments

HYDRATES

1. **Water of Crystallization.** Heat a crystal of blue vitriol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ rather cautiously in a dry test tube holding the latter 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 wall 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 crystallization in crystals is in a true state of chemical combination, for the hydrated crystal shows all the characteristics of a chemical compound.

First: its physical properties such as color (in this instance) and crystalline form are altogether different from those of the anhydrous salt or of water.

Second: it follows the law of definite proportions, every sample of blue vitriol for example having exactly the composition expressed by the formula $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. (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 clay 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 $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ (atomic weights in appendix).

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 much inferior to that holding the elements together in the simpler compounds.

3. Efflorescence. Leave some crystallized sodium sulphate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ or zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or soda crystals $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ uncovered on a watch glass for some time.

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

This change is caused by the loss of water of crystallization from the crystal, leaving either the anhydrous salt or a less hydrated salt (of definite composition however). If the experiment is repeated leaving the hydrated salt under a bell jar in which was also set a dish of water no efflorescence is observed. Pure water exerts a higher pressure of aqueous vapor than does the crystal hydrate, and hence the hydrate is prevented from efflorescing. In the average laboratory air, however, the pressure of aqueous vapor is rarely over 50 percent of the saturation value. If the existing pressure is less than that which the hydrate can exert, the hydrate will effloresce, otherwise not. Blue vitriol exerts a rather low vapor pressure, one which is ordinarily exceeded by the aqueous vapor in the air; but on very dry days the pressure of aqueous vapor in the air sometimes falls below that of the blue vitriol and, on such days only, may this salt be observed to effloresce.

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

4. Deliquescence. Leave small lumps of calcium chloride, zinc chloride, potassium hydroxide, sodium hydroxide, or ferric chloride in a watch glass and note that in a few minutes the surface becomes covered with liquid, and that after a longer time the lumps have completely changed to liquid.

This liquefaction is due to condensation of the water vapor of the air and the dissolving of the solid material in the condensed water. All deliquescent substances are extremely soluble in water. The tension of the vapor escaping from water is always lessened by substances dissolved in the liquid water, and when this tension is lowered to below that of the water vapor existing in the atmosphere the water vapor ceases to escape. Indeed the opposite takes place, namely water vapor condenses. In general substances will deliquesce when the aqueous tension of their saturated solutions is less than the tension of water vapor in the air.

If these deliquescent substances were put under a bell jar, together with a shallow dish containing concentrated sulphuric acid to absorb the water vapor, it is obvious that they would not deliquesce; in fact, if they have already deliquesced and are placed in such a dry atmosphere the water will evaporate and they will again change to dry solid substances.

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. This indicates that the "primary" valence of the element is satisfied in the simple compounds, and that it is only some sort of a minor or "secondary" valence which holds the substances in combination.

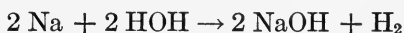
When elements react with water, however, a change in the primary valences is usually involved.

A rather unusual instance of a hydrate of an element is chlorine hydrate, $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$, 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. Fill a small beaker to about 2 cm. depth with cold water; place it on a desk top well removed from any bystander, and at arms length drop a small bit of metallic sodium on to the water. 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. This explosion is accidental and may be due to an impurity in the sodium.

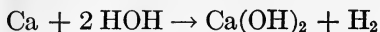
The gas evolved is hydrogen; the alkaline character of the solution is due to sodium hydroxide which is left dissolved in the water



Sodium is a much more active element than hydrogen and has displaced an equivalent amount of the latter from water. Sodium hydroxide then may be regarded as water in which sodium has taken the place of one half of the hydrogen.

6. Calcium and Water. Calcium is a very tough metal and is difficult to cut or break. A lump of it may be taken to a silversmith and rolled into a thin sheet and the latter may be cut into small pieces with tinsmith's shears. Drop one or two small bits of calcium 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 due to the separation of a white finely divided 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



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 $\text{Ca}(\text{OH})_2$ shows that an atomic weight in grams of calcium can take the place of two gram atomic weights of hydrogen, in other words the valence of calcium is two.

Although 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 on 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. Note that the magnesium is without perceptible action on water, either cold or boiling.

(b) To try the effect of hot magnesium in dry steam, clamp a piece of hard glass tubing 1 cm. in diameter (arsenic tubing) in position at an angle of about 5° with the horizontal. Connect the lower end of the tube with the wash bottle in such a manner that steam generated by boiling the water may be conducted through the tube. Connect the upper end of the tube with a delivery tube, 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 hard glass tube. Pass steam through it, and cautiously commence heating 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 is so much colder than the kindling temperature. As soon as the magnesium catches fire make the steam pass vigorously again and slip a test tube full of water over the mouth 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 caught in the trough 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. Since a good deal of rubbing is necessary, it is obvious that 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.

Drop a small lump of magnesium amalgam into a test tube of cold water. A violent reaction takes place. A gas is freely evolved which burns like 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 surface of the amalgam is liquid or at least semi liquid so that no coherent film of magnesium hydroxide can adhere.

That magnesium must be a vastly 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 sensibly diminish the vigor of the reaction for the incandescence was practically as bright as if the magnesium ribbon had been burning in oxygen.

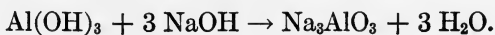
8. Iron and Water. Iron filings do not produce any measurable evolution of hydrogen either in cold or hot water. Arrange to pass steam through a tube arranged as in experiment 7b and containing iron filings. Heat cautiously to dry the liquid water and then heat the iron filings strongly. As the steam from the delivery tube condenses in the water in the trough it is now seen that an occasional bubble of gas rises. Before long enough collects to test and it proves 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 measureably rapid.

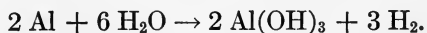
9. Removal of protective coating by chemical action. Note that aluminum metal is like magnesium in that it displays a brilliant metallic luster when its surface has just been scraped but it quickly loses the brightness of its luster.

Drop some aluminum turnings into some sodium hydroxide solution. Note that gas is immediately given off, which a test shows to burn like hydrogen and that the aluminum in time dissolves completely.

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



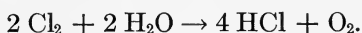
With the aluminum hydroxide coating thus continually removed in this way there is nothing to prevent the progress of the primary reaction



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 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 cc. of a colorless gas collects 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 and is thus shown to be 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



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

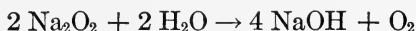
OXIDES AND WATER

Nearly all of the elements are capable of combining with oxygen to form oxides, but there seems to be some sort of a residual combining power, for all of the oxides have a greater or less tendency to combine with water or with other oxides. The oxides of metals combine with water to form bases: the oxides of non-metals combine with water to form acids.

11. Sodium Oxide and Water. Support a porcelain crucible cover or a broken piece of a porcelain dish on a triangle

and heat it to redness; while it is thus hot, place upon it, by means of iron pincers, a small piece of sodium the size of a small pea. Remove the lamp and let the sodium burn. When cold dissolve the 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. This oxide has twice as much oxygen to a given weight of sodium as another oxide Na_2O . The latter can be prepared by heating together sodium peroxide and sodium out of contact with the air. When sodium peroxide is treated with water it reacts according to the equation



thus losing one half of its oxygen and yielding the same soluble product as when the ordinary oxide of sodium combines with water

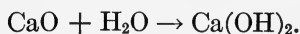


Sodium hydroxide, NaOH , is very soluble in water; it is one of the strongest *bases*.

12. Calcium Oxide and Water. The well known substance quick lime is calcium oxide. Calcium oxide could be made by burning bits of the metal calcium, but the oxide so coats over the surface of the lump that it is difficult to make the interior portions of the lump burn. So for this experiment take a lump of quick lime 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 and gives off clouds of steam, and swells up and tumbles apart to form a fluffy white powder. Stir some of this powder with water. It makes a milky looking suspension which will turn litmus blue. If some of this suspension is placed in a tall bottle the white powder settles and a clear liquid remains above. This liquid colors litmus blue. Taste it by taking a teaspoonful

of it in the mouth; note the taste and remember that it is described as an *alkaline* taste. The liquid is called lime water.

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



The same substance is formed here, calcium hydroxide, as is obtained by the action of calcium metal on water, only in this case no hydrogen is displaced. The primary valence of the calcium is already satisfied in calcium oxide and it is not necessary to dispossess hydrogen in order to get the oxygen or hydroxide radical to satisfy that valence. Calcium hydroxide is not very soluble in water and mainly on that account it is not as strong a base as sodium hydroxide.

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 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 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.

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 less soluble 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 amounts 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 chalk with a

piece of wire, and scooping out one end, but the charcoal, of which a much larger piece should be taken, 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. Instead of preparing the carbon dioxide solution in the above way a siphon of "soda water" may be bought at a drug store. In this bottle water has been saturated with carbon dioxide under a high pressure, and consequently there is a good deal more of the substance dissolved and its properties are more easily detected. Take a little of the soda water in the mouth and compare its taste with that of lime water. This has an *acid* rather than an alkaline taste.

This experiment shows that oxides of non-metals produce acids and also that the acids vary a good deal in their strength.



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

WATER CONTAINS TWO SEPARATELY REPLACEABLE PORTIONS OF HYDROGEN

In the formation of a base by the direct action of a metal on water hydrogen was displaced, and the substance sodium hydroxide or calcium hydroxide was left. The formula NaOH or Ca(OH)_2 shows our knowledge that the compound still contains one half of the hydrogen of the original water, but let us think ourselves for a moment 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 an amount was displaced from the hydroxide just equal to that displaced by the metal from the water when the hydroxide was prepared they drew the conclusion that water contained two parts of hydrogen in combination with one part of oxygen, and this experiment was

one of the strongest 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, and place the mixture in a hard glass test tube fitted with a delivery tube. Heat the mixture in the tube and 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 are 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. The following definitions make clear the methods of stating concentrations and the problems illustrate the advantages of the method.

DEFINITIONS

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 the dissolved substance in one liter of the solution. Note. 1 liter of the solution contains less than 1000 grams of water, but the weight of the whole solution is usually more than 1000 grams.

Equivalent. An equivalent weight of a substance is identical with the mole when the valence of both radicals is one. *e.g.* HCl , HNO_3 , $NaCl$. When the radicals have higher valences, the equivalent weight contains that weight of each radical which could either combine with or replace 1 gram atomic weight of hydrogen. Thus the moles of $CuSO_4$, H_2SO_4 , $CuCl_2$ each contain 2 equivalents.

Normal Solution. A normal solution contains one equivalent weight of the dissolved substance in 1 liter of solution.

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 term mole has no certain meaning, 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.

Concentration. The concentration of a solution may be expressed in terms of the molal, normal, or formal amounts of dissolved substance. Thus 10 liters of 0.1 normal HCl contain the same amount of acid as 1 liter of normal or as 100 cc. of 10 normal HCl.

PROBLEMS

- How many times normal is each of the following solutions?
 - molal H_2SO_4 .
 - formal $\text{Al}_2(\text{SO}_4)_3$.
 - molal AlCl_3 .
 - 0.1 molal Na_3PO_4 .
 - 3 molal H_2SO_4 .
 - 6 molal HNO_3 .
 - 2.5 formal MgSO_4 .
- How many times formal are the following solutions?
 - 6 normal HCl.
 - Normal Na_3PO_4 .
 - 0.5 normal K_2SO_4 .
 - 0.1 normal $\text{K}_4(\text{FeC}_6\text{N}_6)$.
 - 0.4 normal $\text{Ba}(\text{OH})_2$.
 - normal CuSO_4 .
- What is the normality of a solution of HCl containing 39 percent by weight of HCl and of spec. grav. 1.19?
 - of a solution of HCl containing 20 percent by weight and of spec. grav. 1.12?
 - of a solution of HNO_3 containing 68.6 percent by weight and of spec. grav. 1.41?
 - of sulphuric acid containing 96 percent H_2SO_4 and of spec. grav. 1.84?
- What is the percent by weight of the following solutions?
 - 6-normal HNO_3 , spec. grav. 1.195.
 - 6-normal HCl spec. grav. 1.100.

(c) 6 normal H_2SO_4 spec. grav. 1.181.

(d) 0.5 normal $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ spec. grav. 1.00.

5. How many cc. of the concentrated sulphuric acid of 3 (d) should be taken to make one liter of normal solution?

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

7. (a) How many cc. of 6 normal HCl are needed to dissolve 1 gram of zinc. $\text{Zn} + 2 \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$?

(b) How many cc. of hydrogen are evolved?

8. (a) What weight of calcium carbonate will react with 1 liter of 6 normal HCl ? $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$.

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

9. It is desired to find the concentration of a solution of calcium hydroxide. 500 cc. of this solution are carefully measured into a beaker, litmus is added and a 0.5 normal 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 percent by weight (spec. grav. = 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

When a substance dissolves in a liquid it becomes dispersed just as a gaseous substance is dispersed. It behaves in every way similarly to a gas except that the space between its molecules is occupied by the liquid instead of being vacant. Indeed the dissolved substance, the *solute*, obeys almost quantitatively the gas laws (see Chapter I).

But abnormality is observed with a certain class of dissolved substances which are called electrolytes. Solutions of electrolytes conduct electricity very well, although the pure substance, and the pure solvent by themselves do not conduct. Methods of determining the number of molecules present in solutions of electrolytes — freezing point method, osmotic pressure method, etc. — show more molecules to be present than could be accounted for if the substance existed as an ordinary gas. These facts are accounted for by the Theory of Ionization according to which electrolytes in solution are dissociated into their radicals, and furthermore these radicals are electrically charged. These charged independent radicals are free to move in opposite directions under electrical attractions and thus the solutions conduct electricity. Since by the act of ionization an ordinary molecule breaks up into two (Na^+Cl^-) three ($\text{Ca}^{++}\text{Cl}^-\text{Cl}^-$) ($\text{K}^+\text{K}^+\text{SO}_4^{--}$) four ($\text{Fe}^{+++}\text{Cl}^-\text{Cl}^-\text{Cl}^-$) ($\text{Na}^+\text{Na}^+\text{Na}^+\text{PO}_4^{---}$) or even five ($\text{K}^+\text{K}^+\text{K}^+\text{K}^+\text{Fe}(\text{CN})_6^{----}$) charged radicals, or ions, each of which behaves in most respects like an independent molecule, it is clear that the theory of ionization accounts for the abnormally large number of molecules as well as for the electrical conductivity.

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. Success of the experiment depends on using *small 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.

In fact, the salts at once commence to dissolve, forming thin layers of very concentrated solution about each lump. At the surface separating each of these layers of solution from the water glass, there forms a coherent film of the insoluble silicate of the metal. This film is an osmotic membrane which allows water to pass either in or out; but the molecules of salt, not being able to pass through, exert against it their osmotic pressure, and cause it to stretch or even break. If it breaks, a new surface of the salt solution is exposed to the sodium silicate, and a new film forms. Since the film is thinnest at the top the growth is mainly at the top and thus the little tubes of silicate of the metal shoot up through the solution. Clusters of these tubes of various colors give an appearance of plant growth within the liquid.

Record this experiment in the note book, giving a description and an explanation in your own words. Wash out 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 ends of desks, a diagram of which is given in Figure 14.

Electrodes A consist of stout copper wires, and are to be used in testing the conductivity of solid substances, lumps of which are held with the fingers in such a way as to come into contact with each electrode. A 16-candle power lamp may be used in the socket above.

Electrodes B consist of similar copper wires, but bent far enough apart so that they will pass into the two arms of a U-tube 8 mm. internal diameter and 7 cm. high, when the latter is raised from underneath. A 50-candle power lamp (or, somewhat less satisfactorily, a 32-candle power lamp) should be used with these electrodes, which are then designed to show differences in conductivity among good conductors.

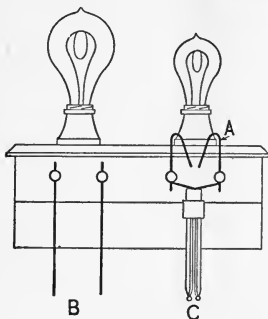


FIG. 14

Electrodes C consist of fine platinum wires supported upon glass rods, and are to be used with a 16-candle power lamp. They are to be used in testing the conductivity of liquids, the latter to be placed 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 pure water until when they are held for 10 seconds or more immersed in distilled water no sign of a *glow* is seen in the lamp filament. To illustrate the necessity for this precaution, immerse the electrodes, first in hydrochloric acid solution, then, without rinsing, immerse them in pure water.

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 C 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, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

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 $\frac{1}{4}$ 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 $\frac{1}{4}$ 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 $\frac{1}{2}$ gram sugar, $\frac{1}{2}$ gram urea, $\frac{1}{2}$ cc. alcohol, $\frac{1}{2}$ cc. glycerine each in 10 cc. of water, and test the conductivity of the solutions.

3. Acids. 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 diluted with 10 to 20 parts of water, and also of other common laboratory acids diluted with water.

Look up the percent of ionization in 0.1 normal solution of each of the acids. What component is common to all acids and is responsible for the characteristic properties of acids? Name three 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 normal hydrochloric and acetic acids by diluting 5 cc. of acid from bottle labeled 1-normal with 45 cc. water. Carefully compare the conductivity of these 0.1 normal acids using Electrodes C. Carefully compare the intensity of the sour or acid taste. Quite a bit of experimenting is necessary to find just the amount of acid to take and how long to hold it on the tongue in order to get a fair estimate of the comparative acidity. It must also 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, rinse out the mouth and wait a short time before tasting another. Compare the effect of the two 0.1 normal 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 likewise to be proportional to the degree of ionization; even the weaker acid contains enough hydrogen ions to completely 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 normal solution:

(1) water, (2) un-ionized acid, (3) hydrogen ion, (4) acid radical ion. Arrange the tabulation for each acid somewhat on the following plan.

COMPONENTS IN 1 LITER OF 0.1 NORMAL ACETIC ACID

total acetic acid	$0.1 \times 60 =$	6.0 grams
water	$1000 - 6 =$	994 "
ionized acetic acid	$\dots\dots\dots =$	"
un-ionized acid	$\dots\dots\dots =$	"
H ⁺ ion	$\dots\dots\dots =$	"
C ₂ H ₃ O ₂ ⁻ ion	$\dots\dots\dots =$	"

5. Bases. 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 6-normal 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 6-normal KOH and again with a drop of 6-normal NH₄OH.

Look up the percent of ionization in 0.1 normal solution of each of the bases. What component is common to all bases and is responsible for the characteristic properties of bases? Name three 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 one liter of 0.1 normal solution.

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

Run 10 cc. of molal hydrochloric acid into a beaker, add 1 drop of litmus solution, and then add molal 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. Also write the ionic equation.

Write ionic equations from now on whenever it is possible. Use the intersecting method as described in the notes in the second part of this chapter.

8. Neutralization of a Weak Acid and a Weak Base. Test separately the conductivity of molal acetic acid and of molal ammonium hydroxide, this time using electrodes C. Neutralize 10 cc. of the molal acid by adding the molal base in the same manner as in No. 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.

Remember the injunction at the end of the preceding experiment to write ionic equations as a part of the explanation of every reaction. Do not however neglect to give the explanation in words as well as by means of ionic equations.

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 quite a different kind of electrodes 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 contained. Remember that the neutral solution in each experiment is one half normal 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 C.

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.

10. Displacement of a Weak Acid from its Neutral Salt by Means of a Stronger Acid. (a) Heat 2 cc. of a solution of sodium acetate to boiling in a test tube and observe if there is any odor. Add a few drops of a strong acid and observe if the odor of acetic acid (vinegar odor) can be detected.

How does this experiment illustrate the displacement of a weak acid from its salt? Suppose that exactly equal volumes of 0.2 normal $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.2 normal HCl had been used, what percent of the way to completion would the reaction have taken place? Compare the completeness of this reaction with that of neutralization.

(b) To 2 cc. of a solution of sodium sulphite add hydrochloric acid and observe the odor. Compare this odor with that of the bottle of sulphurous acid. Is this reaction more or less complete than the one in *a*? Sulphurous acid dissociates non-electrolytically



and sulphur dioxide is expelled from a solution by boiling. What effect would boiling the solution have on the degree of displacement of the weak acid?

(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? If the gas had been prevented from escaping by holding the solution under high pressure, state what components the solution would hold, and roughly the relative amounts of each.

(d) Treat a small quantity of marble dust (calcium carbonate)

with an excess of dilute hydrochloric acid, and see if it will all dissolve. Calcium carbonate usually passes as an insoluble substance, nevertheless it is slightly soluble in pure water. Look up its exact solubility. How would the acid react with the small amount 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. The Displacement of a Weak Base from its Neutral Salt by Means of a Stronger Base. Warm 2 cc. of ammonium chloride solution, and observe if there is an odor. Add 2 cc. of sodium hydroxide solution, and again observe if there is an odor.

The odor is that of the gas NH_3 and it indicates the presence of ammonium hydroxide in the solution. If equal volumes of cold 0.2 normal solutions of NH_4Cl and NaOH are mixed to what degree of completion does the reaction proceed? The amount of NH_3 gas escaping from such a cold solution is negligible. If the solution is boiled, facilitating the escape of NH_3 what will be the final result?

12. The Displacement of an Insoluble Base from its Neutral Salt by Means of a Strong Base. To 2 cc. of magnesium sulphate solution add a little sodium hydroxide solution. Look up the solubility and the degree of ionization of magnesium hydroxide.

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 instantly 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 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 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.

13. Chloride Ions. To solutions of various chlorides, say hydrochloric acid, sodium chloride, and calcium chloride, add a few drops of a solution of a silver salt — silver nitrate or silver sulphate.

To a solution of potassium chlorate (be sure that it is 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?

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

Repeat the experiment using lead nitrate instead of barium chloride as the reagent.

15. Copper Ions. (a) To a solution of cupric salt, say CuSO_4 , add NH_4OH in small amount and then in excess.

In writing ionic equations consider the light blue precipitate as $\text{Cu}(\text{OH})_2$, for the sake of simplicity, instead of the rather indefinite basic salt. To explain the deep blue color see note on Ammoniates later in this chapter.

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

16. 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 demonstrate the presence of a small amount of zinc salt in a solution containing copper salt.

17. Ferrous Ions. Repeat *a* and *b* of Experiment 15 upon a ferrous salt instead of a cupric salt.

(c) to a solution of ferrous sulphate add potassium ferricyanide $K_3(Fe(CN)_6)$.

18. Ferric Ions. (a) To a solution of ferric salt say $FeCl_3$ 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.

19. Silver Ions. (a) Recalling Experiment 13 state how chloride ions may be used as a reagent for silver ions.

(b) To 2 cc. of $\frac{1}{15}$ -normal silver nitrate solution add NH_4OH very carefully. Even a few drops of the 6-normal reagent will prove an excess. So dilute 1 cc. of the reagent with 10 cc. of water in another test tube, dip a stirring rod in this solution and carry it, hanging to the rod, a drop at a time to the $AgNO_3$ solution.

Find in a reference book the formula of the ammonio-silver ion.

20. Electromotive Series of the Metals. (a) Place a few pieces of zinc in 5 cc. of $\frac{1}{5}$ -normal 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 0.2 molal $CuSO_4$ solution and some clean pieces of iron wire.

(c) Again repeat (a) using 5 cc. of $\frac{1}{15}$ -normal $AgNO_3$ 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.

21. Hydrolysis. Dissolve about half a 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.

22. Hydrolysis a Reversible Reaction. Place $\frac{1}{2}$ gram of solid zinc chloride in a dry test tube and add water a single drop at a time with constant shaking until the solid dissolves giving a clear sirupy solution. Then fill the tube half full with water and observe the flocculent precipitate. Now add hydrochloric acid, drop by drop, till the precipitate disappears.

Assuming the precipitate to have been basic zinc chloride, $\text{Zn} \begin{cases} \text{OH} \\ \text{Cl} \end{cases}$ explain its formation from the components of the solution, and explain why a slight excess of hydrochloric acid causes it to disappear.

23. Solubility Product. Recall that a saturated solution can be prepared by stirring an excess of the powdered substance for a very long time with water. The undissolved material can be allowed to settle and the clear saturated solution may be decanted off or poured through a filter. Note however that the solubility of silver acetate and potassium chlorate, the salts used in this experiment, varies very greatly with the temperature. If a saturated solution were prepared one day in a stock bottle and the bottle allowed to stand on the reagent shelf over night, at the lower temperature during the night the solution would become supersaturated and crystals of the salt would separate out. In the morning when it warmed up again the solution would be very much undersaturated, and it would take prolonged stirring to get it again saturated. Hence it is useless to perform this experiment unless one makes certain that he really has a saturated solution to start with.

(a) Place 2 cc. of a saturated solution of silver acetate in each of three test tubes. Add to one tube a small crystal of silver nitrate (not more than 0.05 gram). Agitate the solution until the crystal has completely dissolved. If no change is noticed at once, set the tube aside for several minutes and observe again.

To the second tube add a small crystal of sodium acetate instead of silver nitrate, and to the third tube add a crystal of ammonium nitrate somewhat larger than either of the crystals already used. The ammonium nitrate should have been tested to see that it contains no chloride.

Silver acetate is only slightly soluble, that is, about 10 grams per liter at 20° C.

Put all the waste from this experiment in the bottle marked *silver residues*.

(b) Repeat the above experiment, substituting a saturated solution of potassium chlorate and crystals of potassium chloride, sodium nitrate, and sodium chlorate.

24. Effect of Its Neutral Salt on 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 or hydroxyl ions. In the presence of hydrogen ions it is pink, and of hydroxyl ions yellow; with varying very small concentrations of hydrogen ions it shows intermediate colors.

In four test tubes place respectively 10 cc. normal HCl, 10 cc. normal HAc, 10 cc. normal HAc, 10 cc. normal NaOH, and to each add two drops of methyl orange solution. The first tube shows the pink color imparted by strong acids and the fourth the yellow color imparted by bases. 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, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ and dissolve the salt by shaking. Now compare the colors of the second and third tubes, still keeping the first and fourth 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 20 cc. of normal acetic acid, the other of 20 cc. of normal acetic acid in which an equivalent amount, about 3 grams of sodium acetate $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ 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 entirely dissolve.

Notes and Problems

MEASUREMENT OF IONIZATION

Molal Lowering of the Freezing Point. Dissolved substances have the effect of lowering the temperature at which the solvent freezes, and a very remarkable *law* is found to hold in regard to the extent of this effect, namely:

Equimolal amounts of all dissolved substances whose solutions do not conduct electricity have the same effect upon the freezing point of the solvent, irrespective of the weight in grams or the chemical nature of the substance.

The freezing point lowering is proportional to the number of moles of solute in a given weight of solvent, and for one mole of solute in 1000 grams of water the lowering is 1.86 degrees Centigrade. This figure is known as the *molecular lowering of the freezing point* for water.

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 1000 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° ?

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. When a substance dissolves in a solvent its molecules lose their cohesion for each other just as when a solid or liquid substance is changed to a gas. The dissolved state is like the gaseous state, in that the molecules of the dissolved substance are widely separated; it differs, in that the space between the molecules is filled with the solvent.

A dissolved substance will diffuse so as to make its concentration uniform throughout the solution, just as a gas will expand to fill uniformly the vessel in which it is confined. The pressure with which dissolved substances tend to diffuse from a part of the solution at any given concentration into an adjacent portion of pure solvent is called osmotic pressure, and this pressure is not only of the same nature as gas pressure, but it also obeys the same laws, — Boyle's, Charles', and Avogadro's laws. One mole of any

non-electrolyte in 22.4 liters of water at 0° has an osmotic pressure of 1 atmosphere — the same pressure as 1 mole of a gas exerts at the same temperature and volume.

Of course the osmotic pressure is manifest only between different points within the body of liquid in question. The dissolved substance not being able to escape beyond the surface of the solution, because of the cohesive power of the whole solution, osmotic pressure will obviously not be exerted against the glass walls of a containing beaker, or against the air above 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, $\text{CO}(\text{NH}_2)_2$, 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?

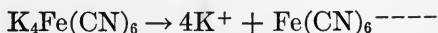
Ionization. The ions of a substance in solution exert, of course, enormous attraction for ions of opposite charge, but since there are ions of opposite charge lying in every direction from each individual ion, the effect of this electrostatic attraction is nullified and each ion exists as a freely moving independent unit in the solution. As such it should exert the same osmotic pressure and have the same effect upon the freezing point as any complete un-ionized molecule.

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 $\text{K}_4\text{Fe}(\text{CN})_6$ in 500 grams of water?



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 1000 grams of water if the salt is 86 percent ionized?

21. — of 0.1 mole of BaCl_2 in 1000 grams of water if the salt is 72 percent 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 1000 grams of water freezes at -0.454° , we know that 0.1 mole of un-ionized substance will lower the freezing point $0.1 \times 1.86 = 0.186^\circ$, and that 0.1 mole of a completely ionized substance giving 3 ions will lower the freezing point $3 \times 0.186 = 0.558^\circ$. 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, $0.454 - 0.186 = 0.268^\circ$, by that which would be caused by 100 percent ionization, $0.558 - 0.186 = 0.372^\circ$, thus giving $0.268/0.372 = 0.72$. Thus the salt is 72 percent ionized.

22. If 9.45 grams of chloroacetic acid, $\text{H}(\text{C}_2\text{H}_2\text{O}_2\text{Cl})$, dissolved in 1000 grams of water show an osmotic pressure of 2.51 atmospheres, find the percent 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 1000 grams of water freezes at -3.05 . Calculate what percent of the salt is ionized.

EXTENT OF IONIZATION

The solvent is undeniably the agent which causes ionization. Hence the more solvent, in other words, the more dilute the solutions, the greater the percent of the molecules that will be ionized. In very dilute solutions (1 mole of solute in 10,000 liters of solvent) strong electrolytes are practically completely ionized. In concentrated solutions they are less ionized; for example, hydrochloric acid in 12-normal solution is only 13 percent ionized.

In the following table are given the degrees to which various typical electrolytes are ionized; it will be noticed that the figures given represent the percent of the solute that is ionized when the solute is in 0.1 equivalent solution. It must be remembered that

in more concentrated solutions this percent is always smaller, and in more dilute solutions it becomes larger and approaches 100 percent as a limit at great dilution.

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 , $Ba(NO_3)_2$, $FeCl_3$, $K_3[Fe(CN)_6]$, K_2SO_4 , and $ZnSO_4$, respectively.

Type of salt	Percentage ionization in 0.1 equivalent solution
R^+R^-	86
$R^{++}R^-R^-$	72
$R^+R^+R^{--}$	72
$R^{+++}R^-R^-R^-$	65
$R^+R^+R^+R^{--}$	65
$R^{++}R^{--}$	45

ACIDS

Substance	Percentage ionization in 0.1 equivalent solution
HCl, HBr, HI, HNO_3 }	90
$HClO_3, HClO_4, HMnO_4$ }	
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	90
$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$	30
$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	50
$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	20
$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$	1
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	27.
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$	0.2
$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$	0.0002
$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	20
HF	9
HNO_2	7
$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.4
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	0.12
$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$	0.002
$H_2S \rightleftharpoons H^+ + HS^-$	0.05
$HS^- \rightleftharpoons H^+ + S^{--}$	0.0002
$HCN \rightleftharpoons H^+ + CN^-$	0.01
$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	0.01

BASES

Substance	Percentage ionization in 0.1 equivalent solution
KOH, NaOH.....	86
Ba(OH) ₂ ⇌ Ba ⁺⁺ + 2 OH ⁻	75
NH ₄ OH.....	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 percent 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 much less basic than AgOH, while hydroxides of the type Fe(OH)₃, Cr(OH)₃, Al(OH)₃ are least basic of all.

Pure water contains 0.0000001 mole of H⁺ ions and 0.0000001 mole of OH⁻ ions per liter.

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. But this is more or less in the realm of speculation. 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. These reactions conform to the law of definite proportions and to all the ordinary principles of chemistry. According to the present state of our knowledge we class these reactions as non-ionic, and for most purposes 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, since if a pure substance, for example, sodium chloride, which is of course un-ionized, is dissolved in water it becomes largely changed into what we may justly regard as two new substances, $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$. We know (see table of ionization values) that if 0.1 mole NaCl is dissolved in 1 liter of water, 86 percent becomes changed to ions. In other words, the reaction just written proceeds 86 percent of the way towards completion. We have also learned that if 0.1 mole of NaCl is dissolved in 10,000 liters of water the ionization becomes practically complete. In other words, the reaction has proceeded 100 percent of the way towards completion. If now this very dilute solution is evaporated until but 1 liter of water is left, we have the 0.1 mole of NaCl again in 1 liter, and at this concentration we know it is but 86 percent ionized. In other words, the reaction of association (the opposite of ionization) $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$ must have progressed 14 percent of the way towards completion. Obviously, this reaction is reversible, and such a condition is indicated in an equation by employing arrows pointing in both directions:



Equilibrium. When 0.1 mole of NaCl is dissolved in 1 liter of water and the two opposing reactions have adjusted themselves so that 86 percent of the salt is in the ionized condition and 14 percent 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 case 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 a salt 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 two volumes of hydrogen (uncombined hydrogen, not hydrogen ions) are mixed with one 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 catalyzers, the two gases will combine completely to form water, even if the tem-

perature 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 $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, and yet at ordinary temperature and without catalyzers the reaction is so slow that it will not have reached an equilibrium condition in a 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:

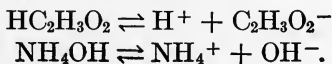
(1) Solid substances are underlined: *e.g.*, NaCl.

(2) The un-ionized part of substances in solution is shown by the molecular formula without ionic charges: *e.g.*, $\text{HC}_2\text{H}_3\text{O}_2$.

(3) Ionized substances in solution are shown by the formulas of the ions: *e.g.*, Na^+Cl^- .

(4) All salts, and strong acids and bases (that is, those which are as much as 45 percent 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^- ; $2\text{H}^+\text{SO}_4^{--}$.

(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.*:



(6) Solid substances formed in a reaction and thus precipitated are indicated by an arrow pointing downward: *e.g.*, $\text{AgCl} \downarrow$

(7) Gaseous substances formed in a reaction and thus escaping from the solution are indicated by an arrow pointing upward: *e.g.*, $\text{CO}_2 \uparrow$

(8) Intersecting equations. The ionization of a substance is itself a reaction which requires an equation; when the products of this reaction enter other reactions, the whole course of the process can be shown only by a series of equations. To show their interdependence these equations should be arranged to intersect, the formula of the component common to two equations being written at the point of intersection.

METATHESIS

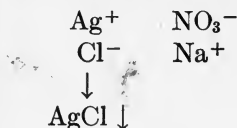
Metathesis, or double decomposition, is one of the main types of chemical reaction, and it takes place between two compounds, consisting merely in an interchange of radicals, the positive radical of the first compound pairing off with the negative radical of the second, and the negative radical of the first pairing off with the positive of the second. Such a reaction involves no change whatever 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 extremely soluble, and reference to the table of ionization values shows that each of the three is highly ionized; on the other hand, AgCl is highly insoluble. The latter salt, therefore, precipitates

until there are left in solution only the extremely few of its ions corresponding to the solubility of silver chloride.



For writing the equations of ionic reactions the set of rules given on page 86 has been devised. Silver nitrate and sodium chloride are each about 86 percent ionized, according to the table. In the equation these substances both appear as completely ionized, the 14 percent 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 percent 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 percent ionized at the start.

Sodium nitrate, according to the table, is 86 percent ionized. Hence 14 percent 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 $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$, which, for convenience, was arranged in a vertical line.

Experiments have shown that any ionized silver salt, *e.g.*, Ag_2SO_4 , $\text{AgC}_2\text{H}_3\text{O}_2$, AgClO_3 , may be substituted for AgNO_3 , and any ionized chloride 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, as, for example, BaSO_4 .

The above principles do not apply solely to silver salts and chlorides, but to all solutions. A mere turning to a table of solubilities will inform one whether 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 86. 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. $\text{AgNO}_3 + \text{NaCl}$.
25. AgCl (solid) + NaI .
26. 1 mole $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$ (solid) + 1 liter normal HNO_3 .
27. 1 mole Ag_2SO_4 (solid) + 2 liters normal HNO_3 .
28. $\text{BaCl}_2 + \text{Na}_2\text{CO}_3$.
29. $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$.
30. PbSO_4 (solid) + Na_2S .
31. $\text{Cd}(\text{NO}_3)_2 + \text{Na}_2\text{S}$.
32. $\text{CaCl}_2 + \text{Na}_2\text{SO}_4$.
33. CaSO_4 (solid) + Na_2CO_3 .
34. BaSO_3 (solid) + HCl .
35. BaSO_4 (solid) + HCl .

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 of 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.

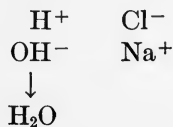
Since we may see in the table of ionization values that pure water contains but 0.000,000,1 mole of H^+ ions and 0.000,000,1 mole of OH^- ions per liter, we may know in advance that when an acid and a base are mixed the H^+ and OH^- ions cannot remain in the presence of each other, but must unite according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



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 reaction consists essentially only of the formation of water from its ions.



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)

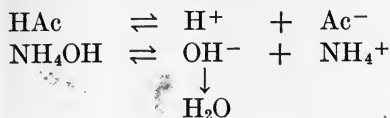
	HCl	HNO ₃	HC ₂ H ₃ O ₂	H ₂ S
NaOH.....	13,700	13,700	13,300	3,800
KOH.....	13,700	13,800	13,300	3,800
NH ₄ OH.....	12,400	12,500	12,000	3,100

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 percent ionized in 0.1 normal solution. Ammonium hydroxide is typical of a rather weak base, it having the same degree of ionization, namely, 1.4 percent in a 0.1 normal solution, as acetic acid. 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:

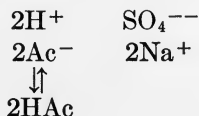


As this train of reactions proceeds it is obvious that NH_4^+ and Ac^- ions, that is, the ions of the salt ammonium acetate, accumulate in the solution, and that their presence accounts for the high conductivity of the neutral solution.

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 for 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 1700 calories must have been absorbed in the ionizing of the acid and the base.

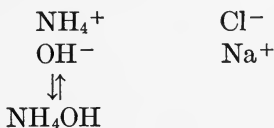
Displacement of a Weak Acid from its Salt. Sodium acetate is a salt of acetic acid, but a solution of this salt has none of the pungent odor of acetic acid, not even if it is warmed. If, however, a strong acid like sulphuric acid is added to the solution, an unmistakable odor of acetic acid is at once manifest.

The neutral salt contains acetate ions, but the attraction of oppositely charged sodium ions prevents them from escaping from the solution to give an odor, even if one could expect charged ions to have any of the same properties as uncharged HAc molecules. With the addition of sulphuric acid, however, the ions of acetic acid are brought into the presence of each other, and they must at once reach a condition of equilibrium with the un-ionized molecules. From the table of ionization values we see, therefore, that $100 - 1.4 = 98.6$ percent of these ions unite to form un-ionized acetic acid; and since this substance is known to be somewhat volatile and to possess a very powerful odor, the observed effect is accounted for.



This process is usually spoken of as the displacement of the weak acid from its salt; the ions of the salt of the stronger acid remain in the solution. If we were always to think solely from the ionic viewpoint, perhaps we should want to describe this process as the formation of the weak acid from its ions.

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.



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,



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,

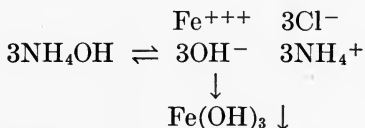


Therefore, whenever NH_4^+ and OH^- ions are brought together, they must come to equilibrium with a large proportion of NH_4OH and the latter must come to equilibrium with NH_3 and H_2O and, through the NH_4OH , the NH_3 and H_2O must be in equilibrium with the ions. In dilute solutions where the proportion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

ucts 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 Metal Hydroxides. The metallic elements as a class are characterized chemically in that their hydroxides are basic. The hydroxides of the alkali metals, of which sodium and potassium are the most common, are very strong and very soluble bases. The hydroxides of the alkaline earth elements, calcium, strontium, and barium, are very strong bases, but they are not as soluble as the alkali metal hydroxides.

The hydroxides of the heavy metals are, as a rule, very insoluble and very weakly basic. Addition of a soluble base, even as weak a base as ammonium hydroxide, may be expected to displace the hydroxide of a heavy metal from a solution of its salt. Thus when ammonium hydroxide is added to a solution of ferric chloride a voluminous reddish brown precipitate of ferric hydroxide separates.

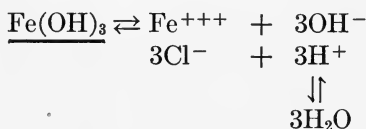


If an amount of ammonium hydroxide equivalent to the ferric chloride is taken, this reaction runs so nearly to completion that no detectable trace of Fe^{+++} ions is left in the solution.

The hydroxides of such metals as iron, copper, silver, and lead do not show to any marked degree the characteristic properties of turning litmus blue, or of alkaline taste, or of producing a slippery feeling when rubbed between the finger tips. Their main claim to classification as bases lies in their ability to neutralize acids; to illustrate, let us consider the cases of ferric hydroxide and copper oxide.

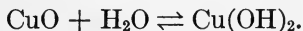
If the ferric hydroxide produced by the addition of ammonium hydroxide to a ferric chloride solution is collected on a filter and washed with water, a reasonably pure substance of the composition given by the formula $\text{Fe}(\text{OH})_3$ is obtained. If this substance is rinsed into a beaker with a considerable amount of pure water and stirred, a thick reddish brown suspension is obtained, but after this has stood for some time it separates, the insoluble $\text{Fe}(\text{OH})_3$ col-

lecting at the bottom, clear water only remaining in the upper part of the beaker. Litmus dipped into the liquid is unaffected. If now such an amount of hydrochloric acid is added to the beaker that 3 moles of HCl are used for every mole of $\text{Fe}(\text{OH})_3$, and the whole is stirred, the reddish brown substance dissolves and a perfectly clear yellow solution fills the beaker. Furthermore, this solution is not strongly acid, as we should expect had the $\text{Fe}(\text{OH})_3$ not been suspended in the water to which the HCl was added. It is true that this solution will color litmus red, showing that the acid is not fully neutralized, but an accurate measurement of the H^+ ion concentration (by methods which we will not elaborate here) will show that it corresponds not to the strength of hydrochloric acid, but very nearly to that of the weak acetic acid. The very weak base, $\text{Fe}(\text{OH})_3$, then is able to neutralize to a large extent the effects of a strong acid. Why the acid is not completely neutralized will appear under the discussion of hydrolysis in the next section.

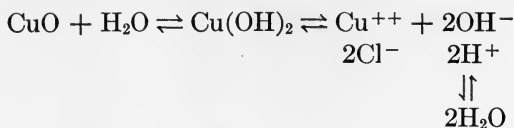


If black, finely powdered copper oxide, CuO , is stirred with water, it settles out again very quickly, and the water has not acquired sufficient basic properties to affect litmus. If an equivalent amount of hydrochloric acid, that is, 2 moles for every mole of CuO , is added and thoroughly stirred, the solution immediately acquires a blue green color and in sufficient time the whole of the black copper oxide is dissolved. This solution, like the one previously discussed, shows very little acid strength.

Copper oxide is not itself a base, but it is very closely allied to copper hydroxide,



Mere contact with water does not seem to cause the copper oxide to change appreciably to the hydroxide, but we can at least assume a slight tendency for this to happen. Addition of acid would neutralize the copper hydroxide and removal of the latter would allow the conversion of more copper oxide to hydroxide; thus the train of reactions may be pictured as follows:



If the solution of copper salt is kept at ordinary temperature the addition of a soluble base causes a light blue precipitate to appear, having a variable composition but approximating to the formula $[\text{Cu}(\text{OH})_2]_3 \cdot \text{CuCl}_2$. If we direct our attention particularly to the $\text{Cu}(\text{OH})_2$ in the formula, the reaction becomes essentially a combination of Cu^{++} and OH^- ions to form the weak base $\text{Cu}(\text{OH})_2$.

The oxides of the alkali and alkaline earth metals combine energetically with water to form hydroxides which are strong bases. By comparison the oxides of the heavy metals combine sluggishly with water, but the oxides themselves may be said to possess somewhat the same basic properties as the hydroxides, because they do have the property of neutralizing acids.

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, as in the case of precipitation.

When the products of a reaction taking place in solution are all 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 complete escape of one of the products as a gas, just as in the case of precipitation, and consequent removal of one of the products 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:

36. $\text{HNO}_3 + \text{NaOH}$.
37. $\text{HC}_2\text{H}_3\text{O}_2 + \text{NH}_4\text{OH}$.
38. $\text{Mg}(\text{OH})_2$ (solid) + HNO_3 .
39. CuO (solid) + H_2SO_4 .

40. H_2S (gas) + NaOH .
41. NH_3 (gas) + HCl .
42. $\text{H}(\text{C}_7\text{H}_5\text{O}_2)$ (solid) + NaOH .

Benzoic acid $\text{H}(\text{C}_7\text{H}_5\text{O}_2)$ is sparingly soluble and a little stronger than acetic acid.

43. $\text{K}(\text{C}_7\text{H}_5\text{O}_2)$ + HCl .
44. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ + HNO_3 . Note odor.
45. $(\text{NH}_4)_2\text{SO}_4$ + NaOH . Note odor.
46. NH_4Cl (in excess) + $\text{Ca}(\text{OH})_2$ (solid).
47. CaCO_3 (solid) + HNO_3 .
48. CaCO_3 (solid) + $\text{HC}_2\text{H}_3\text{O}_2$.
49. FeS (solid) + HCl .
50. MgCl_2 + NaOH .
51. MgCl_2 + NH_4OH .
52. MgCl_2 + NH_4Cl + NH_4OH .
53. $\text{Ca}(\text{OH})_2$ (solid) + FeCl_3 .

54. $\text{Ca}(\text{OH}_2)$ (saturated solution) + CO_2 (gas, in moderate amount and then in excess).

COMPLEX IONS

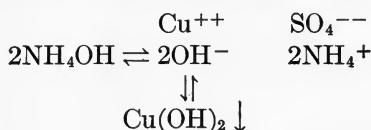
Ammoniates. Review what was said in Chapter II about water of crystallization and hydrates. Two definite crystalline compounds of sodium carbonate and water are the monohydrate and the decahydrate. Both of these will dissolve in water but both solutions are absolutely identical. Furthermore, either one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

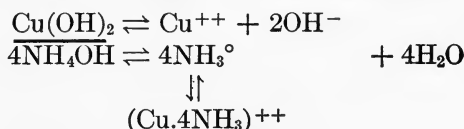
There are other substances than water, notably ammonia, which form compounds similar to hydrates, in this case ammoniates. Numerous solid compounds containing ammonia of crystallization are known, for example ammonio-copper sulphate $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ which is the subject of one of our later preparations. 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.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 for simplicity we shall treat as the simple hydroxide.

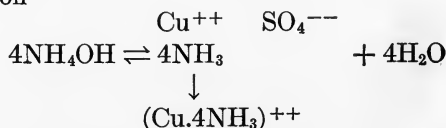


Addition of more ammonia quickly causes this precipitate to redissolve giving an intensely deep blue solution



The hydroxide of the ammonio-cupric radical, unlike that of the simple cupric radical, is very soluble and highly ionized.

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 $2\text{NH}_4\text{OH}$, which will cancel. The total result when four moles of ammonia are added to one mole of copper salt is given by the equation



the resulting solution containing ionized $(\text{Cu.4NH}_3)\text{SO}_4$ 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

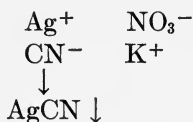
in basic strength with one of sodium hydroxide. Such a solution is known as Schweitzer's reagent and it has the remarkable property of being able to dissolve cellulose (wood fiber and filter paper are composed of cellulose).

It is most interesting that the addition of ammonia to the simple ions of several of the heavy metals produces similar effects. The basic 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:

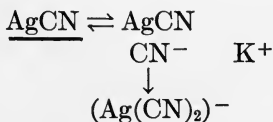
copper	(ous)	(Cu.2NH ₃) ⁺
	(ic)	(Cu.4NH ₃) ⁺⁺
silver		(Ag.2NH ₃) ⁺
zinc		(Zn.4NH ₃) ⁺⁺
cadmium		(Cd.4NH ₃) ⁺⁺
nickel		(Ni.4NH ₃) ⁺⁺
cobalt	(ous)	(Co.4NH ₃) ⁺⁺
	(ic)*	(Co.6NH ₃) ⁺⁺⁺

Aluminum, iron, tin, lead, and some other metals seem to be wholly devoid of the power of forming such ammonio compounds.

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



When another equivalent of potassium 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.

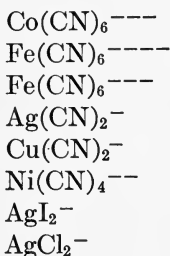


We assume that the very few dissolved un-ionized AgCN molecules in equilibrium with the solid, combine with CN⁻ ions to form the

* The ammonio-cobaltic and similar cobaltic compounds are very numerous and very complicated; the formula given represents the most typical.

complex ion $(\text{Ag}(\text{CN})_2)^-$. Continual removal of AgCN molecules from the solution prevents an equilibrium with the solid being restored and the latter thus dissolves completely.

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



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

The ions NO_3^- , SO_4^{--} , PO_4^{---} are so very stable that we do not think of them as other than simple ions. Nevertheless they are obviously complex and they are probably similar in nature to the complex ions just considered except for the fact that any simple ions out of which they might be supposed to be built have never been identified.

PROBLEMS

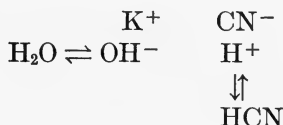
Describe observable effects and write the fully ionized equation for the following cases, when the reagent (second formula) is added (a) in limited amount, and (b) in excess.

55. $\text{ZnSO}_4 + \text{NH}_4\text{OH}$.
56. CuCl solid + NH_4OH .
57. $\text{Ag}_2\text{SO}_4 + \text{NH}_4\text{OH}$.
58. $(\text{Cu} \cdot 4\text{NH}_3)\text{SO}_4 + \text{HNO}_3$.
59. $(\text{Ag} \cdot 2\text{NH}_3)\text{Cl} + \text{HNO}_3$.
60. $\text{AgNO}_3 + \text{KI}$.
61. AgCl (solid) + NaCl (saturated solution, in very large excess).
62. $\text{FeSO}_4 + \text{KCN}$.
63. $\text{FeCl}_3 + \text{KCN}$.

HYDROLYSIS

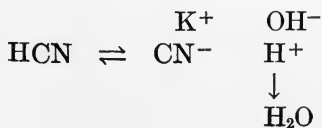
The ionization of water is so small that in most cases it can be totally disregarded. It cannot be neglected, however, in solutions of salts when either the acid or the base — or both — from which the salt is derived, is extremely weak.

Potassium cyanide is the salt of the weak hydrocyanic acid, HCN (ionization = 0.01 percent in 0.1 equivalent solution), and the strong base, potassium 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:



The salt, in accordance with the general rule for salts, will exist in solution in the ionized condition. Water is in equilibrium with an almost infinitesimal 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 immediately reestablished 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 potassium hydroxide are mixed:

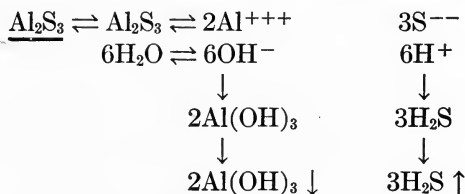


The few ions furnished by the acid combine at once with OH^- ions of the base to form water, and this removal of H^+ ions allows more of the acid to ionize. This cycle of operations repeats itself until we have the same state of equilibrium as existed in the solution obtained by dissolving pure potassium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

The reaction of neutralization in this case goes about 99 percent of the way to completion when equivalent amounts of the acid and base are mixed. The reverse reaction, that is, the hydrolysis of potassium cyanide, progresses only about 1 percent 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.

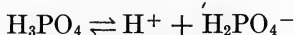
Aluminum sulphide furnishes a good example of this, for when it is treated with water its hydrolysis is complete:



Note in this reaction that solid $\underline{\text{Al}_2\text{S}_3}$ disappears, and solid $\text{Al}(\text{OH})_3 \downarrow$ and gaseous $\text{H}_2\text{S} \uparrow$ 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

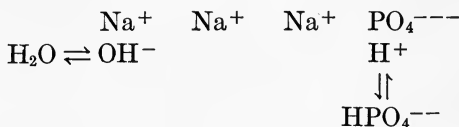


to the extent of 27 percent in 0.1 equivalent solution. The fairly high concentration of H^+ ions thus established prevents appreciable ionization of the H_2PO_4^- ion, but if one equivalent of NaOH is added for each mole of H_3PO_4 , the H^+ ions from the first H radical are entirely removed and the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

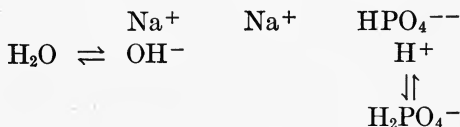


to the extent of 0.2 percent. If a second equivalent of NaOH is now added, the HPO_4^{--} ion is enabled to ionize to the extent of 0.0002 percent.

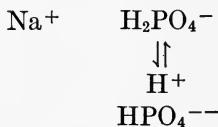
When the hydrolysis of the salt of a polybasic acid is considered, the different H radicals must be treated separately. Thus when 1 mole of tertiary sodium phosphate, Na_3PO_4 , is dissolved in water, hydrolysis takes place very extensively as follows:



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.

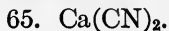


When primary sodium phosphate, NaH_2PO_4 , is dissolved, a weakly acid solution is obtained, this effect being due to the tendency of the second hydrogen radical of the acid to ionize.



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 with a fully ionized equation.



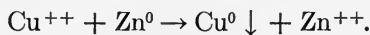
- | | |
|---|---------------------------------|
| 68. $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$. | 73. NaH_2PO_4 . |
| 69. Na_3AsO_4 . | 74. Na_2HPO_4 . |
| 70. Na_2CO_3 . | 75. Na_3PO_4 . |
| 71. NaHCO_3 . | 76. AgNO_3 . |
| 72. NaHSO_4 . | |

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 hydrogen 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 hydrogen 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 has consisted 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:



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:

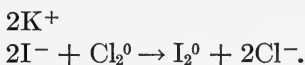


The metals, including hydrogen, may be arranged in the order in which they strive to pass into the ionic condition, as, in this case, zinc does at the expense of copper. Such a series is known as the Electromotive Series, because the electromotive force of such reactions, if properly disposed in a cell, may be made to send a current through an external wire connector. (See Electromotive Series, Appendix. p. 310.)

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, *viz.*: F, Cl, Br, I, S, 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 minus one to zero; as, for example, in the reaction,



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

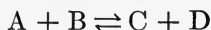
In the left-hand column state the observable effect and in the right-hand column write the fully ionized equations.



79. Cu (metal) + HCl.
80. Ag (metal) + AuCl₃.
81. Cu (metal) + PtCl₄.
82. AgCl (finely divided solid) + Zn (zinc dust).
83. Ag (in a photographic print) + PtCl₄.
84. FeCl₂ + Cl₂.
85. CuCl (solid) + Cl₂.
86. Na (metal) + H₂O

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

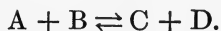


to proceed to the right is determined by the concentrations of A and B, whereas the tendency to proceed to the left is determined by the concentrations of C and D and that equilibrium is reached when the effects of these two opposing changes exactly nullify each other.

A fairly exact quantitative relationship exists among the concentrations of all the components of a reversible reaction when this reaction is at equilibrium and 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⁺, C₂H₃O₃⁻ and HC₂H₃O₂. *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 6 grams (0.1 mole) of HC₂H₃O₂. Dividing the amount (0.1 mole) by the volume, 0.1 liter, gives the ratio 1 and thus the concentration of the total acetic acid is 1 F. W. (formula weight)

per liter. Since the fraction ionized is 0.014 the concentration of hydrogen ion $[H^+]$ * is 0.014; the concentration of the acetate ions $[C_2H_3O_2^-]$ is also 0.014 and the concentration of un-ionized acetic acid $[HC_2H_3O_2]$ is $1 - 0.014 = 0.986$.

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



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

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

exactly undo the effect of each other making the total change zero. Therefore

$$\text{vel } (\rightarrow) = \text{vel } (\leftarrow)$$

$$k_1 [A] [B] = k_2 [C] [D]$$

or

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

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



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

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

The speed of the opposing reaction is given by

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

and the condition of equilibrium is given in the expression

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

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° .



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

$$\text{vel } (\rightarrow) = k_1 [\text{SO}_3] [\text{SO}_3] = k_1 [\text{SO}_3]^2.$$

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

$$\text{vel } (\leftarrow) = k_2 [\text{O}_2] [\text{SO}_2] [\text{SO}_2]$$

$$= k_2 [\text{O}_2] [\text{SO}_2]^2$$

and the equilibrium condition is determined by the expression

$$\frac{[\text{SO}_2]^2 \cdot [\text{O}_2]}{[\text{SO}_3]^2} = K.$$

Interesting as the foregoing line of reasoning is, and logical as the deductions seem to be, the scientists who thought it 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.

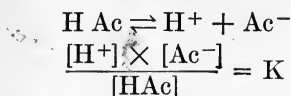
Thus actual measurements of the three components in solutions containing acetic acid, hydrogen ions, and acetate ions show that, whatever the actual concentrations, the ratio always has the same value, namely that of the equilibrium constant.

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 figured 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. In many respects all strong electrolytes do actually behave in solution as if they were in fact completely ionized. Some chemists are inclined to believe that this is really true, and that the methods used for measuring degree of ionization, — electrical conductivity and freezing point, — by which the figures printed in the table in this chapter are determined, do not really give the true results. Be this as it may, there is good justification for employing the approximation of considering strong electrolytes as completely ionized, when no great degree of accuracy is needed. On the other hand the degree of ionization of weak electrolytes follows with a high degree of accuracy the law of molecular concentration.

PROBLEMS

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



88. Find the percent 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 percent 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 percent 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 moles of NH_4Cl per liter assuming the latter to be completely ionized.

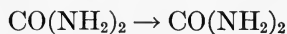
93. What is the ionization constant of hydrocyanic acid if the ionization in 0.1 normal solution is 0.01 percent?

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 percent ionized?

SOLUBILITY AND SOLUBILITY PRODUCT

The dissolving of a substance has been variously considered as a physical and a chemical change, but at all events it is a reversible change which like reversible chemical reactions is subject to the law of molecular concentrations.

When a solid non-electrolyte such as urea is placed in water it begins to dissolve according to the reaction



but, as the urea accumulates in solution, the reverse reaction becomes more and more rapid until its speed is just equal to the rate of solution, at which point equilibrium is established. Applying the expression for equilibrium

$$\frac{[\text{CO(NH}_2)_2]}{[\underline{\text{CO(NH}_2)_2}]} = \text{constant}$$

we arrive at a conclusion which is quite in accord with the facts. For the concentration of the solid urea is a perfectly definite and unchangeable quantity, in other words it is a constant; then by transposing the equation we obtain

$$[\text{CO(NH}_2)_2] = \frac{[\text{CO(NH}_2)_2]}{[\underline{\text{CO(NH}_2)_2}]} \times \text{constant} \\ = \text{constant}_2$$

This is simply an expression of the well-known fact that the solubility of urea is a perfectly definite quantity for a definite temperature. It should be particularly noticed that the solubility depends in no way on the quantity of solid material left in contact with the solution. Equilibrium can exist as well between a single small fragment of the solid and the solution as it can when there is a large amount of the solid present.

Now that we have considered the simplest case of equilibrium between a solid and its solution we are in a position to understand the more complex case in which the dissolved substance is ionized. Let us consider for example the sparingly soluble silver bromate



If we consider the soluble portion to be entirely ionized as a justifiable approximation when only moderate accuracy is desired, it is apparent that, to add a particle to the crystal, an Ag^+ ion and a BrO_3^- ion must collide at the same instant at the same spot

of the crystal surface. The velocity of crystallization is therefore proportional to the product of the concentration of the two ions

$$\text{Vel} (\leftarrow) = k_1 \times [\text{Ag}^+] \times [\text{BrO}_3^-]$$

whereas the velocity of solution is proportional to the fixed quantity, the concentration of the solid AgBrO_3 of the crystal

$$\text{Vel} (\rightarrow) = k_2 \times [\text{AgBrO}_3].$$

The equilibrium constant therefore is given by the expression

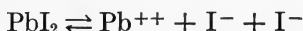
$$\frac{[\text{Ag}^+] \times [\text{BrO}_3^-]}{[\text{AgBrO}_3]} = K$$

or since $[\text{AgBrO}_3]$ is constant

$$[\text{Ag}^+] \times [\text{BrO}_3^-] = K_2 = \text{solubility product.}$$

This is known as the solubility product.

Let us consider a solid salt which gives three ions in solution, lead iodide for example



In this case three ions must collide simultaneously at the surface of the crystal to produce a building up and the velocity of crystallization is

$$\begin{aligned} \text{Vel} (\leftarrow) &= k_1 \times [\text{Pb}^{++}] \times [\text{I}^-] \times [\text{I}^-] \\ &= k_1 \times [\text{Pb}^{++}] \times [\text{I}^-]^2 \end{aligned}$$

Whereas the velocity of solution is again proportional to the fixed concentration of the solid crystal or

$$\text{Vel} (\rightarrow) = k_2 \times [\text{PbI}_2].$$

Therefore the solubility product is given by the expression

$$[\text{Pb}^{++}] \times [\text{I}^-]^2 = K_2 = \text{solubility product.}$$

It has already been stated that the ionization of strong electrolytes in solution does not conform closely to the law of molecular concentrations. However in the case of saturated solutions the equilibrium between the solid salt and its ions in solution does conform very closely to the general law and this specific case is known as the *principle of solubility product*.

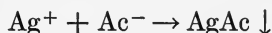
In a saturated solution of any electrolyte the product of the concentrations of its ions is a constant at any given temperature. This

principle is of great value in calculating the solubility of any given salt in a solution containing another salt with an ion in common with the given salt.

An example will make the application of this principle clear.

Let us prepare a saturated solution of silver acetate by shaking some of the solid salt for a long time with pure water. Let the surplus salt settle, then pour a little of the clear solution into a small beaker. Now drop a clear lump of sodium acetate into the beaker. The latter salt is excessively soluble and will have completely dissolved within a few moments. Very shortly there is seen a cloud of fine flaky crystals settling from all parts of the solution. This clearly is a different substance from the sodium acetate added, and tests upon it easily show that it is silver acetate.

The solution was already saturated with silver acetate. The excess of acetate ions supersaturated the solution and the solid separated according to the reaction



until the solution was left exactly saturated, at which point the product of the concentrations of the two ions was exactly equal to the solubility product. Naturally, under this new condition of equilibrium, there are many more acetate ions than silver ions in solution, but the product is equal to the same value as in a solution of silver acetate alone, in which the concentration of the two ions is the same.

If a little more of the saturated solution of silver acetate is poured into another beaker and a small crystal of silver nitrate is dropped in, the same thing occurs. The silver nitrate is excessively soluble and entirely dissolves in a few moments. Very soon a similar flaky precipitate of silver acetate crystals falls out.

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 grams per liter?

CHAPTER IV

THE NON-METALLIC ELEMENTS IN BINARY COMPOUNDS

The distinctive chemical property of non-metallic elements is their ability to combine with metals forming simple 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: fluorine, chlorine, bromine, iodine, oxygen, sulphur, and nitrogen.

PREPARATION 4

COPPER OXIDE

This preparation is typical of the preparation of oxides of the metals. The most obvious method of making an oxide is to heat the substance 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.

In the method here used the metal is treated with a reagent which yields a soluble compound. The latter is obtained by evaporating, and is then decomposed, by heating, into a gaseous oxide and the solid oxide of the metal.

Materials: Copper metal (turnings or wire), 13 grams = $\frac{1}{2}$ gram atom.
6-normal HNO_3 , 89 cc.
anhydrous sodium carbonate, 21 grams.

Apparatus: 2 liter common bottle.
5-inch filter funnel with plain filter.
4-inch evaporating dish.

Procedure: Dissolve the copper in the nitric acid observing Note 7, page 13. Add 500 cc. water and filter if the solution is not clear. Dissolve the sodium carbonate in 500 cc. water, filter if the solution is not absolutely clean and pour this solution into the copper nitrate solution in a 2 liter common bottle. The

precipitate of basic copper carbonate is now to be washed free of the soluble sodium nitrate. Wash by decantation (Note 5(b), page 10) until not more than one one-thousandth of the original NaNO_3 is left. Then pour the sludge of basic copper carbonate in a filter folded in a 5-inch funnel and let it drain and partially dry until it has stiffened to a jelly. Then remove the filter and contents, and, without tearing the filter, spread it out flat on some paper towels. When the copper carbonate is dry place it in a 4-inch evaporating dish and warm it by playing the flame underneath. A very low temperature suffices to decompose the copper carbonate. When the substance has changed to a uniform black powder and no more gas is evolved the preparation is complete. Put it up in a 6-inch cork stoppered test tube.

QUESTIONS

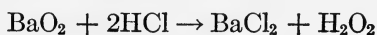
1. Could hydrochloric acid take the place of nitric acid in this preparation? Explain.
2. Refer back to Experiment 1, Chapter I for the method of obtaining zinc oxide from zinc. What would be the advantages and disadvantages of using that method in this preparation?

PREPARATION 5

HYDROGEN PEROXIDE AND BARIUM PEROXIDE HYDRATE

The ordinary oxide of barium has the formula BaO and it is an ordinary metal oxide, that is, it forms the corresponding base $\text{Ba}(\text{OH})_2$ when it combines with water, and the ordinary barium salts are formed when this base is neutralized with acids. But 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 is not an ordinary oxide; it does not for example react with water to give such a base as $\text{Ba}(\text{OH})_4$ nor with acids to yield such a salt as $\text{Ba}(\text{NO}_3)_4$. The entire oxygen seems to behave as a single radical having the same valence, namely two, as the simple oxygen radical in ordinary barium oxide; because, when barium peroxide is treated with acids, the ordinary barium salt is formed and hydrogen peroxide, *e.g.*

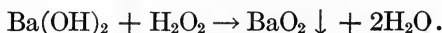


The name *peroxide* has been given to such oxides containing the O_2 radical which is interchangeable with the negative radicals of acids so as to yield hydrogen peroxide.

The common heavy metals have not the ability to form peroxides; only the most strongly metallic elements such as barium and the alkali metals do so. For example, when sodium metal burns freely in air the peroxide Na_2O_2 is formed. It is a matter of a good deal of difficulty 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 an acid to obtain a solution of hydrogen peroxide. 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, being no more ionized than water itself. Yet its acid character is manifest from the way it reacts with the barium hydroxide:



Were the barium peroxide soluble this reaction would shortly come to equilibrium, but since the barium peroxide is very insoluble, crystallizing as the hydrate, the reaction is fairly complete.

Materials: crude BaO_2 34 grams = $\frac{1}{8}$ F.W.
 6-normal HCl 67 cc. = $\frac{2}{3}$ F.W.
 barium hydroxide $Ba(OH)_2 \cdot 8H_2O$ 63 grams = $\frac{1}{8}$
 F.W.
 ice.

Apparatus: 2-600 cc. flasks.
 5-inch filter funnel with plain filters.
 2-liter common bottle.
 600 cc. beaker.
 suction filter.

Procedure: Dissolve the barium hydroxide in 500 cc. of warm water and pour through a filter without suction into a 600 cc. flask. While the filter is draining place the HCl, 250 cc. ice water, and about 100 grams ice in a 600 cc. beaker. Grind the BaO_2 in a mortar with water until a smooth uniform paste is ob-

tained 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, or until it is all added. Now add a few cc. of the $\text{Ba}(\text{OH})_2$ until a light precipitate is formed. This will be colored reddish due to ferric hydroxide. The solution should be slightly alkaline at this point. Make sure of this by testing with litmus paper. Then filter the solution without suction into a 600 cc. flask. Pour the $\text{Ba}(\text{OH})_2$ solution into a 2-liter bottle, and add 1 liter of cold water. Then pour in a thin stream with constant stirring the hydrogen peroxide solution into the barium hydroxide solution. 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, 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 as well as barium hydroxide.
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 6

HYDROCHLORIC ACID

Sulphuric acid and sodium chloride are the sources respectively of the positive and negative radical in this preparation. The hydrogen and the chlorine radical combining give hydrogen chloride, the only volatile product possible, and this is led off to be dissolved in water in another part of the apparatus.

Materials: rock salt, NaCl, 117 grams = 2 F.W.
36-normal sulphuric acid, 222 cc.

Apparatus: 1500 cc. round bottom flask.
1 wide mouth bottle of 300-500 cc. capacity

with as wide a mouth as possible (or better a 3 necked Woulfe bottle).

1 common 300 cc. bottle.

1 thistle tube.

1 2-hole rubber stopper to fit flask.

1 3-hole rubber stopper to fit first bottle.

glass delivery tube fitted as in diagram.

drying tube packed with glass wool.

1 1-hole rubber stopper to fit drying tube.

pan of cold water in which first absorption bottle is to set.

Procedure: Study the diagram of the apparatus thinking out the purpose of each part so that it may be put together intelligently. Build the apparatus. Place the dry rock salt in the

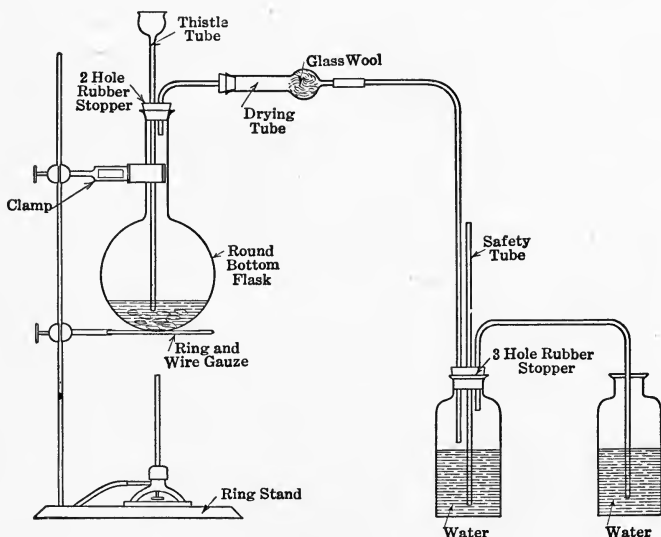


FIG. 15

flask, and 167 cc. of water in each absorption bottle. Adjust the inlet tube of first absorption bottle so that it reaches to within $\frac{1}{2}$ inch of the surface of the water.

Pour enough of the sulphuric acid, perhaps 50 cc., through the thistle tube into the flask to cover the lower end of the thistle

tube. Watch the action carefully to see that the foam does not rise and threaten to go up 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.

Danger: The contents of the flask are very hot and must not be poured out, least of all into water. Let the contents cool completely (best until next exercise), then add cold water and wash out the flask.

Most of the hydrogen chloride has been dissolved in the first bottle, unless the latter was allowed to get too hot, and any remainder has been caught in the second bottle.

To find the concentration of the acid in the first bottle determine the specific gravity using a Westphal Balance, or a hydrometer, or the apparatus shown in the diagram.

Look up in a specific gravity table the normality corresponding to the specific gravity, measure the total volume of the acid and compute the number of formula weights and the number of grams of HCl obtained in the first bottle. If a satisfactory yield cannot be accounted for, determine in the same way the acid in the second bottle. The contents of this however is not to be saved. Preserve

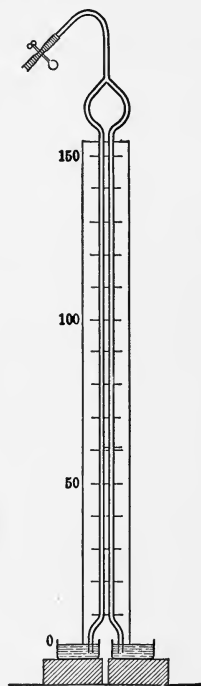


FIG. 16

FIGURE 16.

The scale at the back is marked off in divisions of $\frac{1}{10}$ 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.

the acid from the first bottle in a 250 cc. narrow-necked glass-stoppered bottle.

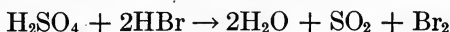
QUESTIONS

1. How much of an excess of sulphuric acid was used in this preparation? What is the advantage of using such an excess?

PREPARATION 7

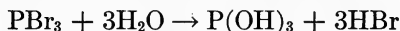
HYDROBROMIC ACID

The method of the preceding preparation would be the obvious one for making hydrobromic acid were it not for the fact that hydrogen bromide reacts to some extent with concentrated sulphuric acid according to the equation



and the gas passing over to the absorption bottles would be contaminated with sulphur dioxide and bromine.

Hence the method we shall choose starts with bromine and allows this to react with red phosphorus and water. Phosphorus and bromine combine very easily to form PBr_3 , but the phosphorus bromide hydrolyzes at once completely:



and hydrogen bromide passes over to the absorption flask.

Materials: bromine, 40 grams = 12.5 cc. = $\frac{1}{4}$ F.W.
red phosphorus, 7 grams.

Apparatus: dropping funnel.
250 cc. flask.
4-inch side arm U-tube.
8-inch plain U-tube of $\frac{3}{4}$ to 1-inch bore.
1 1-hole rubber stopper to fit flask.
2 solid rubber stoppers to fit small U-tube.
1 1-hole rubber stopper to fit large U-tube.
glass delivery tube as in diagram.
5 grams broken glass.
glass wool.

Procedure: After carefully studying the diagram construct the apparatus. Place 6 grams of the phosphorus, 12 grams of sand and 6 cc. of water in the flask. Mix 1 gram of the phosphorus with the broken glass, place it in the bottom of the small U-tube, and press into each arm above it a small wad of glass

wool. Add 12 cc. water, or enough to close the bend, to the larger U-tube.

Danger: Use extreme care in handling bromine as it produces very severe burns in the flesh. Be sure the stop cock of the dropping funnel is tight and turns easily. When manipulating it after

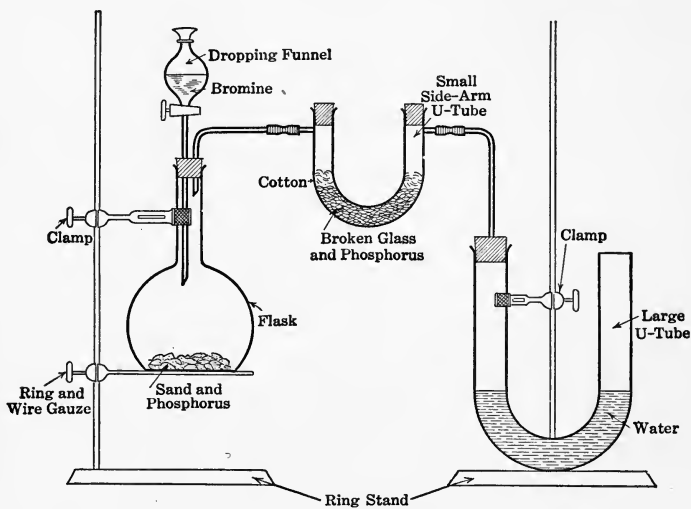


FIG. 17

the bromine is added, steady the bulb with one hand while turning the cock with the other and 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 pour the bromine into the funnel. Then let a single drop of bromine fall into the flask watching its effect then add the rest of the bromine a drop at a time as rapidly as proves safe. After the gas ceases to flow pour the contents of the absorption tube into a graduate, note its volume, and preserve it in a 25 cc. 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-tube.

3. Explain why at the outset of the process bubbles pass outward through the second 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 Exp. 13.) Write the equations. What property possessed by hydrogen bromide, but not by hydrogen chloride, is shown?

PREPARATION 8

HYDRIODIC ACID

The method employed in the preparation of hydrochloric acid is inapplicable here for the same reason that it is in the preparation of hydrobromic acid. Hydriodic acid can be prepared by the same method which we used for hydrobromic acid, that is, by letting iodine, phosphorus, and water react; but in order to illustrate a different principle we shall employ another method.

The position of sulphur in the negative electromotive series is lower than that of iodine because the latter displaces sulphur from a solution of hydrogen sulphide. This is the principle on which this preparation is based.

Materials: iodine, 32 grams = $\frac{1}{4}$ gram atomic weight. (Keep the iodine stoppered in a test tube until ready to use.)

hydrogen sulphide generator, see Note 13, page 19.

Apparatus: 200 cc. Erlenmeyer flask.

two 75 cc. flasks.

150 cc. distilling flask.

thermometer.

condenser.

carbon dioxide generator.

hydrogen generator.

cork or rubber stoppers to fit condenser to distilling flask and receiving flask.

Procedure: Grind the iodine to a fine powder in a mortar, and quickly replace it in the stoppered test tube. Place about 0.5 gram iodine and 100 cc. water in the Erlenmeyer flask. Pass hydrogen sulphide into the solution until the brown color of iodine has disappeared. Add about 1 gram more of iodine and again

pass hydrogen sulphide until the iodine is used up. After 10 grams of iodine have reacted in this way, add the remaining 20 grams and allow the mixture to stand, with repeated shaking, until the iodine is entirely dissolved (half an hour or more). Then pass hydrogen sulphide slowly until the solution is decolorized. Pour the solution into another flask, leaving the clotted lumps of sulphur behind, and rinse the first flask and the residue with a few cc. of water. Pass a current of carbon dioxide through the solution until the excess of hydrogen sulphide is entirely removed; then shake the flask vigorously to cause the suspended sulphur to clot together, and filter the solution. In this way a rather weak solution of hydriodic acid is obtained.

Fit a distilling flask with a thermometer and an inlet tube for hydrogen, and pass the side arm of the flask into a condenser. After introducing the hydriodic acid solution, fill the whole apparatus with hydrogen, and keep a slow current of this gas passing during the distillation. On distilling, nearly pure water passes over at first, and the thermometer does not register appreciably above 100° . When the thermometer rises to 105° change the receiving vessel and collect the distillate until the temperature has risen to 120° . Change the receiver again and collect the rest of the distillate. The temperature rises quickly to 126° , and remains very close to this point until practically all of the acid has passed over. This last fraction is the desired concentrated acid. Preserve this acid in a 50 cc. glass-stoppered bottle.

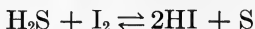
QUESTIONS

1. Compare the stability of the hydrogen halides as judged (a) by the heat produced when they are formed from the elements; and (b) by the temperature at which the compounds are decomposed. Look up the data.

2. What are the products of the reaction of concentrated sulphuric acid and potassium iodide (Experiment 14)? Write the equations. What property of hydrogen iodide is shown? Compare hydrogen iodide, hydrogen bromide and hydrogen chloride as reducing agents.

3. Is sulphur invariably a less active element than iodine? Look up the decomposition temperatures of hydrogen sulphide and hydrogen iodide. Find in reference book the effect of heating sulphur in dry hydrogen iodide.

4. What explanation can you offer for the fact that the reaction



goes in one direction in aqueous solutions and in the other direction in the dry gases? Look up the heats of solution of HI and H₂S.

PREPARATION 9

BARIUM BROMIDE, BaBr₂·2H₂O

A universal method of preparing a salt is by neutralizing the respective acid and base. It is almost as effective to use the carbonate of the metal as the base itself, because carbonic acid is so easily displaced. When both the acid and the base are soluble, it is necessary to get the solution exactly neutral if a perfectly pure salt is to be made; but in this preparation the barium carbonate used to react with the acid is so very insoluble that it may be used in excess and the excess may be filtered off. Thus the tedious process of balancing the base against the acid to get the exact neutral point is avoided.

Materials: hydrobromic acid. Use product obtained in No. 7.
barium carbonate BaCO₃, 50 grams.

Apparatus: 5-inch filter funnel.
500 cc. flask.
4-inch evaporating dish.

Procedure: Place all but 2 grams of the barium carbonate in the flask, add 100 cc. of water and then the hydrobromic acid cautiously enough not to cause too violent frothing. When even with shaking, effervescence ceases, add the other 2 grams of barium carbonate. If this also goes into solution, add more barium carbonate until an excess remains undissolved. Boil the contents of the flask 5 minutes. Filter without suction and partially evaporate the filtrate. Let the solution cool and crystallize. Collect the crystals, and evaporate the mother liquor. In this way practically the entire amount of salt should be obtained in the crystalline form. Wrap the product in paper towels and leave it to dry (Note 9(b), page 15). Put up the product in a 2-ounce cork-stoppered bottle.

QUESTIONS

1. Explain the method employed in this preparation of obtaining an exactly neutral salt solution. Write ionized equation.
2. Could a neutral solution of barium bromide be obtained by adding excess of barium hydroxide to hydrobromic acid? Explain.
3. Could a neutral potassium salt solution be obtained by treating the appropriate acid with excess of potassium carbonate?

PREPARATION 10

ALUMINUM SULPHIDE

Although the obvious method to prepare 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 the process is so difficult to control that we shall not attempt it. When finely divided aluminum and sulphur 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, when it does react, the reaction is not too violent, because 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
= 1.5 F.W. (a fairly pure sample of the mineral must be used to obtain good results).

Apparatus: clay crucible without cover.
iron pan.
gas furnace.

Procedure: Mix the powdered galena and granulated aluminum and place the mixture in the clay crucible and put the latter 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 thirty seconds in the furnace, then lift 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 in the same way. Compare the basic strength of $\text{Pb}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$. 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

This preparation is to be made by the reduction of the oxy-salt calcium sulphate by means of carbon. Calcium is too active to be reduced by this means, but the sulphur is readily reduced from its valence of + VI to its minimum valence of - II.

The most abundant source of calcium sulphate is the mineral gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. We desire anhydrous CaSO_4 as our starting material, but plaster of paris, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, 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.

The calcium sulphide prepared by the following procedure is not luminescent. The luminescent varieties owe that property to traces of other substances. Directions for preparing samples which will luminesce with almost any desired color are given in Vanino, Handbuch der Präparativen Chemie, Volume I, p. 382.

Materials: plaster of Paris, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, 145 grams = 1 F.W.
powdered charcoal, C, 48 grams = 4 F.W.

Apparatus: 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 and mix the two materials and pack the mixture in the clay crucible. Heat the crucible to between a bright red and a yellow heat for one hour and a half. 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. If the reduction has not been complete, grind the material again after adding 5 grams of charcoal, and heat it again for an hour and a half. Preserve the product in a 12-ounce cork-stoppered bottle.

QUESTIONS

1. Write the equation for and explain the behavior of calcium sulphide with acids.
2. 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?

3. 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

This substance is conveniently made by direct synthesis from the elements. Two modifications of mercuric sulphide are known, one black, which is formed first in this preparation and also by precipitation of mercuric and sulphide ions, and the other a brilliant red (vermillion), which is more stable and into which the black form tends to change.

Materials: mercury, Hg, 20 grams = 0.1 F.W.
 flour of sulphur, 8 grams.
 6-normal KOH, 15 cc.
 saturated Na_2SO_3 solution 50 cc.

Apparatus: 6-inch evaporating dish.
 large porcelain mortar.
 warm closet or plate at about 50° .
 600 cc. beaker.

Procedure: Place the mercury and the sulphur in a large mortar, and triturate the mixture, moistening it with ammonium 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 6-inch dish. Use 10 cc. of water to finish rinsing the material into the evaporating dish. Let this dish stand in a place at a temperature of about 50° , replacing the evaporated water as often as each day, and stirring the mass thoroughly each time with a glass spatula.

When, at the end of a week at most, the mass has become of a pure red color, wash it by decantation (see Note 5(b), page 10) in a tall beaker whereby most of the excess of sulphur is floated off. Then float the red sulphide itself with water back into the evaporating dish, leaving behind in the beaker any lumps of black

sulphide or globules of mercury. Boil the red sulphide with sodium sulphite solution to remove the last of the uncombined sulphur; wash by decantation with boiling water and collect it on the suction filter. Dry the product on the hot plate and preserve it in a cork-stoppered test tube.

QUESTIONS

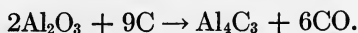
1. Red and black sulphides of mercury have exactly the same composition, as expressed by the empirical formula HgS . Would you regard them as the same or as different substances? Give your arguments.
2. What explanation can you give of the action of sodium hydroxide in facilitating the change of the black to the red modification?

PREPARATION 13

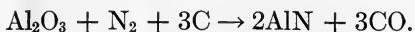
ALUMINUM NITRIDE

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 its ability to cover itself with a thin tenacious coating of oxide, which keeps it physically separated from the reacting material. Aluminum powder alone can not be made to burn in air, but when it is mixed with lamp black 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 remove the surface film of oxide from the grains of aluminum powder, and the action is probably as follows: It is well known that carbon cannot reduce aluminum oxide to metal, because aluminum is more active than carbon. But carbon and aluminum can form a carbide and since we have carbon tending to take oxygen away from aluminum and carbon also tending to take aluminum away from oxygen the two forces working together bring about the reaction



In an atmosphere of nitrogen however, the place of that part of the carbon which combines with the aluminum may be taken by nitrogen



The method used in this preparation was outlined by Doremus, Science 1920, page 635.

Materials: finely powdered aluminum, 45 grams. The material sold for use as pigment and often labeled Aluminum Bronze, although nearly pure aluminum, is suitable for the purpose. The oil which still adheres from the grinding is of no disadvantage.

lamp black, 5 grams.

magnesium ribbon, 4 inches.

Apparatus: 8-inch square of asbestos paper to be laid on a thick iron plate.

large porcelain mortar.

dark colored glasses may be worn to protect the eyes from the blinding light.

Procedure: Mix the aluminum and lamp black thoroughly in a mortar, and heap up the mixture in as compact a mound as possible on the asbestos paper. The latter must be placed in a safe location for the heat will be so intense as to melt through the asbestos. Insert the magnesium ribbon $\frac{1}{2}$ inch into top of 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 so 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 glasses. When the ash is cool, break it up, remove as much of the aluminum oxide crust from the outside as may be and preserve the nitride in a 4-ounce glass-stoppered bottle.

QUESTIONS

1. Examine the aluminum nitride and describe its appearance.
2. Treat a little with cold and 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 Exp. 9, Chap. II.)
5. Treat portions of aluminum nitride with 6-normal nitric, sulphuric, and hydrochloric acid respectively.
6. Heat a little aluminum nitride in the open air to see how easily it can be converted to oxide.

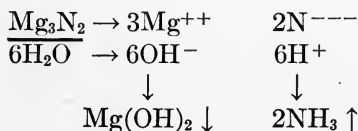
PREPARATION 14

MAGNESIUM NITRIDE AND AMMONIA

The formation of magnesium nitride follows in principle the same method in this preparation as the formation of aluminum nitride in the preceding. 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. Therefore the reaction is here 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 directly with pure water; in fact it does so with extreme violence.

The mechanism of the hydrolysis of magnesium nitride is probably similar to that of such salts as sodium carbonate and ferric chloride, and it would therefore appear as follows:



If magnesium nitride can ionize at all the ions which it would yield are obviously Mg^{++} and N^{---} as shown in the upper horizontal equation. The fact that such an ion as N^{---} is entirely unfamiliar does not weaken our belief in the above mechanism, because, as the direction of the arrow shows, the N^{---} ion is

formed only to be removed according to the right-hand vertical equation.

- Materials:* powdered magnesium, 10 grams.
dry sand, 50 grams.
- Apparatus:* iron crucible and cover of 25 cc. capacity.
300 cc. r.b. flask.
150 cc. flask.
filter bottle (or 500-cc. flask).
U-tube $\frac{7}{8}$ inches wide, $7\frac{1}{2}$ inches tall.
2 thistle tubes.
1 pinch cock.
3 2-hole rubber stoppers.
1 1-hole rubber stopper.

See diagram for fittings.

Procedure: Weigh an iron crucible of about 25 cc. volume 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 with a cylinder of asbestos $2\frac{1}{2}$ to 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 onto 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 the diagram. Have the rest of the apparatus and connections fitted as in the diagram. Pour 50 cc. of water into 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 6-normal HCl in the absorption tube *F* and then add enough water to seal the bend. Remove the stopper and fittings from the generating flask *A*. Pour water into the thistle tube *i* and open the pinch cock until the stem of the tube has filled with water. Replace the stopper in the flask and open the pinch 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 the flask apply a small flame until the liquid boils. Boil gently for 15 minutes. Pour together the

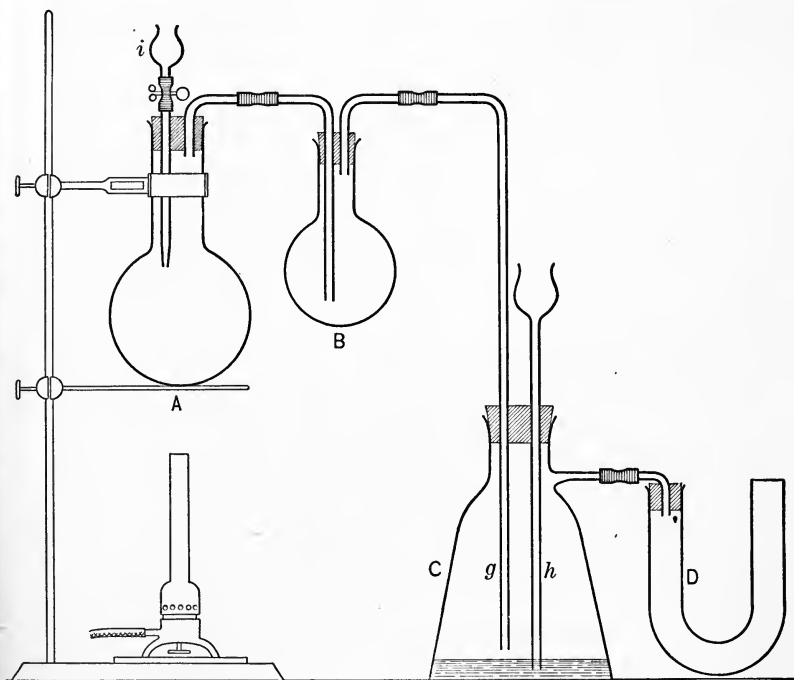


FIG. 18

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.

contents of the absorption flask and the absorption tube, and, using litmus as an indicator, add enough more 6-normal HCl to just neutralize the ammonia. Evaporate the solution to obtain solid ammonium chloride, according to Note 6(b), page 12. Preserve the product in a 6-inch cork-stoppered test tube.

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, and 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, figure 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 electro-positive constituents of compounds, whereas the non-metals form the electro-negative constituents.

It must be remembered that an uncombined element is electrically neutral, but every element 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 negatively. 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. Pure liquid and gaseous compounds are likewise non conductors, the electrostatic forces holding the

constituents of each individual molecule together. But we have seen in Chapter III that many compounds, *viz.* acids, bases and salts, give a conductive solution when they are dissolved in water. 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. That this is the case however seems to be a well warranted conclusion, 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 + III and that of chlorine - I 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

No divalent negative ion of oxygen, O^{--} , has ever been found; nevertheless the valence of oxygen is believed to be - II because of the composition of water. Nearly all of the elements combine with oxygen forming simple binary 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 exchanged for an equivalent amount of chlorine.



The primary valence of all of 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.

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 very slowly, so as to be practically imperceptible; but many substances act as catalyzers for the reaction, especially solid materials which have a rough surface, notably platinum and manganese dioxide.

2. To 10 cc. of a 3 percent solution of hydrogen peroxide in a test tube, add a pinch of powdered manganese dioxide. Note that a vigorous effervescence at once ensues and that the escaping gas will cause a glowing splinter to burst into flame.

3. **Test for Hydrogen Peroxide.** To 2 cc. of the 3 percent 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.* 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 dilutions according to the powers of ten until a solution is obtained which shows a distinct color with the titanium sulphate, while the next dilution

* Prepared by fusing 1 part of titanium dioxide with 15 to 20 parts of potassium bisulphate and dissolving the mass in 500 cc. cold dilute sulphuric acid.

fails to show the test. In the final tests add 1 cc. of reagent to 15 cc. of pure water and hold this side by side with 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.

We have used litmus as a test reagent for acids and bases although we probably have not learned the chemical formula for litmus nor the difference in nature between the red and the blue litmus. When we find by experience that a very pronounced effect is always shown when a substance is treated with a particular reagent, we can use this reagent as a test reagent for the substance. If the effect is given the presence of the substance is proved. In such a way it has been found that titanium sulphate gives a deep yellow color with hydrogen peroxide, and thus we use this reagent and the effect as a test for hydrogen peroxide, without worrying as yet too much about the chemical formula of the yellow substance.

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-normal HNO_3 drop by drop with continuous stirring until the solid has dissolved. Test the solution for hydrogen peroxide by adding titanium sulphate. Treat another sample of barium peroxide with another acid in order to convince yourself whether the effect could have been caused by the nitric acid. Treat 1 gram BaO_2 with 5 cc. of water and 5 cc. 6-normal 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.

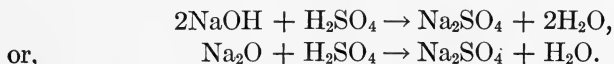
(b) Test barium oxide BaO in the same way. Since this oxide is difficult to get and since it reacts vigorously with water anyway to form the hydroxide $\text{Ba}(\text{OH})_2$ we might as well use

the hydroxide as a starting point, but should bear in mind that it is essentially the same thing as the oxide BaO.

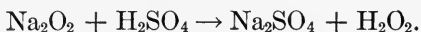
(c) Heat a piece of broken porcelain on a triangle to redness; drop upon it a piece of sodium metal the size of a small pea, and remove the flame. The sodium burns to form sodium peroxide Na_2O_2 . Place 50 cc. of cold water and 5 cc. of 6-normal H_2SO_4 in a small dish; let the porcelain and adhering sodium peroxide cool completely and then drop it into the dilute acid. Test the solution with titanium sulphate.

(d) Prepare another sample of sodium peroxide in the same way. Scrape it off the porcelain and 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.

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 in Chapter II.) This leaves in the solution the oxide Na_2O or rather NaOH the product of the reaction of Na_2O with water. On acidification we get a simple neutralization:

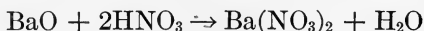


But in (c) the peroxide has not been given a chance to decompose before the treatment with acid. Since hydrogen peroxide was found as a product, the reaction is probably

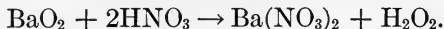


Evaporation of the solution does yield crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ identical in every respect to the sodium sulphate that can be obtained from (d) thus confirming the above equations.

In the same way barium oxide BaO neutralizes an acid, with the formation of water:



and barium peroxide yields hydrogen peroxide:



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 two.

Thus the peroxides are not really simple binary compounds in which the primary positive valence of the metallic constituent is just equalled 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 complex negative radical.

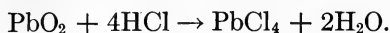
5. Dioxides. To about a gram each of manganese dioxide, MnO_2 , and lead dioxide, PbO_2 , in separate test tubes add 10 cc. of water and 5 cc. of 6-normal H_2SO_4 or HNO_3 and warm for a few moments. Note that the dark colored powders do not dissolve or change their appearance in any way nor is there 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 four, or whether they are peroxides in which the valence of the metal is two like that of barium in barium peroxide.

6. Different Behavior of Dioxides and Peroxides with Hydrochloric Acid. Treat $\frac{1}{2}$ gram of finely powdered lead dioxide with 5 cc. of ice cold 12-nHCl. Note that a yellow solution is formed. Dilute 1 cc. of the solution with 100 cc. water and add 1 cc. of titanium sulphate. Note that no yellow color is produced. Heat the rest of the solution. Note that an evil smelling yellow gas (chlorine) is given off, that the yellow color disappears and that a white crystalline powder settles out as the solution cools. Treat $\frac{1}{2}$ gram of barium peroxide in the same way with 5 cc. of ice-cold 12-nHCl. Add cold water until the crystalline residue is all 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.

The yellow soluble substance is lead tetrachloride PbCl_4 and is formed by the reaction

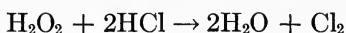


Lead tetrachloride is very unstable and decomposes rapidly into the lower chloride PbCl_2 and free chlorine. This chloride of lead is the same one that is obtained when lead monoxide is treated with hydrochloric acid:



Since the 2 oxygens of lead dioxide are exchangeable for 4 chlorines, and the lead is exchangeable for 4 hydrogens of the acid, the valence of lead is established as four and therefore each of the divalent oxygens are held as separate units by the lead.

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 would expect that it would react with the excess of hydrochloric acid



and set free chlorine.

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 of 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 grains 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 grains and the paper as a vapor —, but it illustrates one of the striking properties of free iodine, namely its power of turning starch deep blue. We will 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.

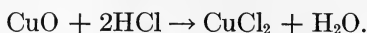
9. Test for the Presence of Chlorine or Bromine. Place 5 cc. each of chlorine and bromine water in separate wide-mouthed bottles. Lower for a moment strips of moistened iodide-starch paper in the mouth of each bottle. The papers are immediately turned deep blue.

Chlorine and bromine are higher in the electromotive series than iodine and thus are able to drive it out of the ionic form

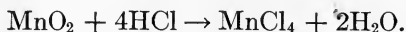


10. Chlorine from Hydrochloric Acid. Place about 0.5 gram each of manganese dioxide, lead dioxide, potassium or sodium dichromate, and potassium permanganate in separate test tubes. Add about 2 cc. of 6-normal hydrochloric acid to each and test for chlorine by holding iodide-starch paper in the mouths of the tubes. Also after warming a very little observe the odor and color of the gas. Rinse out the tubes immediately at the hood under the sink. 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.



There are several ways of explaining the mechanism of the reaction in which chlorine is liberated. Let us imagine that the first step is a metathesis:



But manganese tetrachloride is not stable and it decomposes



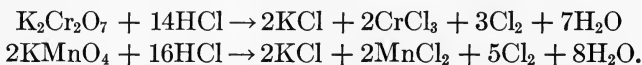
adding these equations we obtain



This is a reaction of oxidation and reduction (see page 105); one atom of manganese changes its valence from + IV to + II and this is compensated by the change of two atoms of chlorine from - I to zero, so that algebraically the total changes of valence add to zero.

The reaction of lead dioxide may be similarly figured out if one has the information that the stable chloride of lead is PbCl_2 corresponding to the oxide PbO .

The reactions of potassium dichromate and potassium permanganate are represented by the equations



These are likewise reactions of oxidation and reduction and the valence changes add up as follows:

2Cr	+ VI to + III	2 × (- 3) = - 6
6Cl	- I to 0	6 × (+ 1) = + 6
Total change		= 0
2Mn	+ VII to + II	2 × (- 5) = - 10
10Cl	- I to 0	10 × (+ 1) = + 10
Total change		= 0

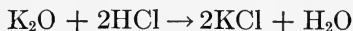
In working out these equations it would be necessary to know that the stable salt forming oxides of chromium and manganese are

Cr_2O_3 and MnO , corresponding to the chlorides CrCl_3 and MnCl_2 respectively.

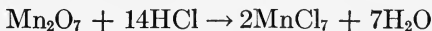
Let us analyze the possible mechanism of one of these reactions: Potassium permanganate is an oxy-salt which could be formed from a basic oxide and an acid oxide (see page 61). Let us imagine the first step of the reaction is to resolve this salt into its simple oxides.



Potassium oxide, being a strongly basic oxide would react with the acid without any question



and manganese heptoxide could be imagined to undergo a metathesis with hydrochloric acid



but the existence of the heptachloride is only hypothetical since such a substance has never been isolated; it will therefore be expected to decompose as soon as formed:



Now these separate steps may be added together and give identically the same equation as printed above for the complete reaction.

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 No. 10, say manganese dioxide, on hydrobromic and hydriodic acids.

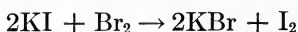
Add a few drops of chlorine water to 5 cc. of a bromide solution, for example NaBr . Then, in order to find whether bromine has been set free, add 1 cc. of carbon disulphide, shake vigorously, and let the heavier liquid settle to the bottom. The free halogen is more soluble in carbon disulphide than in water, consequently it dissolves in and im-

parts 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, 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 No. 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 thus can be liberated by the weakest oxidizing agents. It should be noted that in this connection the halogens themselves are oxidizing agents; for, in the reaction



the bromine has gone from a valence of zero to $-I$, that is, it has been reduced, while the iodine has been oxidized from valence $-I$ to valence zero.

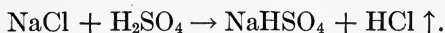
Fluorine is the strongest oxidizing agent of all. It liberates the other halogens from their compounds. It will even liberate oxygen from water and it is of particular interest that a portion of the oxygen so liberated is in the more active form of ozone. The oxidizing power of fluorine must be extraordinarily high in order to build up the very active oxidizing agent ozone. 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. But 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 OF AND PROPERTIES OF THE HYDROGEN HALIDES

12. Hydrogen Chloride. Add 2 cc. of concentrated sulphuric acid (36-normal) to about 0.5 gram of sodium chloride in a test tube and warm it a very little if necessary. 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 ammonia water near the mouth of the tube. The salt effervesces in the concentrated acid. The gas issuing from the tube creates a dense fog with the breath. The gas turns moistened litmus red and it produces a dense white smoke in the vicinity of the paper moistened with ammonia water.

The main reaction consists of the displacement of a volatile acid from its neutral salt by means of a non volatile acid.



Although hydrogen chloride is excessively soluble in water it is not soluble in sulphuric acid.

The fogging of the breath is caused by a condensation of the water vapor. This condensation is possible because of the extreme solubility of hydrogen chloride; such a concentrated solution can be formed that the tension of the water vapor which can escape from it is reduced to a very low point. The water vapor in the breath is at a much higher pressure and thus being out of equilibrium it condenses. 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 paper is due to the precipitation of solid ammonium chloride where the gases HCl and NH₃ meet. The ammonium hydroxide dissociates non-electrolytically



and the ammonia combines with the hydrochloric acid



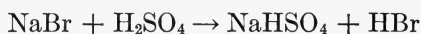
These properties of fogging the breath, reddening litmus, and making a smoke with ammonia, are characteristic of hydrogen chloride and the other hydrogen halides, and one can infer that a hydrogen halide is present when these properties are observed.

13. Hydrogen Bromide. Add 1 cc. of 36-normal sulphuric acid to about $\frac{1}{2}$ gram of powdered potassium or so-

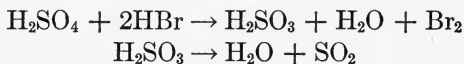
dium bromide in a test tube. Apply the same tests as in No. 12 then look for other new substances formed, applying the following tests, and towards the last heating the tube a little. Observe the color of the gas and also the effect of lowering iodide-starch paper for *a moment only* into the tube. Continued 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 salt effervesces in the concentrated acid. 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, even in the presence of all the other smells.

The fogging, 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:



The properties of hydrogen bromide are very similar to those of hydrogen chloride but differ in that hydrogen bromide reacts with sulphuric acid



which reactions account for the red color of free bromine, the turning blue of iodide-starch paper, and the odor of sulphur dioxide. 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.

It is recalled from Experiment 11, that bromine is a less active

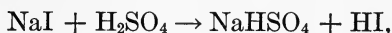
element than chlorine; hence it is but natural that we should find it here displaced from its hydrogen compound by a weaker oxidizing agent. Chlorine is displaced from hydrogen chloride by strong oxidizing agents, MnO_2 , PbO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , but bromine is displaced by 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 + VI to valence + IV in sulphur dioxide.

14. Hydrogen Iodide. Add 1 cc. of 36-normal sulphuric acid to $\frac{1}{2}$ gram of powdered potassium or sodium iodide, and apply all of the test enumerated in Nos. 12 and 13; also inspect the walls of the test tube carefully to see if any solid sulphur condenses.

As in Nos. 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 and the odor of hydrogen sulphide is very obvious. Sometimes a powdery light yellow substance (sulphur) is seen collecting on the walls of the tube.

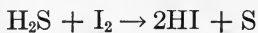
The primary reaction in this experiment,



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 ($\text{PbAc}_2 + \text{H}_2\text{S} \rightarrow \text{PbS} + 2\text{HAc}$), and the odor; sulphur, shown by the light yellow deposit. Their formation can be accounted for by the equations:



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 + IV in sulphur dioxide. Hydrogen iodide can reduce sulphuric acid much more freely carrying the valence all the way from + VI down to the lowest possible, namely - II 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, such as sulphuric acid, but one which would not at the same time behave as an oxidizing agent.

Place about $\frac{1}{2}$ 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, mercury, and lead are soluble in water, but with the ions of these three metals, the halide ions for the most part 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 if 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 may be looked up in the solubility table in the Appendix. The solubility of the silver halides in ammonia solution depends on the formation of the complex ion $(Ag.2NH_3)^+$ (see chapter III, page 97). 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 $(Ag.2NH_3)^+$ 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

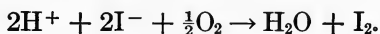
The activity of an element is judged by its power to combine with other elements, or by its ability to pass from the elementary condition into solution in the form of ions, whereby it forces other

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 Exp. 10, Chap. II; yet some substances which give up oxygen readily (oxidizing agents, see Exp. 10) set chlorine free from hydrochloric acid.

17. Observe the color of the solution of hydriodic acid made in Preparation 8, or of the stock solution on the side shelf. If this should chance to be perfectly fresh and 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 if 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



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.

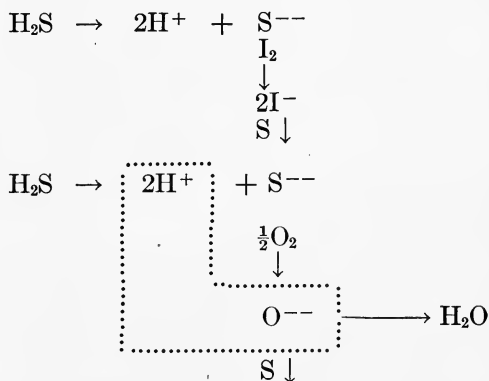
Chlorine and bromine are not liberated by the action of air on hydrochloric acid and hydrobromic acid, still less on neutral solutions of chlorides and bromides.

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.

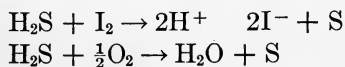
Explain the reaction in each case, and place sulphur, oxygen, chlorine, bromine, and iodine in the order of their chemical activity in acid solutions.

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 difficult to represent them as such.



Hydrogen sulphide, although its ionization is very small, does maintain a certain S^{--} ion concentration, and, as rapidly as the S^{--} ion is driven out, the hydrogen sulphide ionizes further. Thus all of the sulphide constituent of the hydrogen sulphide enters the reaction and is precipitated as free sulphur. Supposedly oxygen strives to form the hypothetical O^{--} ions but this unites with hydrogen ions to form water.

When one is sufficiently familiar with the ionic theory he writes the equations for these reactions in the abbreviated form



but he can read in these equations the whole of the above discussion.

From this experiment and the preceding one we have learned that the non-metallic elements fall in the order F, Cl, Br, O, I, S, (fluorine being strongest) with respect to their activity in acid aqueous solution. This is the order of the electromotive series.

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.

(b) Melt 50 grams of sulphur in a small beaker. Get a special beaker from the Supply Room. After the experiment throw it away. It cannot be cleaned. 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).

(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.

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).

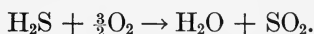
20. Hydrogen and Sulphur. (a) Prepare hydrogen sulphide by the action of dilute sulphuric acid on ferrous sulphide in a generator bottle (see Note 13(a) page 19). Pass the gas through a drying tube containing a plug of cotton wool, which retains any acid spray, then through a piece of hard glass tube 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, dew condenses inside the bottle. Now thrust a piece of cold porcelain half way into the flame and note the deposit of sulphur.

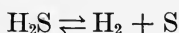
(c) Generate hydrogen gas in exactly the same way as hydrogen sulphide in (a). Place about $\frac{1}{2}$ gram of sulphur in the end of the hard glass tube nearest the generator. When it is ascertained that the hydrogen coming off is pure, heat the further end of the glass tube to redness and gradually 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:



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 pretty well 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.



It is instructive to review the properties of the other non-metals 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 ex-

plasion. 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 iodine begins to show the violet color of free iodine as low as 180° ; hydrogen sulphide does not deposit free sulphur lower than 310° ; hydrogen bromide is first perceptibly decomposed at 800° ; hydrogen chloride at 1800° ; water at 2000° ; and hydrogen fluoride is still undissociated at this temperature.

21. Ionization of Hydrogen Sulphide. Pass hydrogen sulphide, which has been strained 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 C (see page 70) 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 $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ to the extent of 0.05 per cent as found in the tables.

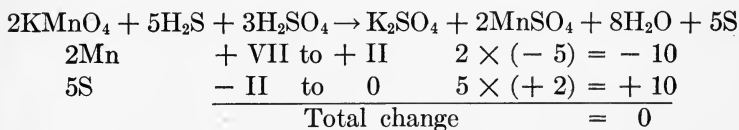
22. Hydrogen Sulphide as a Precipitant. Pass hydrogen sulphide into solutions, acidified or neutral, of salts of the heavy metals; take for example a solution of copper chloride. A heavy black precipitate is formed.

The precipitate is copper sulphide. The table gives the ionization $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{--}$ as 0.0002 per cent but this applies only to a 0.1 equivalent solution of $\text{Na}^+ \text{HS}^-$ 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, then 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 dilute sulphuric acid. 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 $-II$ to $+VI$,—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.



NITROGEN

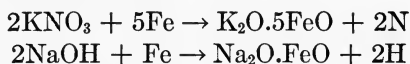
Nitrogen is an extremely inactive element, combining directly only with the most active of the metals. Nitrogen forms no simple ions and it is impossible to give it an exact potential in the electromotive series, but it is obvious enough that it is far less active than sulphur or iodine. Under the influence of electric sparks or of catalyzers 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 con-

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 grams 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



The hydrogen and nitrogen are doubtless 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 slowly burn. Remove 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



The magnesium nitride may be considered as a salt of the base $\text{Mg}(\text{OH})_2$ 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. What is meant by the "activity" of an element. 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 front 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, $\text{M}(\text{OH})_2$, 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 BICARBONATE BY THE AMMONIA (SOLVAY) PROCESS

Materials: table salt, 59 grams.

14-normal ammonium hydroxide, 71 cc.

carbon dioxide, which can be drawn either from an automatic gas generator (see Note 13(c) on 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 (see Note 4, (a) and (b), p. 5).

1-liter flask equipped with 1-hole rubber stopper, delivery tube reaching to bottom, and 24 inches of rubber delivery tube.

300-cc. flask with stopper.

Procedure: Place the salt, the ammonium hydroxide, and 130 cc. of water in the smaller flask and shake vigorously until the salt is dissolved. Pour the solution through a filter into the 1-liter flask (large plaited filter for speed). 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 thirty minutes. When the absorption is complete collect the precipitated sodium bicarbonate on the suction filter (Notes 3, and 4, b), drain it thoroughly with suction, stop the suction, pour over the surface of the product 15 cc. of cold water, and after this has soaked in apply the suction again. Wash a second time with 15 cc. of cold water exactly as at first. Spread the drained product on paper towels and leave it at room temperature 24 hours to dry. Test the preparation for chloride by dissolving about 0.1 gram in a little water, acidulating slightly with nitric acid, and adding a drop of silver nitrate solution. There will be considerable clouding. Put up the product 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 this way (see solubility table)?

2. Why must the solution be acidulated with nitric acid before testing with silver nitrate?

3. Why does shaking greatly increase the rate of absorption?

4. How do you explain the heat produced in the absorption flask?

5. How can you prepare sodium carbonate from sodium bicarbonate?

6. 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?

7. What is an acid salt? How does a solution of an acid salt such as KHSO_4 behave toward litmus? Test the behavior of solutions of NaHCO_3 and Na_2CO_3 towards litmus. Explain the cause of this behavior.

8. Would a precipitate of sodium bicarbonate form if carbon dioxide were passed into a solution of sodium chloride alone? Explain the part played by the ammonia in the formation of the product, giving the ionic equation.

9. Explain how a given amount of ammonia may be used over and over again in the commercial process.

PREPARATION 16

SODIUM CARBONATE FROM SODIUM BICARBONATE

Heat the sodium bicarbonate obtained in No. 15 in a 4-inch evaporating dish by playing the free flame over the bottom of the dish until carbon dioxide ceases to escape. Do not set the burner down under the dish because the flame concentrated in one spot might melt the sodium carbonate. Compare the weight obtained with that calculated. Put up the product in a 6-inch cork-stoppered test tube.

PREPARATION 17

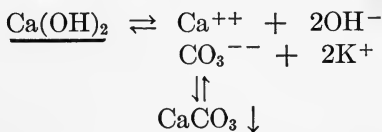
CAUSTIC ALKALI FROM ALKALI CARBONATE

Of the mineral constituents of plants, potassium salts form an important part, and, so far as these are salts of organic acids, they are converted into potassium carbonate when the plant is burned. On an average, wood ashes contain about 10 percent of potassium carbonate, and before the advent of the Leblanc soda process this was almost the sole supply of alkali. Even after this process came into general use, by which sodium carbonate

could be obtained from common salt, wood ashes remained for some time the important source of potassium carbonate. In recent years, however, the greater part of the production of potassium carbonate has been from potassium salts found in deposits in the earth, principally at Stassfurt, Germany.

Potassium carbonate being the principle soluble constituent of wood ashes, it is extracted with water; but the extract so obtained contains, as well, the other soluble mineral constituents, and also a considerable amount of tarry coloring matter which was not destroyed in the combustion of the wood. This tarry matter is destroyed by calcination of the residue obtained on evaporating the aqueous extract, and the calcined mass is what is known as crude potash. A better grade of commercial potash can be obtained by dissolving this mass in water, filtering, and evaporating the solution.

In order to obtain the hydroxide or caustic alkali from potassium carbonate or sodium carbonate, the carbonate in 10 percent solution is treated with excess of milk of lime (calcium hydroxide), the filtrate being a pure solution of the desired 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



until equilibrium between both solids and the solution is attained.

	Solubility in pure water moles per liter	Solubility product
Ca(OH) ₂ ..	0.02	.02 × .04 ²
CaCO ₃	0.00013	.00013 × .00013

At this point the concentration of both Ca⁺⁺ and CO₃⁻⁻ ions is so small (both close to the value .00013) that for practical purposes it is disregarded and the filtered solution is said to be free of either calcium or carbonate. But with so small a Ca⁺⁺ ion concentration the OH⁻ ion concentration can be quite large

without exceeding the solubility product of $\text{Ca}(\text{OH})_2$. In fact the filtered solution has a concentration of nearly 2-molal in KOH. It would obviously be more economical to start with a much more concentrated K_2CO_3 solution, since a more concentrated KOH solution would require less evaporating to give the solid potassium hydroxide. When, however, this is done the high OH^- ion concentration lessens the equilibrium Ca^{++} ion concentration which in turn increases the equilibrium CO_3^{--} ion concentration. In other words if a solution of alkali carbonate more concentrated than 10 percent is taken at the start, the conversion into alkali hydroxide will be incomplete.

Materials: anhydrous sodium carbonate, Na_2CO_3 , 53 grams = $\frac{1}{2}$ F.W. (or any alkali carbonate as for example the aqueous extract from wood ashes.)
slaked lime, $\text{Ca}(\text{OH})_2$, about 50 grams.

Apparatus: 8-inch dish.
suction filter.
burette with normal HCl.
15-cc. pipette.
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.

Test the strength of the solution. Measure 15 cc. with a pipette into a beaker and add a drop of litmus solution. Run into this from a burette a solution of normal hydrochloric acid, drop by drop, until the color just changes from blue to red. If the right point is overstepped begin again with a fresh sample of the solution. From the amount of acid taken to neutralize the sample, calculate the amount of alkali metal hydroxide. Label the bottle with the number of cubic centimeters of the solution, with its strength in mols per liter, 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 although an excess of calcium hydroxide, which is appreciably soluble in pure water, has been used for causticizing.

PREPARATION 18

CHEMICALLY PURE SODIUM CHLORIDE FROM ROCK SALT

Common rock salt may contain other than sodium chloride up to 10 percent of matter, which consists in the main of the sulphates and chlorides of potassium, calcium, and magnesium, not to mention a considerable amount of dirt and insoluble matter. 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 is then passed gaseous hydrochloric acid 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: rock salt, 75 grams.
concentrated sulphuric acid, 95 cc.
concentrated hydrochloric acid, 50 cc.

Apparatus: 1 liter r. b. flask with 2-hole rubber stopper.
300 cc. common bottle with 3-hole rubber stopper.
2-inch funnel.
2 thistle tubes.
delivery tube and connection, see diagram.
beaker, 3 inches wide.

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 pro-

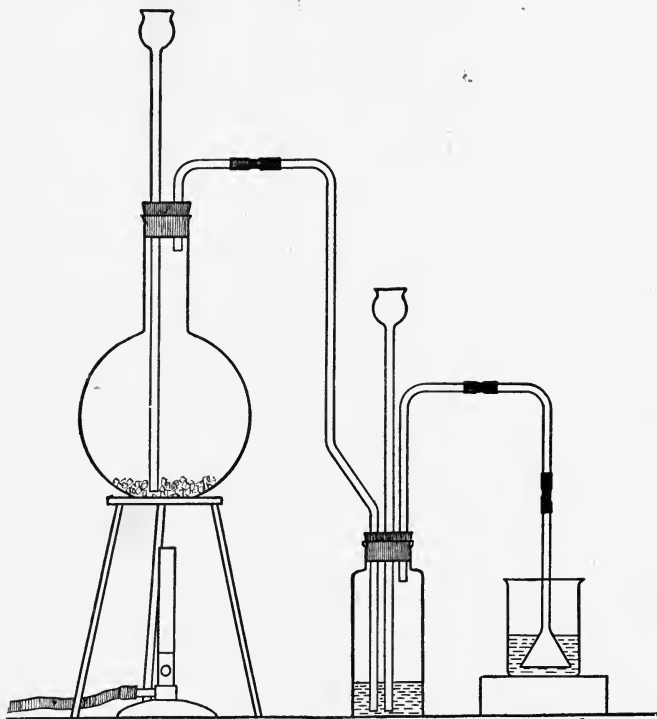


FIG. 19

duced 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)). 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 direction given under the preparations of hydrochloric acid, page 119, and note particularly the caution as to the disposal of the hot residue. The gas is to be purified by being bubbled through the washing bottle containing about 50 cc. of concentrated hydrochloric acid, and then it is passed through

the wide mouth funnel into the sodium chloride solution in the 3-inch beaker. When hydrogen chloride ceases to be evolved on heating the generator, separate the precipitated sodium chloride in a suction filter from its mother liquor. Test the filtrate for sulphate by adding a little barium chloride solution to a small sample of it diluted with water. A strong 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).) Then transfer the crystals to a porcelain dish and heat gently, while stirring, until all decrepitation ceases. Put up the product in a 6-inch cork-stoppered test tube.

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.

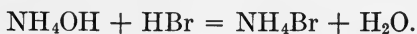
3. Mention two possible causes for the very considerable amount of heat produced when the hydrochloric acid gas is absorbed by the solution in the beaker.

4. Why does not the solution in the washing bottle also grow hot?

PREPARATION 19

AMMONIUM BROMIDE

Ammonium bromide could be prepared by the neutralization of ammonium hydroxide with hydrobromic acid,

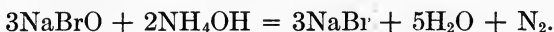


Since, however, hydrobromic acid is a more expensive material than uncombined bromine, the latter would have the preference

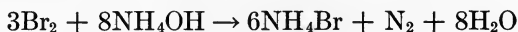
as a source of bromine, provided it yielded as satisfactory a product. Chlorine or bromine reacts as follows upon a cold solution of sodium hydroxide, as, for example, in the manufacture of bleaching liquors,



with the formation of sodium hypochlorite or hypobromite. Sodium hypobromite reacts with ammonium hydroxide according to the equation,



If now we substitute NH_4 for Na in the last two equations and add the equations we obtain



which gives the complete reaction of bromine with ammonium hydroxide.

Materials: bromine, Br_2 , 40 grams = 12.5 cc. = $\frac{1}{4}$ F.W.

NH_4OH 15-normal = 44 cc. = $\frac{2}{3}$ F.W.

Apparatus: 50 cc. dropping funnel.

300 cc. Erlenmeyer flask.

4-inch evaporating dish.

pan of cracked ice and water.

Procedure: Lubricate the stop cock of the dropping funnel lightly with vaseline, and secure it in place with a rubber band, so that it may not slip out when in use and let the bromine spurt out over the fingers. Secure the funnel with a clamp to the lamp stand so that the bottom of the stem is about one 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 in 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 00 page 00). Pulverize the dry salt and put it in a 6-inch cork stoppered test tube.

QUESTIONS

1. What products would be formed if bromine were added to a solution of sodium hydroxide instead of ammonium hydroxide, if the solution were kept cold? — if it were heated?

2. Add about 10 drops of bromine to 10 cc. of a cold 10 percent sodium hydroxide solution. Add this gradually to a solution of ammonium hydroxide, made by diluting 1 cc. of desk reagent with 10 cc. of water. Determine what gas is given off.

3. What fraction of the entire amount of ammonium used is lost through formation of nitrogen gas when ammonium bromide is made by the action of bromine on ammonium hydroxide?

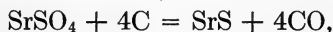
4. Why cannot hydrobromic acid be prepared from potassium bromide by a method analogous to that used in the manufacture of hydrochloric acid?

5. Explain why, from the standpoint of economy, the method of preparation above outlined is superior to the direct neutralization of ammonia with hydrobromic acid.

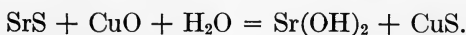
PREPARATION 20

STRONTIUM HYDROXIDE FROM STRONTIUM SULPHATE

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,



and the strontium sulphide by treatment with copper oxide and water can be made to yield strontium hydroxide,



Copper oxide is in the ordinary sense insoluble; nevertheless in contact with water it does yield to an infinitesimal extent, first copper hydroxide, and then Cu^{++} ions,



Therefore, 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, and this action continues until either the copper oxide or the strontium sulphide is exhausted.

Strontium hydroxide crystallizes with 8 molecules of water, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. It is very soluble in hot water, but sparingly soluble in cold water.

Materials: celestite, SrSO_4 , 61 grams = $\frac{1}{3}$ F.W.
powdered charcoal, 35 grams.
copper oxide, 48 grams.

Apparatus: gas furnace.
clay crucible.
large mortar.
8-inch dish.
500 cc. flask.
suction filter.

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 one 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. So 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) the hot solution through a large ordinary filter (Note 4 (c)), 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 of the liquid. 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

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 at-

tacked 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 liter	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, whose solubility product 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 so long as there is a large excess of carbonate ions 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, $\text{SrSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{SrCO}_3 + \text{Na}_2\text{SO}_4$, 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 $[\text{CO}_3^{--}]/[\text{SO}_4^{--}] = \frac{1}{74}$. When this ratio prevails, both solids are in equilibrium with the solution and no change takes place in either direction.

Materials: celestite, SrSO₄, 61 grams = $\frac{1}{3}$ F.W.
 anhydrous Na₂CO₃, 73 grams.
 chlorine water.
 6-normal HCl, 111 cc. = $\frac{2}{3}$ F.W.

Apparatus: 8-inch porcelain dish.
600 cc. tall beaker.

Procedure: Take the powdered celestite. Grind it in a mortar until it is so fine that it no longer feels gritty under the pestle. Cover it in an 8-inch 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 tall, narrow 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 Note 5 (b), first paragraph). The residue is now sufficiently free from soluble sodium sulphate. Transfer about $\frac{1}{10}$ of the moist strontium carbonate to another beaker, to be used in a later part of the process. To the remaining $\frac{9}{10}$ add 50 cc. of hot water, and then add hydrochloric acid, drop by drop, while keeping the mixture at the boiling temperature, 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 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 $\text{Fe}(\text{OH})_3$. 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)); 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 $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in paper towels and leave them overnight 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 equi-molal quantities of sodium carbonate and sodium sulphate, what would be the precipitate formed?

PREPARATION 22

BARIUM OXIDE AND BARIUM HYDROXIDE FROM
BARIUM CARBONATE

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, $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$, is to some extent 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 there is already present in the atmosphere in the furnace enough carbon dioxide to force the reaction towards the left. The carbon dioxide must be chemically removed. This is accomplished by mixing powdered charcoal with the barium carbonate, for carbon reacts with carbon dioxide at a white heat and gives carbon monoxide. In the following procedure, in addition to the charcoal, a little rosin is mixed with the charge. On heating, the rosin decomposes and a deposit of soot is formed, which in this way becomes very intimately mixed with the charge.

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, however, very suitable 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 $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

Materials: barium carbonate, BaCO_3 , 99 grams = $\frac{1}{2}$ 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.
clay or graphite crucible.
8-inch porcelain dish.
5-inch filter funnel and plain filter.
500 cc. flask.

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 $\frac{1}{2}$ inch deep. Place a well-fitting cover on the crucible and heat the whole for one hour to as high a temperature as possible in the gas furnace. 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)), letting the clear liquid run directly into a 500 cc. flask. 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 overnight to dry at room temperature. Put the product in a 6-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, and what resulting substance would be present to a small extent in the final crystallized product and to a greater extent in the mother liquor. (Compare preparation of strontium hydroxide from strontium sulphate.) Test both crystals and mother liquor for this substance. How? The final product can be quite satisfactorily purified from it by one or two recrystallizations. How might it be removed chemically?

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. Preceding experiments which involve the alkali and alkaline earth metals, and which should now be reviewed are:

Chapter II, Experiments 3, 4, 5, 6, 7, 11, 13.

Chapter III, Experiments 2, 5, 6, 7, 8, 9, 11, 12.

Chapter IV, Experiments 4, 6, 25.

1. Place a few small lumps of marble (pure 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. Then wet the product with somewhat more water, and test the reaction of the moist mass towards litmus.

2. Place a few grams of magnesium carbonate in a 3-inch 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 water in a test tube, adding acid, and watching for effervescence.

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. Note the rapidity and intensity with which the litmus is turned blue.

4. To some magnesium chloride solution, add (a) some ammonium hydroxide; (b) some ammonium chloride and then some ammonium hydroxide. Observe in each case whether magnesium hydroxide is precipitated.

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 the latter, it can form a monovalent positive ion, or it can form compounds with acid radicals, for example, NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$; 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. Test the evolved gas for ammonia.

(b) Add a solution of a strong base to a solution of any ammonium salt, warm, and notice whether the odor of ammonia is apparent. Show that this experiment furnishes an instance of the displacement of a weak base from its salt by means of a strong base.

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. In the vapor con-

dition, however, the salt is highly dissociated into two gaseous compounds.

Place 2 grams of ammonium chloride in the middle of an 8-inch piece of hard glass tube and on either side place loose plugs of asbestos. Outside the asbestos plugs place moistened strips of both red and blue litmus paper at both ends. Support the tube in a slightly inclined position by means of a clamp, and heat the section containing the salt, using a flame spreader. Observe the changes in color of the litmus.

Remembering that gases *diffuse* with velocities inversely proportional to the square roots of their densities, account for the effects observed.

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.

Explain why boiling increases the extent of the hydrolysis of the salt.

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 percent of ionization of the hydroxides of the alkali metals, of ammonium, and of the alkaline earth metals in 0.1 normal solution if the substance is soluble to that extent. Give figures for the hydroxyl ion concentration in 0.1

normal NH_4OH solution and in saturated solutions of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. Describe and discuss the results of Experiment 4 in the light of these figures.

5. An oxy-salt, such as $\text{CaCO}_3 (= \text{CaO} \cdot \text{CO}_2)$, can be broken up by a sufficiently high heat into a basic oxide and an acid oxide — for example, $\text{CaO} \cdot \text{CO}_2 \rightarrow \text{CaO} + \text{CO}_2$. 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, $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3 + 28,850$ calories. But more often we will find only the heat of formation from the elements, for example, $\text{Mg} + \text{C} + \frac{3}{2}\text{O}_2 \rightarrow \text{MgCO}_3 + 269,900$ calories. In this case we must look up the heat of formation of magnesium oxide, $\text{Mg} + \frac{1}{2}\text{O}_2 \rightarrow \text{MgO} + 143,400$ and the heat of formation of carbon dioxide, $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 + 97,650$ 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 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 three, 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 the weak boric 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

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 = $\frac{1}{4}$ F.W.
12-normal HCl.
methyl orange solution.

Apparatus: 500 cc. beaker.
suction filter.

Procedure: Dissolve the borax in 300 cc. of boiling water. Add a few drops of methyl orange solution (a dye which is yellow in

neutral or alkaline solution but is pink in distinctly acid solution) and add 12-n HCl until the color of the dye has changed through an orange to a distinct pink and addition of 1 cc. more of the acid does not increase the pink tone. Let the solution cool to 15° or below, drain the crystals on a suction filter. If the filtrate is not distinctly pink (showing it to be acid) add enough 12-n HCl to make it so, shake vigorously, and add any crystals thus obtained to the main crop. Dissolve the crystals in 300 cc. of boiling water, filter if not clear, crystallize by slow cooling with occasional stirring if crystals cake together too much. Collect the crystals and let them dry at room temperature.

Note. — The above procedure yields fine granular crystals. Lustrous flaky crystals can be obtained if a little grease is present in the crystallizing solution. To this end dissolve 1 gram of soap shavings in 300 cc. of boiling water and use this solution to dissolve the boric acid for the recrystallization. This procedure is not recommended if purity of product is required rather than an attractive appearance.

QUESTIONS

1. Explain the relations between normal boric 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 grains of boric acid in a small porcelain dish, cover it with 5 cc. of alcohol, set fire to it, and 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 the preceding experiment, 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 two moles of HCl have been added to one 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

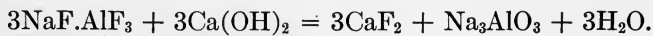
ALUM FROM CRYOLITE

(BY-PRODUCT: SODIUM CARBONATE)

A characteristic series of compounds of the trivalent metals are the alums, of which potassium aluminum sulphate, or common alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, is typical. These compounds are particularly interesting from the readiness with which they can be produced in large and beautiful crystals, and from the fact that any of the univalent alkali metals may take the place of potassium, or any one of a large number of the trivalent metals may take the place of aluminum in the common alum without altering the form of the crystals produced.

Of the many raw materials which might serve as the source of aluminum, cryolite, the double fluoride of sodium and aluminum, $3NaF \cdot AlF_3$ or $Na_3(AlF_6)$, has been chosen, partly because it actually serves as an important source of aluminum compounds, and partly because its decomposition illustrates important chemical reactions and manipulations.

This mineral, although itself insoluble in water, will, if boiled with milk of lime, (a suspension of $Ca(OH)_2$), undergo a metathesis, with the formation of insoluble calcium fluoride, and a soluble salt of aluminum, in which this metal plays the part of an acid-forming element,



By removing the insoluble residue from the liquid, a separation of the aluminum from the fluorine is accomplished; but on the laboratory scale this separation is difficult to carry out on account of the colloidal nature of the residue. If filtration were resorted

to, the pores of the filter would be immediately clogged with the gelatinous precipitate, so that the liquid would run so slowly, even with suction, that an undue length of time would be spent. Therefore the method which will be employed is that of sedimentation after stirring up with a large amount of water. It must be borne in mind, however, that this device is adopted only to meet the requirements of laboratory practice, for on a commercial scale the expense of evaporating the large amount of water to obtain soda, one of the by-products of the process, would be prohibitive. The separated sludge, consisting of calcium fluoride and all excess of calcium hydroxide, is of no great value, and will be discarded, although it could be used as a source of fluorine compounds.

From the clear solution of sodium aluminate the aluminum is precipitated by displacement of the weak aluminic acid from the salt by the action of the stronger carbonic acid,



This precipitated aluminic acid, H_3AlO_3 (or, as more frequently named, aluminum hydroxide, $\text{Al}(\text{OH})_3$), is also a very gelatinous substance, and can likewise only be separated, within a reasonable length of time, by means of sedimentation.

The aluminum hydroxide is treated with the calculated amount of sulphuric acid whereby the soluble salt, aluminum sulphate, is obtained. To this solution is added the calculated amount of potassium sulphate, and then the alum is allowed to crystallize.

The ideal conditions for obtaining large, clear crystals — which constitutes the beauty of this as a laboratory preparation — are, that a solution which is just saturated with alum may be slowly concentrated by spontaneous evaporation at a nearly constant temperature. Such conditions are found in industrial works, where the evaporation of the solution in large vats yields beautiful crystals, often of enormous size; but these necessary conditions are almost impossible to realize in a small laboratory preparation, and another method is adopted to give more rapidly and more surely the desired results.

From the accompanying table it is seen that the solubility increases rapidly with the temperature. If a solution is saturated at 35° and then cooled to $15\text{--}20^\circ$ about one-half of the alum will separate out, but ordinarily in the form of a mass of very minute

100 grams of water dissolve the given number of grams of
 $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Temp.	0°	5°	10°	15°	20°	25°	30°	40°	50°	60°	70°
Grams	5.6	6.6	7.6	9.6	11.4	14.1	16.6	24	36	57	110

crystals. In order to obtain large crystals during the cooling, three precautions are necessary: (1) A few small crystals must be added to serve as nuclei for the crystallization before setting the solution to cool. (2) Dust must be excluded, since dust particles might serve as nuclei for the formation of a great number of little crystals. (3) The cooling must take place very slowly in order that the crystal faces may be built up uniformly. This can be accomplished if the crystallizing dish is insulated by being covered with a watch glass and wrapped with a towel. If the solution set to crystallize is saturated at a much higher temperature than 35°, it will be found that the crystallization will proceed so rapidly that it will be quite impossible, even if the above precautions are all observed, to obtain good crystals.

Materials: cryolite, Na_3AlF_6 , 53 grams = $\frac{1}{4}$ F.W.
 quicklime, CaO, 48 grams.
 36-normal H_2SO_4 , 32 cc.
 potassium sulphate, K_2SO_4 , 22 grams = $\frac{1}{8}$ F.W.

Apparatus: 500 cc. casserole.
 2-liter common bottle.
 8-inch evaporating dish.
 6-inch crystallizing dish and watch glass or plate to cover it.

Procedure: Slake the quicklime and then mix in a large casserole with 250 cc. of water to make milk of lime. Stir into this 53 grams of finely powdered cryolite, and while constantly stirring, heat to boiling. Continue boiling for an hour, adding water to replace that lost by evaporation and stirring sufficiently to avoid spattering. At the end of that time add a part of 1½ liters of boiling water to the thick mass in the dish, and transfer it, together with the rest of the hot water, to a tall, wide-mouth, 2-liter bottle, and set aside to settle until the next period. The sludge should have settled so as to occupy not more than one-fifth of the volume of the liquid.

Siphon off as much clear liquid as possible without drawing over any of the precipitate. Then add $1\frac{1}{2}$ liters more of hot water to the bottle, stir and again let settle, and draw off the clear liquor. The residue in the bottle may be thrown away. Combine all the solution in a large bottle, and pass in carbon dioxide (Note 13(a), page 19), until all of the aluminum is precipitated. Test to see if this is accomplished at the end of $\frac{1}{2}$ hour by stopping the carbon dioxide stream and letting the precipitate settle enough to pour off a little clear liquor into a beaker. Pass carbon dioxide into this for a few minutes; if no precipitation occurs it shows that all of the alumina has already fallen out of the solution. If a precipitate does appear, the treatment of the entire solution with carbon dioxide must be continued until all the alumina is thrown out. Then let the precipitate settle until it occupies less than one-sixth of the entire volume. Siphon off the clear liquid and evaporate it to dryness in a porcelain dish. Powder the sodium carbonate so obtained, and preserve it in a cork-stoppered test tube. Stir up the precipitate left in the bottle with $1\frac{1}{2}$ liters of hot water; let settle, and siphon off and discard the clear liquid, since it will not contain sufficient sodium carbonate to pay for its evaporation. To the suspension of aluminum hydroxide left in the bottle add 32 cc. of 36-n H_2SO_4 , and warm, if necessary, to effect complete solution. Add 22 grams of potassium sulphate, and warm until dissolved. The solution should now be perfectly clear; if not, filter. If the volume exceeds 400 cc. evaporate to that bulk, and while still hot transfer it to the crystallizing dish (an 8-inch porcelain dish will answer). When cooled to $55-50^\circ$, drop 8 to 10 very small alum crystals into the solution, cover immediately with a glass plate, wrap the whole in a towel, and set where it will not be disturbed until the next exercise. Remove the few large crystals formed and preserve them. Evaporate the mother liquor not quite to $\frac{1}{2}$ its bulk (say $\frac{9}{16}$), and set this to crystallize in exactly the same manner as before. Add the crystals so obtained to the first lot. Dry the crystals on paper towels and preserve them in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. Of what does the insoluble residue consist which remains after boiling the cryolite with milk of lime? When this is discarded after partial washing according to directions, what pro-

portion of the soluble aluminum salt is lost with it? (Note that the actual solid material of the slime in question occupies an inappreciable volume as compared with the liquid in which it is suspended, even after the slime has been settling for several days. See Note 5 (b) on page 10.)

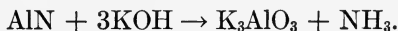
2. State what ions are produced by aluminum hydroxide (1) when it acts as an acid; (2) when it acts as a base. Compare its strength as an acid and as a base with that of other common electrolytes.

Define an *amphoteric* substance.

PREPARATION 25

ALUM AND AMMONIA FROM ALUMINUM NITRIDE

The preparation of aluminum nitride, No. 13, illustrates one of the possibilities in the way of fixation of atmospheric nitrogen. Although this method would hardly be of economic importance unless metallic aluminum could be produced very much more cheaply, it is obvious that if the aluminum nitride were to be utilized as a source of ammonia it would be profitable to recover a useful compound of aluminum. Boiling with a solution of caustic alkali, and still better, fusion with the dry reagent attacks the nitride.



For use as fertilizer ammonia is invariably absorbed in sulphuric acid, and put on the market as the solid and easily handled ammonium sulphate.

Treatment of K_3AlO_3 with sufficient sulphuric acid yields a solution containing the constituents of potash alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, but with three times the necessary proportion of K_2SO_4 . Nevertheless, pure alum can be crystallized from this solution. The mother liquor containing the excess of potassium sulphate is rejected. It is impossible to avoid this excess of potassium sulphate because the amount of caustic alkali prescribed is the minimum which will give a satisfactory reaction with the aluminum nitride.

Materials: aluminum nitride, AlN, 10 grams = $\frac{1}{4}$ F.W. (product of Preparation 13)
 potassium hydroxide, in sticks, 42 grams = $\frac{3}{4}$ F.W.
 6-normal H_2SO_4 , 250 cc.

Apparatus: 400 cc. sheet iron crucible.
5-inch funnel.
strip of asbestos paper for gasket.
2 filter bottles to use as absorption flasks.
2 1-hole rubber stoppers to fit filter bottles.
connections as described.
600 cc. beaker.
1-liter flask.
8-inch crystallizing dish.

Procedure: Place the aluminum nitride and the potassium hydroxide in the iron crucible. Wet the strip of asbestos paper and fold it over the edge of the crucible all the way around. Press the funnel down over this asbestos gasket to make a tight joint and connect the stem of the funnel with the absorption flasks, in the first of which is 40 cc. of water, and in the second 15 cc. of 6-normal H_2SO_4 . The gas delivery tube should come within one half inch of the surface of the liquid in each bottle, but should not dip in the liquid. The delivery tubes should be of good size so that no gas pressure can arise to force the ammonia out past the gasket. Heat the crucible with a very low flame for 20 minutes, then increase the size of the flame gradually and heat the bottom of the crucible to redness for 30 minutes. Pour the contents of the two flasks together and add sulphuric acid, noting amount, until the exact point of neutrality is reached (Note 11, page 17). Evaporate the solution on steam bath to complete dryness (Note 6(b), page 12), and put up the ammonium sulphate in a cork stoppered test tube.

After the crucible has cooled add 250 cc. of water and let the contents disintegrate. Pour the solution and sludge into a beaker and with 50 cc. of water rinse the crucible into the beaker. Boil the contents of the beaker 5 minutes and filter the hot solution into a liter flask. Cool the solution completely. Hold about $\frac{1}{4}$ of it in reserve and add 6-normal H_2SO_4 slowly to the $\frac{3}{4}$, rotating the flask in a pan of cold water to keep the solution from growing hot. Record in the note book the volume of acid which first gives a precipitate that will not redissolve on rotating the contents of the flask persistently, and then that will just redissolve the precipitate. Then add the remaining $\frac{1}{4}$ of the solution, which will bring down a heavy precipitate again; and add H_2SO_4 very

carefully with constant rotation until this precipitate just re-dissolves. Record the total volume of acid used. Filter the solution if it is not perfectly clear and set it in an uncovered 8-inch crystallizing dish, in a place free from dust, to evaporate slowly and crystallize. If preferred the method of crystallizing outlined in the preceding preparation may be followed (Note 8, page 13, on crystallization). Discard the last 360 cc. of the mother liquor since this will contain so much excess of potassium sulphate that this salt would crystallize also. Dry the alum crystals on paper towels and preserve them in an 8-ounce cork-stoppered bottle.

QUESTIONS

1. The aluminum nitride prepared by method of No. 13 contains aluminum carbide as impurity. Find in a reference book the formula of this carbide. What is the product of the hydrolysis of the carbide? Equation?
2. Answer question 2 under No. 24.
3. Write in ionic form the successive reactions as sulphuric is gradually added to potassium aluminate solution. Explain each reaction and state to what type it belongs.
4. Repeat question 3 for the gradual addition of potassium hydroxide to an aluminum sulphate solution.

PREPARATION 26

HYDRATED ALUMINUM CHLORIDE, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

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, $13\frac{1}{2}$ grams = $\frac{1}{2}$ F.W.

12-normal HCl, 125 cc.

90 grams rock salt and 175 cc. 36-n H_2SO_4 for hydrogen chloride generator.

shredded asbestos.

potassium hydroxide in sticks for dessicator.

ice.

Apparatus: 750 cc. flask.

suction filter and marble.

1500 cc. flask for generator (Fig. 15 on p. 118).

3-inch dish.

dessicator (a wide jar covered with a sheet of asbestos paper pressed close to the edge with a heavy plate will serve).

Procedure: Place the aluminum turnings in a 750 cc. flask, add 50 cc. of water and then the 12-n 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(a), page 8) and return it to the 750 cc. flask. Fit up the hydrogen chloride generator and connections so that the gas will pass first through a washing bottle containing a little 12-n HCl and provided with a safety tube (Fig. 19 on p. 164). 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 $1\frac{1}{2}$ 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 $\frac{1}{2}$ 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 3-inch dish in the dessicator in which sticks of potassium hydroxide have been placed. It will take several days for the excess of hydrochloric acid to evaporate from the crystals. When it is dry put the product in a 6-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 casserole 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 27

ANHYDROUS ALUMINUM BROMIDE

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. The fact that aluminum bromide can be purified by distillation is rather typical of the binary halogen compounds, most of which are volatile, — usually very much more so than the oxides.

Aluminum bromide melts at 90° and boils at 265° . 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 = $\frac{1}{3}$ F.W.
bromine, 80 grams = 25 cc. (must be dry and must be measured in a dry graduate).

Apparatus: 2 100 cc. distilling flasks.
100 cc. dropping funnel.
600 cc. beaker.
3 clean dry test tubes.
18 inches hard glass tube of $\frac{5}{8}$ -inch diameter.

Procedure: This preparation must be carried out entirely under the hood. Fit the dropping funnel with a rubber stopper into one of the distilling flasks, clamp the latter upright with the bulb

immersed in water boiling in a 600 cc. beaker on a lamp 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; if it is too large it must be drawn out a little smaller in the blast flame. The hard glass tube should slope somewhat from the distilling flask to the receiving flask, but not enough so that the aluminum turnings, which are to be placed about in the middle of this tube but a little nearer the upper end, will not stay in place.

The entire apparatus must be absolutely dry inside. Place the bromine in the dropping funnel, and open the stop cock so that it drips very slowly into the heated flask and vaporizes. Heat the aluminum fairly strongly 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. If it is necessary in order to sustain the reaction, the glass tube may be heated. 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, as is not likely, 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. 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 three 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 one or two 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 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. If a deposit of aluminum oxide adheres inside the distilling flask add a few cc. of 12-n 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 arms length with the face turned away, pour it all at once into the first beaker. The reaction is startling but not dangerous if one is not too near. Heat the contents of the beaker until the carbon disulphide is all 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. What causes the dense fogging? After the carbon disulphide evaporates let the residue stand on a hot plate until it appears dry and no longer gives off a fog. 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 normal NaOH, one 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 normal NaOH to give Na_3BO_3 , 50 cc. to give NaBO_2 , and 25 cc. to give $\text{Na}_2\text{B}_4\text{O}_7$. 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, $\text{H}_2\text{B}_4\text{O}_7$) 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 salt solution (nitrate, chloride, or sulphate) 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 acid and basic properties.

3. Aluminum Hydroxide Acting as an Acid. To a little aluminum salt solution (nitrate, chloride, or sulphate) 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, $Al(NO_3)_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaNO_3$. That the aluminum hydroxide thus 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.



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 Exp. 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.

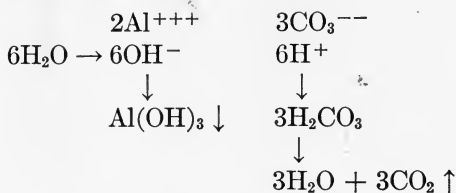
The precipitate is aluminic acid, displaced from its salt by the stronger acid, $\text{Na}_3\text{AlO}_3 + 3\text{HNO}_3 \rightarrow \text{H}_3\text{AlO}_3 + 3\text{NaNO}_3$. That the aluminic acid dissolves in nitric acid indicates that it reacts to form a soluble salt and is itself reacting as a base.

5. Comparative Basic and Acidic Strength of $\text{Al}(\text{OH})_3$. 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 $\text{Al}(\text{OH})_3$ 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 $\text{Al}(\text{NO}_3)_3$ 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 $\text{Al}(\text{OH})_3$. 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:



That aluminum carbonate is thus completely hydrolyzed indicates that the base and the acid are both very weak.

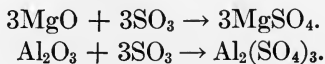
GENERAL QUESTIONS VI

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 if more than one is described in the reference books; 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 stability of magnesium and aluminum carbonates, — of dry magnesium and aluminum sulphates. Find the heat of formation of equivalent amounts of the sulphates according to the equations.



What do the facts thus cited show as to the relative basic strength of magnesium and aluminum oxides. (Compare General Questions V, Nos. 5 and 6.)

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, — they being not greatly, or not at all, affected by the atmosphere or by water. They are distinctly base-forming with the exception of gold, in that their oxides yield fairly stable salts with the strong acids; but their basic properties are comparatively weak, and the oxides of some of them show very feeble acidic properties as well.

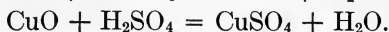
Copper, silver, and gold in Group I show a similarity to sodium and potassium principally in the fact that they form certain compounds of the same type, for example, M_2O and MCl . Zinc, cadmium, and mercury in Group II resemble calcium, barium, and strontium in that they form compounds of the types, 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 28

CRYSTALLIZED COPPER SULPHATE (BLUE VITRIOL) FROM COPPER TURNINGS

On account of the fact that copper has not, like zinc, iron, etc., 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 affect with acids, nevertheless copper *oxide* is readily dissolved; 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 will be employed instead of air as the oxidizing agent.



Materials: copper turnings, 64 grams = 1 F.W.

6-normal HNO_3 .

6-normal H_2SO_4 .

Apparatus: 500 cc. dish.

suction filter.

6-inch crystallizing dish with watch glass or glass plate to cover it.

Procedure: Heat the copper turnings in an iron pan until all oily matter is burned and the metal has become coated with oxide. In a 500 cc. porcelain dish treat the ignited copper turnings with the calculated volume of 6-n H_2SO_4 and 6-n HNO_3 . Warm in the hood for 20 minutes; if any metallic copper remains undissolved, pour the solution off from it and dissolve 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 crystal meal, throwing away the mother liquor from this crystallization. Dissolve all of 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 and save 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 a 12-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 concentrated 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?

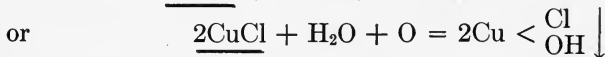
PREPARATION 29

CUPROUS CHLORIDE

Although copper itself is not readily oxidized, yet when oxidation is once induced it proceeds under most conditions at once to the "ic" state (corresponding to the oxide CuO). This is in accordance with the fact that cuprous salts are oxidized with the greatest readiness, so that, in the presence of any oxidizing agent powerful enough to oxidize metallic copper, any cuprous salt which might first be formed would instantly be oxidized to cupric. When metallic copper is placed in a cupric chloride solution, the former soon becomes coated with a white deposit of cuprous chloride,



the copper acting as a reducing agent, and the cupric ion as an oxidizing agent. This insoluble coating soon prevents further contact of the reacting substances with each other, and the reaction becomes very slow, or ceases. But if concentrated HCl is added to the solution, the cuprous chloride is dissolved and the reduction of the cupric salt continues to completion. The cuprous chloride and chloride ions unite to form the complex cuprochloride ions CuCl_2^- and CuCl_3^{--} . But these complex ions are not very stable, and if the concentration of chloride ions is diminished by diluting the solution, they dissociate, and cuprous chloride precipitates. Cuprous chloride is so readily oxidized that, even in contact with moist air or suspended in water containing dissolved air, it is changed to a cupric salt:



Hence a great deal of care will be necessary in washing and drying the cuprous chloride to prevent its becoming discolored in consequence of oxidation. When perfectly dry, however, or when covered with dry ether, the oxidation takes place very slowly.

Materials: cryst. cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 43 g. = $\frac{1}{4}$ F.W.
 clean copper wire, 25 grams.
 12-normal HCl 100 cc.
 95% alcohol, 30 cc.
 ether, 30 cc.

Apparatus: 300 cc. flask.
short stemmed funnel.
2-liter common bottle.
suction filter.

Procedure: Dissolve the crystallized cupric chloride in 100 cc. of water and 100 cc. of 12-n HCl. Place the solution, together with the clean copper wire in a flask and suspend a short-stemmed funnel in the neck of the flask to prevent in part the escape of acid vapors. Warm the mixture in the flask to about 80° and hold it at that temperature by placing the flask over a very tiny flame or on a warm plate, but do not allow the solution to boil. The green color disappears gradually and the solution becomes colorless, but usually, the moment this point is reached, an intense brown color, arising from some unexplained impurity, develops within a few seconds, and unless one watches all the time, he will fail to see the transition. Test for complete reduction by pouring $\frac{1}{2}$ cc. of the solution in a test tube and adding water. White cuprous chloride is precipitated and if the cupric salt is all reduced the solution will show no blue color. Pour the contents of the tube into the 2-liter bottle, and if the test was satisfactory, put 2 liters of cold water in the bottle and pour into it, in a thin stream, all the solution from the flask, leaving the remnants of copper wire behind. Rinse the flask into the bottle with about 25 cc. of water. Mix the contents; let the white precipitate settle; pour off most of the liquid, stir up the precipitate with the rest and pour the suspension into the suction filter; add a few drops of HCl and 50 cc. of water to the bottle and rinse out the last of the cuprous chloride into the filter. Continue the suction until the last drop of liquid is drawn into the cake of cuprous chloride; 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. Apply the suction until the last drop of alcohol is sucked into the cake, then stop the suction. In exactly the same way, wash the sides of the funnel and the cuprous chloride with one more 15 cc. portion of alcohol and with two successive 15 cc. portions of ether. Transfer the caked cuprous chloride to paper towels, break up the cake with a spatula, and leave the preparation on the warm plate 5-10 minutes, until the adhering ether has evaporated. Pulverize

the product and put it up in a warmed (to thoroughly dry) 6-inch cork stoppered test tube. The product should be pure white.

QUESTIONS

1. Metallic copper placed in a cupric sulphate solution causes no easily observed reaction, as is probably well known to the student. Nevertheless, very careful experiments are capable of showing that cuprous ions, Cu^+ , are formed to a very small extent in the solution, $\text{Cu}^\circ + \text{Cu}^{++} \rightleftharpoons 2\text{Cu}^+$. But this reaction is reversible and it has already reached a state of equilibrium when the concentration of cuprous ions is so small as to escape detection except by the most refined methods of measurement.

In view of the fact that cuprous chloride is extremely insoluble, state why the above reaction can proceed to completion towards the right in a solution containing chloride ions.

2. Place 2 to 3 grams of cuprous chloride in the bottom of a dry test tube. Fill it completely with 6-n 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. Unstopper the tube and quickly pour its contents into a bottle of about 300 cc. capacity, and immediately cork the latter air-tight. Shake the bottle vigorously for 3 minutes, then place the mouth under water and remove the cork. From its quantity, infer what gas is absorbed from the air in the bottle. What is the change in the condition of the copper salt which causes its change in color? Equations?

3. Spread about $\frac{1}{2}$ 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. 6-n HCl . What causes the solid to again become white and the solution blue? Equation?

PREPARATION 30

CUPROUS OXIDE

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 alkalies 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. Such a solution is known as *Fehling's solution*.

Materials: blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50 grams = $\frac{1}{2}$ F.W.
Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6$, 75 grams.
sodium hydroxide in sticks, 75 grams.
grape sugar, 100 grams.
alcohol, 45 cc.

Apparatus: 8-inch evaporating dish.
2-liter common bottle.
suction filter.
350 cc. casserole, 3 beakers, and 3 8-inch common filters.

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 solution results, but one of so deep blue a color as to appear almost like ink. Dissolve the grape sugar in 150 cc. of water, filter if necessary, add it to the solution in the dish, and boil the mixture until the copper has precipitated as the bright red cuprous oxide, and the blue color has disappeared from the liquid. Transfer the contents of the dish to the 2-liter bottle, add water to fill the latter, mix the contents thoroughly, and 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 folded paper towel on the warm plate, and as soon as the alcohol is evaporated, put up the product in a 6-inch cork stoppered test tube.

QUESTIONS

1. Treat small samples of the product with 6-n H_2SO_4 , 6-n HCl and 6-n NH_4OH respectively. What reaction would you expect to take place with these reagents, and what evidence of such reactions do you actually observe?

Place 0.5 gram of cuprous oxide in a test tube, fill the tube with 6-n HCl , and stopper it tightly with a rubber stopper. Let it stand at least 24 hours, shaking as often as convenient, and letting the tube lie on its side the rest of the time in order to expose a larger surface of the solid material to the reagent. Finally pour some of the clear solution into a large beaker of water. Does this furnish any evidence that the cuprous oxide has reacted with the acid?

PREPARATION 31

AMMONIO-COPPER SULPHATE, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$

Preparation 3 illustrated the formation of a double salt, potassium and copper sulphate, and one of the experiments following that preparation showed that ammonium could be substituted for potassium to give the ammonium and copper sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$. 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 in 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. 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 $\text{Cu}(\text{NH}_3)_4^{++}$, 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 97.)

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.

blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 25 grams = $\frac{1}{10}$ F.W.

6-normal NH_4OH , 85 cc.

alcohol, 165 cc.

ether, 20 cc.

Apparatus: 100 cc. dropping funnel.

300 cc. tall common bottle.

2 250 cc. flasks.

400 cc. beaker.

Procedure: Pulverize the blue vitriol, place it in a flask and dissolve it in the 85 cc. of cold 6-n NH_4OH . (See Note 7, page 13.) 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 and 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 6-inch test tube, 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)) with the same liquids as were used for the larger crystals. Preserve the large crystals and the crystal meal separately, each in a 6-inch cork stoppered test tube.

QUESTIONS

1. What is the reaction between Cu^{++} and OH^- ions? To a little 1-n CuSO_4 add 6-n NaOH drop by drop, until it is present in large excess. Save the solution.

2. When ammonium hydroxide is added instead of sodium hydroxide, explain what successive reactions occur.

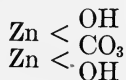
3. Add ammonium chloride to the solution saved from (1) and explain the results.

4. To 5 cc. of 1-n 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 32

ZINC OXIDE

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 to its formation are brought together. The simplest formula for the basic carbonate is



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.

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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystallizes isomorphously with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ a preparation of the latter cannot be freed of the former by recrystallization. By addition of chlorine water 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 $\text{Fe}(\text{OH})_3$. 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, No. 21.)

Materials: white vitriol, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 57 grams = $\frac{1}{5}$ F.W.
anhydrous sodium carbonate, Na_2CO_3 , 23 grams = $\frac{1}{5}$ F.W.
chlorine water, 15 cc. (must be fresh and smell strongly of chlorine).

Apparatus: 2 2-liter common bottles.
5-inch filter funnel.

Procedure: Dissolve the zinc sulphate in 1.5 liters of hot water in the 2-liter bottle. Add the chlorine water, and stir well. Dissolve the sodium carbonate in 250 cc. of water; add 12 cc. of this solution at once to the large bottle, stir and observe the color of the precipitate. If it is reddish brown ($\text{Fe}(\text{OH})_3$) add 12 cc. more of the sodium carbonate solution, which ought to precipitate white basic zinc carbonate. The entire precipitate when mixed, ought to be of a light buff color showing it to contain basic zinc carbonate. Hold the rest of the Na_2CO_3 solution in reserve. Let the solution in the bottle stand (best over night) until the precipitate has settled. Decant the clear solution through a large filter catching the filtrate in another 2-liter bottle. Finally pour the sludge on the filter and let it drain. Filter the rest of the Na_2CO_3 solution unless it is clear and add it to the zinc sulphate

solution. The precipitate should be pure white. Note the effervescence. Let the precipitate settle, — to $\frac{1}{3}$ or $\frac{1}{4}$ the volume of the solution. 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 percent of the soluble sodium sulphate present at first (see Note 5 (b)). Finally, transfer the slime to a large, ordinary filter (Note 4 (c)), 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. Pulverize the basic zinc carbonate, and heat it moderately in a porcelain dish over a free flame until all the carbon dioxide has been driven off. Test the product by wetting 0.1 gram with 2 cc. of water and adding a few drops of 6-n HCl. The zinc oxide should dissolve, and there should be no trace of effervescence. Put up the preparation in a 6-inch cork stoppered test tube.

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?

To some solution of zinc sulphate add a solution of sodium hydroxide, drop by drop, until the precipitate first formed re-dissolves. How is zinc hydroxide similar to aluminium hydroxide in respect to its behavior towards strong acids and strong bases? Write ionic equations.

PREPARATION 33

MERCUROUS NITRATE, $\text{HgNO}_3 \cdot \text{H}_2\text{O}$

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 , from which are derived respectively 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 = $\frac{1}{8}$ F.W.
6-n HNO₃, 20 cc.

Apparatus: 50 cc. flask.
3-inch evaporating dish.

Procedure: Treat 25 grams of mercury in a flask at the hood with 20 cc. of 6-n HNO₃, 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 10 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 of 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 34

MERCURIC NITRATE

When mercury is heated with an excess of nitric acid, mercuric nitrate is produced. This salt is exceedingly soluble in water, and it can only be crystallized 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, $\text{Hg} < \begin{matrix} \text{NO}_3 \\ \text{OH} \end{matrix}$. 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 = $\frac{1}{8}$ F.W.
6-normal HNO_3 , 60 cc.

Apparatus: 50 cc. flask.
100 cc. casserole.
25 cc. glass stoppered sample bottle.

Procedure: Heat 25 grams of mercury in a flask with 60 cc. 6-n HNO_3 until it is all dissolved. Test a drop of the solution by adding to it in a test tube $\frac{1}{2}$ 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 over a very small free flame until the liquid has assumed a sirupy consistence and crystals just commence to form on the surface. Then remove the whole mass to the 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.)
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 35

MERCURIC SULPHOCYANATE

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.

Thus potassium sulphocyanate, $KSCN$, yields the ion SCN^- just as potassium chloride yields the ion Cl^- . 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 an 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 99). 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 intensely 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 so long as any of the latter are present, the solution remaining colorless and the precipitate $Hg(SCN)_2$ forming towards the end; but so soon as the Hg^{++} -ions are exhausted, then the SCN^- -ions unite with Fe^{+++} -ions, producing the red compound, and the appearance of the red color is the indication to stop.

Mercuric sulphocyanate has the peculiar property that when ignited it burns with the production of a very voluminous coherent ash, which, from the form which it assumes, is called "Pharaoh's Serpent." It should not be burned in an open room 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.

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 moulds about 1 cm. wide and 1 cm. deep, and letting it dry out and harden.

QUESTIONS

1. Find out what is the degree of ionization of the soluble halides of mercury, *i.e.*, HgCl_2 , $\text{Hg}(\text{CN})_2$. 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 Chap. III Exps. 15, 16, 19, 20, and 21 and the discussion of the basic properties of metal hydroxides, p. 94, and of complex ions, p. 97. In Chap. IV, review Exps. 16 and 22.

1. Stability of the Carbonates. (*a*) Make unacidified solutions of CuSO_4 , ZnSO_4 , CdSO_4 , by dissolving 1 gram of each in about 15 cc. of water, and of AgNO_3 by dissolving 0.5 gram in 10 cc. of water. To each solution add 1-n Na_2CO_3 until no further precipitate is formed and notice very carefully whether any bubbles of gas escape. In those cases in which a gas did escape, collect the precipitate on a filter wash it 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 $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$. This shows that the basic character of the hydroxides is

weak, but not so weak as that of $\text{Al}(\text{OH})_3$, because not even a basic carbonate of aluminum can be formed. Since no effervescence took place with the silver salt, the precipitate must have been the neutral carbonate, Ag_2CO_3 , which indicates that silver oxide is 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 , $\text{Hg}(\text{NO}_3)_2$, and ZnCl_2 , do not dissolve in pure water to give a clear solution but that a flocculent residue of basic salt, $\text{HgNO}_3 \cdot \text{HgOH}$, HgOHNO_3 , ZnOHCl , is left. The formation of the basic salt is a partial hydrolysis, it leaves the solution faintly acidic; but, 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 1-n CuSO_4 ; (b) 10 cc. of .05-n AgNO_3 ; (c) 1 cc. of 1-n ZnSO_4 ; (d) 1 cc. of 1-n CdCl_2 ; (e) 5 cc. of 0.1-n HgNO_3 ; and (f) 5 cc. of 0.2-n $\text{Hg}(\text{NO}_3)_2$. To each tube add water to make a volume of 10 cc. and then add 6-n NaOH one 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 $\text{Cu}(\text{OH})_2$, (b) brown Ag_2O ; (c) white $\text{Zn}(\text{OH})_2$, (d) white $\text{Cd}(\text{OH})_2$, (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; 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 Exps. 2, 3, 4, and 5 in Chap. VI).

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 latter 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 Exp. 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 of 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 pp. 97-99). 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, as 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. 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 small crystals 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 $\text{K}^+ \text{CuI}_2^-$, 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, Chap. IV, Exps. 12, 13, and 14.)

(b) To 1 cc. of 0.2-n $\text{Hg}(\text{NO}_3)_2$ 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.

(c) To 1 cc. of 0.05-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 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, $\text{AgCl}_2^- \rightleftharpoons \text{AgCl} \downarrow + \text{Cl}^-$, 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 p. 99.) The negative radical ions show differ-

ing 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 are due to some such cause.

7. Sulphides. (a) To separate tubes containing diluted heavy metal salt solutions as in Exp. 3, (a) to (f), add 2 cc. of 6-n $(\text{NH}_4)_2\text{S}$ 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 cc. of 6-n HCl.

The precipitates are CuS , dark brown; Ag_2S , black; ZnS , white; CdS , yellow; $\text{HgS} + \text{Hg}$, 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, $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{--}$, 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, p. 111, and Exp. 22, p. 154).

8. Electromotive Series. Review Exp. 20, Chap. III, 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, $\text{KAg}(\text{CN})_2$, and the instability of sodium argentichloride, NaAgCl_2 .

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, insofar as they enter binary compounds, in which they act as the negative constituents.

When two non-metallic elements unite, the one which is the least strongly non-metallic is regarded as the positive constituent; it is, so to speak, compelled to play the positive role 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, + VI, and oxygen, — II, 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, $\text{SO}_3 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4$; $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$. 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 one sulphur, with a valence of + VI, and four oxygens, with a valence of — II each, would leave the unbalanced valence of — II 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 electro-negative 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 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; indeed it is probable that if the elements which should fit into the places below tellurium and iodine, respectively, are ever found, they will display rather marked metallic properties.

The characteristic valences of the sixth and seventh groups are VI and VII, 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 in every way 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_2^{--} , whereas the A family elements form positive ions, Cr^{++} , Cr^{+++} .

PREPARATION 36

POTASSIUM BROMATE AND POTASSIUM BROMIDE

Bromine, like chlorine, hydrolyzes to a considerable extent according to the reversible reaction:



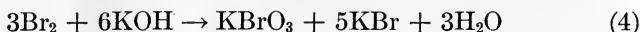
In presence of a base both acids are neutralized as fast as formed and reaction (1) proceeds to completion. Thus the complete reaction in presence of KOH is:



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:

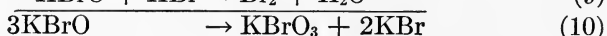
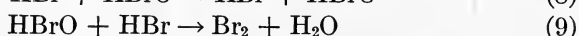
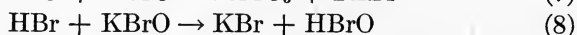
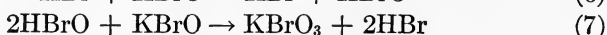
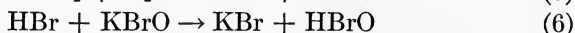
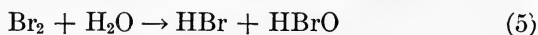


Multiplying equation (2) by 3 and adding equation (3) the equation



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, in 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 of the hypobromite into bromate. The addition of all of the equations (5) to (9) in the train gives the equation (10) for the total net change which is identical to equation (3)



Materials: potassium hydroxide: 1 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: Br_2 , $\frac{1}{4}$ F.W. = 40 grams = $12\frac{1}{2}$ cc.

Apparatus: 300 cc. flask.

30 cc. iron crucible.

suction filter.

small ordinary filter.

4-inch evaporating dish.

graduate.

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 filtrate to obtain by-product.

Dissolve 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 crystals. Add mother liquor to that reserved for obtaining the by-product, potassium bromide.

Dissolve .05 gram of crystals in 2 cc. hot water, add 1 drop of AgNO₃ solution. A precipitate while the solution is at 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 of 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. 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 cork-stoppered test tubes.

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 37

POTASSIUM CHLORATE

Chlorine hydrolyzes to an even greater extent than bromine. (Study the discussion of the preceding preparation.) 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 } the stick form of
sodium hydroxide, 44 grams }
these hydroxides, as free of carbonate as possible, should be used. Allowing roughly 10 percent as water gives the net amounts: KOH, $\frac{1}{4}$ F.W.; NaOH, $1\frac{1}{4}$ F.W.

chlorine, to be generated from coarse manganese dioxide and 12-n HCl.

Apparatus: 500 cc. flask with 2-holed rubber stopper.

chlorine generator, use 1500 cc. round-bottomed flask.

suction filter.

Procedure: Calculate the amount of manganese dioxide and 12-n HCl required to generate the chlorine necessary to react with the alkalis. Take 10 percent 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 6-n 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, while still at boiling temperature onto 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 onto the salt crystals in the filter, and, after it has soaked in, apply the suction. In this way nearly all of 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 cork-stoppered test tube.

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 tabular outline of the method to be followed if the mother liquors are worked over.

2. The modern 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 38

POTASSIUM IODATE

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,



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 = $\frac{1}{4}$ F.W.
iodine, 36 grams.

Apparatus: 800 cc. flask.
short stemmed funnel.
pan of cold water.
suction filter.

Procedure: Dissolve 31 grams of potassium chlorate by warming it with 100 cc. of water in an 800 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 if this prediction is borne out by the facts.

PREPARATION 39

IODIC ACID; IODINE PENTOXIDE

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 easily 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 = $\frac{1}{5}$ F. W.
barium nitrate, $\text{Ba}(\text{NO}_3)_2$, 26 grams = $\frac{1}{10}$ F.W.
36-n H_2SO_4 , 8 cc.

Apparatus: tall 600 cc. beaker.
500 cc. casserole.
suction filter.

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 dish, suspend it in 250 cc. of water, heat to boiling, and stir in a solution of 8 cc. 36-n 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, and evaporate until solid iodic acid separates in some quantity. Cool completely and rinse the crystals with three successive portions of 10 cc. each of 16-normal 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 sample bottle.

To obtain completely anhydrous iodine pentoxide, the product could be heated for some time in an oven at about 200° . Crys-

tallized 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 $\frac{1}{2}$ 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 40

POTASSIUM PERCHLORATE

When potassium chlorate is heated to about 400° it may decompose according to either of the following independent reactions:



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.

Materials: potassium chlorate, KClO_3 , 61 grams = $\frac{1}{2}$ F.W.

Apparatus: 100 cc. porcelain crucible.
suction filter.

Procedure: Place 61 grams of potassium chlorate in a dry, clean 100 cc. porcelain crucible, the glaze of which is in perfect condition. Place a small watch glass over the crucible to prevent loss of particles of the salt by decrepitation, and heat gently until the charge just melts. Then remove the watch glass 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 50 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) on 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 (ClO_2) when treated with a few drops of concentrated 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 dissociated electrolytically 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 41

SODIUM THIOSULPHATE, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

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 *thiosulphate* instead of sulphate is formed.

The sulphur so taken up certainly plays a different function than 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: 2 350 cc. flasks with 2-hole rubber stoppers and delivery tubes.

600 cc. beaker with watch glass to cover it.

5-inch funnel and 10-inch filters.

8-inch porcelain dish.

6-inch crystallizing dish.

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; 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 of 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 if 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 a 6-inch crystallizing dish until an abundant crop of crystals is obtained; discard the final 30 cc. of mother liquor. Sodium thio-sulphate 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 a 10-ounce cork-stoppered bottle.

QUESTIONS

1. Dissolve $\frac{1}{2}$ 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 thio-sulphate? 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

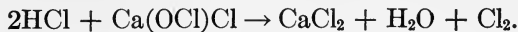
unabsorbed. Look up the degree of ionization of both hydrogens, both of sulphurous and carbonic acids. Write equations for the reactions taking place during each of the stages enumerated above.

Experiments

1. Hypochlorites. (a) 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.

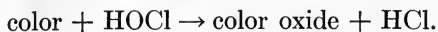
Calcium chloride and calcium hypochlorite are both extremely soluble; but bleaching powder always contains a considerable excess of calcium hydroxide which has not reacted with the chlorine, and also a good deal of calcium carbonate. It is for this reason that it does not appear to the eye to dissolve. That hypochlorite dissolves freely out of the bleaching powder is shown by the action with hydrochloric acid.



(b) Soak a piece of colored cotton cloth in one half of the filtrate obtained in (a). 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 Prep. 37) 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, $\text{H}^+ + \text{OCl}^- \rightarrow \text{HOCl}$, the ionization of this acid in 0.1-n solution being 0.06 of one percent. 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).

Add the rest of the solution to a solution of $\frac{1}{4}$ 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,



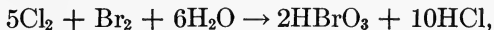
3. Chlorates and Bromates. The formation of chlorate and bromate by heating hypochlorite and hypobromite respec-

tively, is illustrated in Preps. 36 and 37. 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 Exp. 11, Chap. IV, 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 + V.



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 sul-

phate 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 + III and + V respectively,



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 + V to one of - I.

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.

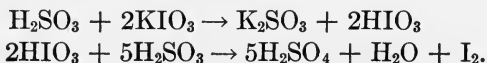
Iodate and iodide ions alone have no action on each other, but with hydrogen ions present a mutual oxidation and reduction of the iodine takes place.



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 iodide to free iodine which gives the blue color.



The iodine is then reduced by more sulphurous acid to hydriodic acid which is colorless,



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 Exp. 6.

Sulphur burns forming sulphur dioxide SO_2 . The effect with the potassium iodate-starch paper constitutes a convenient test for sulphur dioxide.

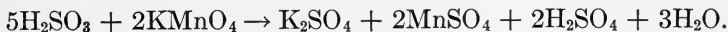
8. Sulphurous Acid. (a) Bubble sulphur dioxide into a bottle of water and note that it dissolves freely. The solution colors litmus red and it conducts electricity fairly well.

(b) **Test for Sulphurous Acid.** To 5 cc. of sulphurous acid add 1 cc. of 6-n 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 of the sulphuric acid. Then the addition of bromine oxidizes the sulphurous acid to sulphuric acid and another precipitate of barium sulphate is produced.



9. Reducing Action of Sulphurous Acid. To 5 cc. of potassium permanganate solution add sulphurous acid. The deep red solution becomes colorless.



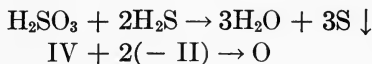
10. Oxidizing Action of Sulphur Dioxide and Sulphurous Acid. (a) Fill a 250 cc. wide-mouthed bottle with sulphur

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 Exp. 6 (a) in which an element existing in different states of oxidation mutually oxidizes and reduces itself.

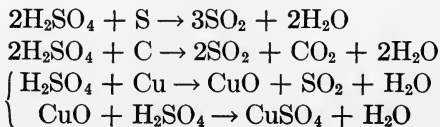


11. Dehydrating Action of Sulphuric Acid. Add 10 cc. of 36-n H_2SO_4 to 5 grams of sugar in a porcelain dish. If necessary warm the mixture a little to start a reaction. Once started the reaction proceeds vigorously giving off a good deal of heat, and the sugar swells up and grows black. Finally, there is left a bulky brittle charcoal like mass.

The formula of sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ 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 36-n 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. Exps. 13 and 14 in Chap. IV) it being reduced usually to sulphurous acid (SO_2).



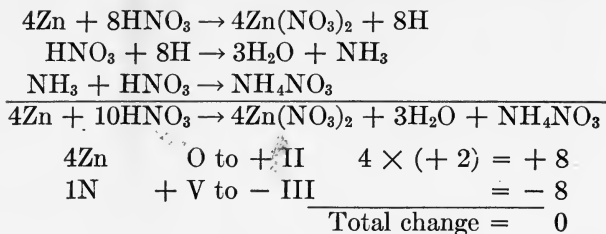
This experiment should be compared with Exps. 6 (b), 8 (b) and 9, in which sulphurous acid reduces iodic acid, bromine, and permanganate it itself being oxidized to sulphuric acid. The latter is not an oxidizing agent in dilute solution.

13. Nitric Acid as an Oxidizing Agent. (a) To 3 grams copper turnings in a test tube add 5 cc. water and 5 cc. of 6-n HNO_3 . Fit stopper with 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. Nitric acid first oxidizes copper, it itself being reduced to nitric oxide, $3\text{Cu} + 2\text{HNO}_3 \rightarrow 3\text{CuO} + \text{H}_2\text{O} + 2\text{NO}$; 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, $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$.

(b) To 2 grams of zinc turnings 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 limit represented by ammonia. The ammonia does not escape from the solution because it combines with the excess of nitric acid.

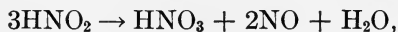


Explain how the final step in the experiment is an example of the displacement of a weak base from its salt by a stronger base and that it involves no change in the primary valence of any of the elements.

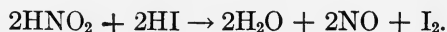
14. Nitrous Acid. (a) Dissolve $\frac{1}{2}$ gram of sodium nitrite in 5 cc. of ice water and add 1 cc. of cold 6-n H_2SO_4 . A blue solution results which at 0° effervesces very slowly. Add a few drops of this solution to a half test tube of water containing a few drops of iodide-starch solution. An 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 red 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,



the NO giving the red color when it comes in contact with air. Nitrous acid is an oxidizing agent, liberating iodine from hydriodic acid,

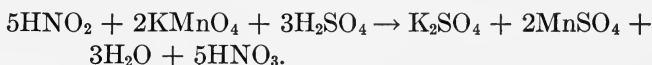


Since nitric acid does not liberate iodine under similar circumstances, the nitrous acid is shown to be the more vigorous oxidizing

agent. This is quite in accord with what we have already found in other cases, namely, that the stability of the acid is greatest 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 sodium nitrate 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,



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, the four corresponding acids of bromine and of iodine with 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 fifth column the word gas, liquid, solid, or hyp., according as to the state of aggregation of the anhydride at ordinary temperature, hyp. signifying hypothetical or non-existent; in the sixth column the percent ionization of the acid in 0.1 normal 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 THE 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. As in the case of 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, while the elements of high atomic weight are almost entirely base-forming. Between these extremes there is an almost regular gradation of properties.

Titanium, although it is a fairly abundant constituent of the earth's crust, is an element of comparatively little importance.

Cerium and thorium, the heaviest two elements of Family A, have acquired some importance on account of the use of their oxides in incandescent gas-lighting mantles.

PREPARATION 42

PRECIPITATED SILICA

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 syrup like consistency and is sold on the market under the name of "water glass." Several grades of water glass of different ratios $\text{Na}_2\text{O}:\text{SiO}_2$ are sold, but perhaps the most common grade approximates the composition $\text{Na}_2\text{Si}_4\text{O}_9$ ($= \text{Na}_2\text{O}.4\text{SiO}_2 = \text{Na}_2\text{SiO}_3.3\text{SiO}_2$).

The addition of an acid to a sodium silicate solution causes a separation of silicic acid which appears as a jelly-like substance. Ortho-silicic acid has the composition H_4SiO_4 , meta-silicic acid, H_2SiO_3 ; the acid corresponding to the sodium salt of the above formula, $\text{H}_2\text{Si}_4\text{O}_9$. Suspended in water these different silicic acids are more or less easily interchangeable one into the other, 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.

Apparatus: 6-inch evaporating dish.
tall 600 cc. beaker.
suction filter.

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 at 130° is available the dish and contents should be baked for one hour at this temperature. Otherwise heat the dish over a flame for fifteen minutes avoiding, if possible, letting any part of the con-

tents 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 tall 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 cork-stoppered test tube.

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 $\frac{1}{2}$ 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. Explain all of the reactions, with equations, and state what rather unusual properties are shown by this experiment to be possessed by hydrofluoric acid and by silicon tetrafluoride.

PREPARATION 43

STANNOUS CHLORIDE ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)

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, by its action upon a metal, reduced only to the oxide NO ; 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 HNO₃, 25 cc.
500 cc. casserole.

Apparatus: shredded asbestos for filter.
suction filter.
6-inch evaporating dish.

Procedure: Place 100 grams of feathered tin in a large casserole, cover with 175 cc. of 12-n HCl and add (at the hood) 25 cc. of 6-n HNO₃, 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 a 6-inch evaporating 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 SnCl₂·2H₂O 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 latter 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 44

STANNIC SULPHIDE (MOSAIC GOLD)

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, $\text{Sn}(\text{OH})\text{Cl}$. 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 of the tin to sulphide, the sulphides being very much less soluble than the products of the hydrolysis.

Materials: stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 45 grams = $\frac{1}{2}$ F.W.
hydrogen sulphide (Note 13, page 19).
powdered sulphur.
ammonium chloride.

Apparatus: large common bottle.
hydrogen sulphide generator.

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 1500 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 1500 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 throw 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 $\frac{2}{3}$ 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 $\frac{1}{4}$ -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 $\frac{1}{4}$ gram powdered stannous sulphide with sodium sulphide (Na_2S) solution warming for about 3 minutes. Does the solid dissolve? Then add about $\frac{1}{10}$ 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 6-normal HCl , — in warm $(\text{NH}_4)_2\text{S}$. 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 $(\text{NH}_4)_2\text{S}$ solution.

PREPARATION 45

STANNIC CHLORIDE (ANHYDROUS)

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 $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$, or $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. 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, 150 grams.
chlorine.
tin foil.

Apparatus: 350 cc. tubulated retort.
5 300 cc. bottles.
chlorine generator (1500 cc. flask).
36-inch condenser.
200 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.

This preparation is only to be attempted if four 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 1500 cc. flask in which place 33 percent 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 150 grams of tin in a tubulated retort, and place the retort on a sand bath. The neck of the retort should pass into a long condenser, and the latter should empty into a 200 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

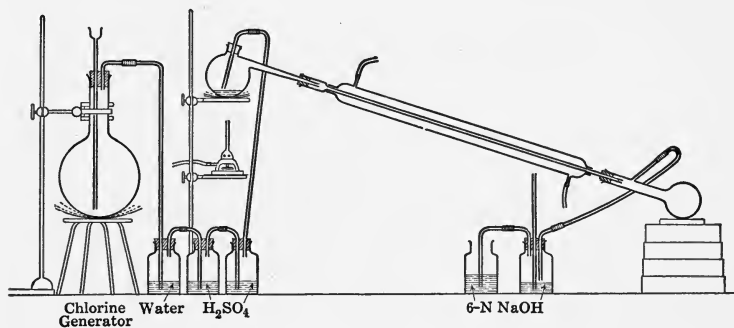


FIG. 20

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.

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 distill the tin tetrachloride into the prepared container. During the distillation this container should not be open to the air, but should be con-

needed 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 $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ might be made, starting with stannous chloride.
3. What happens if hydrated stannic chloride is heated? (Compare aluminum chloride and bromide, Preps. 26 and 27.)

PREPARATION 46

LEAD NITRATE

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, $\text{Pb}(\text{NO}_3)_2$. 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°
$\text{Pb}(\text{NO}_3)_2$	36	44	51	56	79	127

Procedure: Take 56 grams, or $\frac{1}{4}$ F.W., of litharge, PbO . Calculate the amount of 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 $\text{Pb}(\text{NO}_3)_2$ solution forming the basic salt $\text{PbOH} \cdot \text{NO}_3$ 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. Give 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

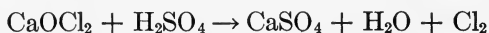
LEAD DIOXIDE

The compounds of lead in which its valence is II are the most stable, but with strong oxidizing agents the valence may be raised to IV. 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, $\text{Pb}(\text{OH})_4$ or $\text{PbO}(\text{OH})_2$. 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 Exps. 10 and 6, Chap. IV). 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.

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 $\text{Pb}(\text{OH})_2$, as well as calcium hydroxide and calcium carbonate from the bleaching powder, and possibly the salts calcium plumbate and calcium plumbite, CaPbO_3 and CaPbO_2 . 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 labelled with the percent of available chlorine. This is the percent by weight of chlorine which would be given of if the material were treated with dilute H_2SO_4 .



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 percent if the package is not marked) that would be required to oxidize the lead acetate used for this preparation.

Materials: lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, 95 grams = $\frac{1}{4}$ F.W.
bleaching powder containing 30 percent available chlorine, 66 grams.
6-n HNO_3 , 250 cc.

Apparatus: 8-inch porcelain dish.
2-liter common bottle.
suction filter.

Procedure: Dissolve the lead acetate in 200 cc. of cold water in the 8-inch 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 in a mortar with a little water. Warm the mixture slowly to the boiling temperature, stirring frequently, and finally boil it for 10 minutes. Transfer the contents of the casserole to a 2-liter common bottle and wash the precipitate by decantation with cold water (see Note 5 (b) on page 13) until the wash water gives but a slight test for chlorine ions. Then transfer the remaining slime 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) on page 9). 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. Dissolve 0.1 gram of lead nitrate in 1 cc. of water and add 5 cc. of 16-n HNO_3 . What is the white precipitate. Explain the application of the solubility product principle. Note particularly that nitric acid does not oxidize divalent lead.

2. Show the relation among ortho-plumbic acid, meta-plumbic acid, and lead dioxide. Give the symbol of sodium meta-plumbate; of calcium ortho-plumbate.

3. Why could not lead dioxide be prepared equally well by treating a solution of lead chloride with chlorine?

4. Compare the reaction of lead dioxide and of lead monoxide upon hydrochloric acid.

5. Compare the action of lead dioxide upon hydrochloric acid with that of manganese dioxide.

6. Why should not lead dioxide and manganese dioxide dissolve in dilute nitric acid as well as in hydrochloric acid?

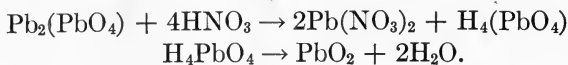
7. Treat $\frac{1}{2}$ gram samples of lead dioxide in separate test tubes with 5 cc. of 16-n HNO_3 and 5 cc. of 36-n H_2SO_4 . What is the gas evolved and what is the white residue in each case?

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 of 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, $2\text{PbO} \cdot \text{PbO}_2 = \text{Pb}_2(\text{PbO}_4)$. 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,



The following procedure 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.

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 latter 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.

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 ortho-plumbic acids.
2. Boil a little of the red lead with nitric acid. What is the residue, and what soluble salt is formed? Test the solution 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.

Experiments

1. **Carbon Dioxide.** From a generator (Note 13(a), page 19) fill with carbon dioxide several test tubes inverted in a pan of water, and use them in the following experiments.

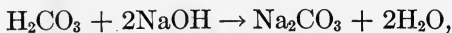
(a) Place the thumb over the mouth of a test tube of carbon dioxide and transfer it to a beaker of freshly drawn water. Clamp it in position and note the level of the water at intervals of about 15 minutes.

(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 sixty 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 normal 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,



and since 5 cc. of *n*-NaOH reacts, according to the equation, with carbonic acid equivalent to 56 cc. of carbon dioxide, all of the gas is dissolved.

(d) Repeat (c) using 5 cc. of normal 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.

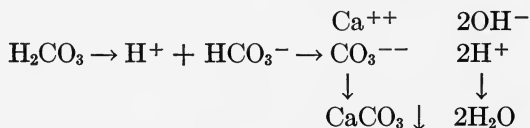
According to the equation, $\text{Na}_2\text{CO}_3 + \text{H}_2\text{CO}_3 \rightarrow 2\text{NaHCO}_3$, 56 cc. of carbon dioxide should be dissolved in this experiment.

(e) Repeat (c), using 10 cc. of lime water (saturated $\text{Ca}(\text{OH})_2$ solution) instead of 5 cc. of normal NaOH. Note the appearance of the solution during and after the absorption.

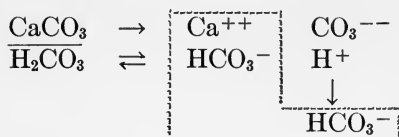
Write equation to account for this appearance. What volume of CO_2 should 10 cc. of saturated $\text{Ca}(\text{OH})_2$ be able to absorb (the $\text{Ca}(\text{OH})_2$ is 0.02 molal) if (1) CaCO_3 is formed, (2) $\text{Ca}(\text{HCO}_3)_2$ is formed?

(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, Chap. III, p. 102),



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:



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; the affinity of carbon for hydrogen and for sulphur is not extremely great and both hydrogen and sulphur, as well as carbon have a great affinity for oxygen. Chlorine on the other hand will not form stable compounds with oxygen, and it does form very stable compounds with carbon. 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. Carbon tetrachloride is extremely poisonous and any advantage it may have as a fire extinguisher is neutralized by the great danger attending its use.

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.

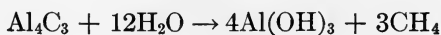
3. Carbon Monoxide. Place a plug of shredded asbestos *loosely* 2 inches from one end of a piece of difficultly fusible glass tube. Fill the tube with granulated (not powdered) charcoal for a length of about 4 inches and insert another plug of asbestos. Join this tube to a carbon dioxide generator, and 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 6-normal NaOH in a shallow dish and 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 very combustible which fact may be attributed to the tendency of carbon to return to its usual valence of IV.

4. Carbides. (a) The aluminum nitride made in Prep. 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 of the ammonia. Test the combustibility of this gas and find that it burns with a nearly colorless flame.

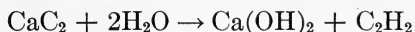
(b) Drop a little calcium carbide, CaC_2 , into water in a test tube, note that a gas is evolved and that this gas will burn with an intensely luminous and very smoky flame.

Nearly all of the metals form carbides which will hydrolyze more or less readily. The hydrolysis product of aluminum carbide is methane



from which it is concluded that in aluminum carbide the carbon is acting as a simple negative radical with a valence of IV. Note that the maximum negative valence of carbon is IV 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 equalled.

The hydrolysis product of calcium carbide is acetylene



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 II for the whole radical. (Compare peroxides.)

5. Luminosity of Flame. (a) Note the color of the Tirrill or Bunsen flame both when the air inlet at the bottom is open and closed. The following experiments throw some light on the cause of the difference.

(b) Fit up a gas holder as shown in the diagram. Through *a* allow illuminating gas to pass in until the bottle is one-half full. Then pass in carbon dioxide until the bottle is filled. Agitate the bottle enough to ensure thoroughly mixing the gases. Attach the capillary jet *b* to the delivery tube, allow the gas to issue from the jet, light it, and observe the color of the flame.

Repeat with varying proportions of illuminating gas and carbon dioxide, finding what proportions of the latter is sufficient to give a colorless flame.

(c) Fill the gas holder with acetylene. Note the color and character of the acetylene flame.

(d) Repeat (b), using acetylene in place of illuminating gas.

(e) The object of this part of the experiment is to show

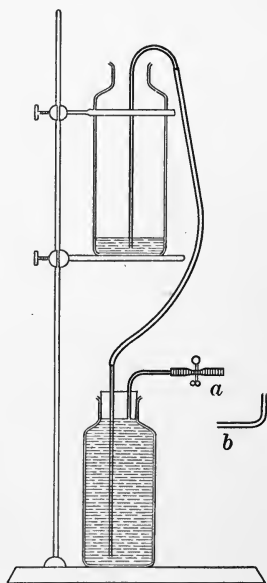


FIG. 21

the effect of admixture with an inert gas upon the decomposition of illuminating gas or acetylene.

Fill the gas holder with the mixture to be tested. Attach a piece of infusible glass tube to *a*, and at the other end attach a rubber connector with a pinchcock and the capillary *b*. Open the pinchcock until the glass tube is full of the gas mixture. Then heat the tube as strongly as possible, every now and then opening the pinchcock for a moment.

Test in this way whether illuminating gas and acetylene are decomposed by heat. What is the solid product of such a decomposition? How does the presence of some of this solid product affect the luminosity of a flame? If the gases alone are thus decomposed, find if they are or are not so decomposed when admixed with CO_2 in the proportion that gave a colorless flame.

It is believed that the luminosity of a gas or candle flame is caused by incandescent particles of carbon within the hot part of the flame, first, because when a cold object is held in a luminous flame soot (finely divided carbon) is deposited, whereas the cold object held in the non-luminous flame does not become sooted; second, because hot gases are known not to emit light whereas hot solid substances do give off light.

The presence of a very moderate proportion of inert gas in illuminating gas suffices to render its flame non-luminous. Nitrogen exerts the same effect as carbon dioxide.

Acetylene burns with a very much more brilliant flame than illuminating gas and it takes a larger proportion of inert gas to take away its luminosity.

Experiment (*e*) shows that acetylene heated alone out of contact with air is very easily decomposed giving a dense deposit of carbon inside the tube; admixture of inert gas lessens the ease with which the carbon is deposited. Illuminating gas does not give any deposit of carbon within the tube unless the tube is heated very hot.

The facts above enumerated all strengthen the theory that luminosity is due to the particles of carbon produced by the decomposition of the gases by the heat of the flame. These particles heated to incandescence, give the luminosity until they reach the outer part of the flame where the oxygen of the air burns them.

When a flame smokes the carbon particles get cooled to below the kindling temperature before they come in contact with sufficient oxygen for combustion.

The question now arises why mixture with an inert gas should stop the formation of the particles of free carbon. One obvious reason is that the inert gas absorbs part of the heat of the flame and thus prevents a temperature high enough to decompose the hydrocarbon being reached. But this does not explain why the mixture of acetylene and carbon dioxide does not decompose in the glass tube at the temperature that decomposed the acetylene alone. The explanation for this fact is that the *rate* of decomposition of the hydrocarbon depends on its concentration (law of molecular concentration); the presence of inert gas lessens the concentration, and therefore the rate of decomposition, of the hydrocarbon.

To return now to the colorless Bunsen flame the explanation of its lack of luminosity which one would at first be inclined to advance is that the air admitted at the base burns the carbon particles before they have a chance to glow. When, however, we consider the fact that carbon dioxide, or nitrogen also prevents the luminosity, we see that the diluting action of the air also must be an important factor in causing the absence of luminosity.

6. Silicon Dioxide and Silicic Acid. (a) Wet a little silicon dioxide (very finely powdered quartz, or better the product of Prep. 42), 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, $\text{SiO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2 \uparrow$, 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 and the latter will not again take up water.

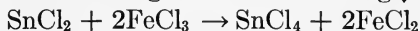
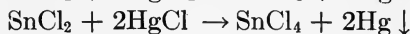
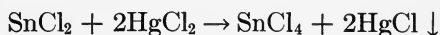
7. Hydrolysis of Stannous Salts. Dissolve $\frac{1}{2}$ gram crystallized $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a few drops of water. Note that a clear solution can be obtained if the preparation is fresh. Dilute the solution with water and note the white precipitate. Add a little HCl and note that the precipitate redissolves.

Stannous salts in which tin displays the lower valence of II are derivatives of the hydroxide $\text{Sn}(\text{OH})_2$. 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, $\text{SnCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{SnOHCl} \downarrow + \text{HCl}$, indicates that base is a weak one.

8. 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 $\text{K}_3\text{Fe}(\text{CN})_6$, and note the deep blue precipitate.

Tin has a marked tendency to develop the valence IV characteristic of the group and in consequence stannous compounds are strong reducing agents.



9. 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.

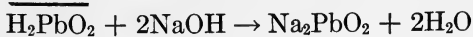
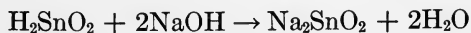
(b) Moisten some litharge (PbO) with water and test with litmus, noting that the latter is turned blue. Boil the litharge a few minutes with 10 cc. of water, filter, and add hydrogen sulphide water to the filtrate, noting a little black precipitate.

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 $\text{Pb}(\text{OH})_2$.

10. Amphoteric Character of the Hydroxides of Tin and Lead. Dilute 2 cc. of normal 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 normal $\text{Pb}(\text{NO}_3)_2$ instead of SnCl_2 and note that a very much larger volume of the NaOH is necessary to redissolve the precipitate.

$\text{Pb}(\text{OH})_2$ is much more basic than $\text{Sn}(\text{OH})_2$; it is correspondingly more weakly acidic as is shown by the greater excess of base required to convert it to the soluble salt.



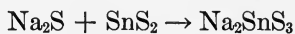
Sodium stannite and sodium plumbite both hydrolyze easily but the latter much more so, consequently the greater amount of base to overcome its tendency to hydrolyze.

11. Stannic Acid. Heat $\frac{1}{2}$ 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.

12. Thio-Salts of Tin. Perform Exp. 1 under Prep. 44. 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.



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 .

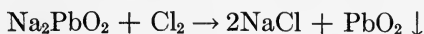
Addition of an acid displaces the very weak thio-stannic acid from its salt solution, $2\text{HCl} + \text{Na}_2\text{SnS}_3 \rightarrow 2\text{NaCl} + \text{H}_2\text{SnS}_3$; this acid is very unstable and decomposes into stannic sulphide, the yellow precipitate, and hydrogen sulphide, $\text{H}_2\text{SnS}_3 \rightarrow \text{H}_2\text{S} \uparrow + \text{SnS}_2 \downarrow$.

13. Lead Dioxide. (a) To 2 cc. of $\text{Pb}(\text{NO}_3)_2$ 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

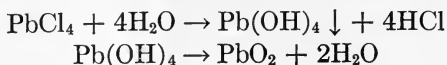


This highest oxide of lead has practically no basic properties and it does not react with nitric and sulphuric acids. Neither are its acidic properties highly developed for it does not react with NaOH . The action with HCl has already been discussed; it depends on the reducing action of this acid. The next experiment however throws a little more light on this subject.

14. 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, etc. Furthermore it combines with excess HCl to form the complex acid H_2PbCl_6 , of which the ammonium salt $(\text{NH}_4)_2\text{PbCl}_6$ can be crystallized. By comparison, if nitric acid reacted with lead dioxide, the tetranitrate, $\text{Pb}(\text{NO}_3)_4$, 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



giving the brown precipitate. In concentrated solution it decomposes into chlorine and PbCl_2 , the white crystalline precipitate.

15. 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; *w. a.*, *w. b.* = 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 , Pb_3O_4 .

3. Make a table for the tetrachlorides of all of 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 THE 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. But 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 of the elements of Family B are of frequent occurrence and considerable importance.

The characteristic valence of the group is five, corresponding to the oxide M_2O_5 , but the elements likewise exhibit a valence of three in the oxide M_2O_3 . It is noteworthy that the valence is nearly always either three or five.

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.

PREPARATION 49

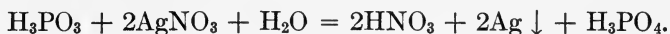
ORTHO-PHOSPHORIC ACID, H_3PO_4

A rather impure grade of phosphoric acid can be obtained from natural calcium phosphate by decomposition with sulphuric acid, but a pure product may be most readily obtained by oxidizing phosphorous by means of nitric acid.

The solution first obtained by the action of dilute nitric acid upon phosphorus contains a considerable quantity of phosphorous acid, H_3PO_3 ; but upon boiling down this solution, a point is reached at which a rather strong 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, unless removed by hydrogen sulphide, would contaminate the preparation of phosphoric acid.

Phosphorous acid may always be present in the product in case 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,



Materials: red phosphorus, P, 31 grams = 1 F.W.

6-n HNO_3 , 295 cc.

16-n HNO_3 , 20 cc.

seed crystal of H_3PO_4 .

Apparatus: 2-liter round bottom flask.

condenser to hang in neck of flask (Fig. 22).

8-inch evaporating dish.

thermometer.

100 cc. casserole.

2-ounce glass-stoppered sample bottle.

Procedure: Place the 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 nearly stopped add a little more of the phosphorus, and again wait until action has nearly stopped, and so on, until all of the phosphorus is used. Then add 20 cc. of 16-n HNO_3 ; transfer the solution to an 8-inch evaporating dish and boil it under the hood until a rather violent reaction begins to take place. Remove

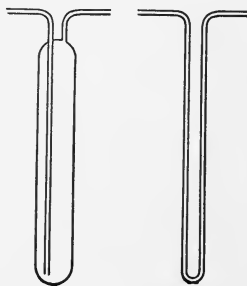


FIG. 22. Condensers to Hang in Mouth of Flask

The one at the left is more efficient; the one at the right may be made in a few minutes by bending common delivery tube.

the flame and let the reaction proceed; it grows very violent and then, in the most remarkable fashion ceases altogether.

The solution should now be clear and almost colorless, and should contain no phosphorous acid. If it contains a fine black suspension, dilute it with an equal volume of water and filter it without suction. Test for phosphorous acid by adding a few drops of the liquid to 10 cc. of water, adding 1 cc. of .05-n AgNO_3 and warming; a dark coloration, or black precipitate, appearing within two 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 small 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 ortho-phosphoric acid become changed partially into pyrophosphoric acid, but it attacks very strongly the material of the dish, and the preparation becomes contaminated. Pour the liquid while still warm 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 overnight. 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 obtainable the sirupy acid can be made to crystallize spontaneously if it is placed in a vacuum desiccator over concentrated sulphuric acid and 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 ortho-phosphoric 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 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 phosphoric acid.

6. Give an example of phosphorous acid acting as a reducing agent.

PREPARATION 50

CRYSTALLIZED ARSENIC ACID $(\text{H}_3\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$

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. By the nitric acid this is oxidized 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 evap-

oration 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 boiled down 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 that 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 = $\frac{1}{4}$ F.W.
16-n HNO_3 , 75 cc.
seed crystal of $(H_3AsO_4)_2 \cdot H_2O$.

Apparatus: 500 cc. casserole.
150 cc. casserole.
thermometer.
2-ounce glass-stoppered sample bottle.

Procedure: Place 50 grams of arsenious oxide in a good-sized casserole; add 20 cc. of water, and then at the hood add 75 cc. of 16-n 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, the original white powder should have all 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 even although a plentiful excess of nitric acid may be present. When this does happen the addition of 5 cc. of 6-n 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 $(\text{H}_3\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$, 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 ten 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 over heating. 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 16-n 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 if 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

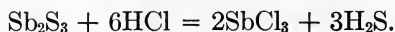
one preceding. Recall a previous instance in which the direction of a reaction of oxidation and reduction is changed on passing from an acid to an alkaline solution.

PREPARATION 51

ANTIMONY TRICHLORIDE FROM STIBNITE

(BY-PRODUCT: ANTIMONY OXYCHLORIDE)

Native antimony sulphide (stibnite) dissolves quite readily in hydrochloric acid, yielding antimony trichloride,

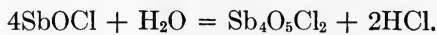


If the solution so obtained is distilled, there pass off at first only steam and hydrochloric acid, later a mixture of hydrochloric acid and antimony trichloride, and finally pure antimony trichloride.

Antimony trichloride hydrolyzes with a moderate amount of water, giving a precipitate according to the reactions,



with more water a further hydrolysis takes place:



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 = $\frac{1}{2}$ F.W.
12-n commercial concentrated HCl, 840 cc.
shredded asbestos for filter.

Apparatus: 8-inch porcelain dish.
suction filter.
350 cc. retort.
1-liter flask.
2-liter common bottle.

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)) which has previously been moistened with hydrochloric acid, and rinse the residue onto 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 is placed, to prevent bumping, about a teaspoonful of small bits cracked from an unglazed porcelain dish. Place the retort on a sand bath and distill, 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 the liquid is all 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. In case 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 liable to interfere with obtaining distinct fractions of the distillate. In such a case distill until the residue in the retort is left dry, but with making the final change in receiving vessels. Then pour all of the distillate containing any of the antimony salt into a fresh retort and distill again, this time separating the fractions.

Antimony Oxychloride. — Pour the 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?

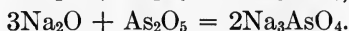
2. Pass hydrogen sulphide into the solution of antimony trichloride. What is the color of the precipitate? How could it be converted into a product like stibnite?

3. Compare the reactions of phosphorus, arsenic, and antimony trichlorides with water. Is hydrolysis more or less complete in the case in which a precipitate forms?

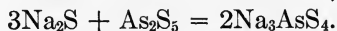
PREPARATION 52

SODIUM SULPHANTIMONATE $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$

The oxides of arsenic and antimony, and more particularly the higher oxides, are acidic in nature, and form salts with basic oxides.



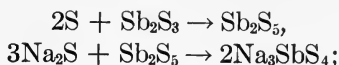
Sulphur, in accord with its similarity to oxygen, can be substituted for the latter in many of its compounds without essentially altering their chemical nature, and the compounds thus obtained have the same nomenclature as the corresponding oxygen compounds, except that the syllable *thio* or *sulpho* is inserted. Thus sulpho-salts are produced in the same manner as the oxy-salts above:



The sulpho-salts of arsenic, antimony, and stannic tin are particularly characteristic of these metals. (See Prep. 44, and Exp. 12, Chap. IX.) 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:



Sodium sulphantimonate can be prepared from stibnite by the combined action of a solution of sodium sulphide and sulphur,



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 = $\frac{1}{5}$ F.W.
sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 140 grams, or use
47 grams of anhydrous sodium sulphide and an
additional 93 cc. of water.
powdered sulphur, 13 grams.

Apparatus: 500 cc. casserole.
suction filter.
6-inch crystallizing dish with watch glass or glass
plate to cover it.

Procedure: To the 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, 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 stopper them tightly in an 8-ounce cork-stoppered bottle as soon as they are dry.

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 precip-

itate if its formula is Sb_2S_5 ? Write equation for change of Sb_2S_5 to $nSb_2S_5 \cdot mSb_2O_5$. Explain why both Na_2S and $NaOH$ are capable of repressing the hydrolysis.

3. What general principle is illustrated in the fact that Sb_2S_5 dissolves much less readily than Sb_2S_3 in Na_2S solution?

PREPARATION 53

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 much used in vulcanizing rubber.

Materials: sodium sulphantimonate, $Na_3SbS_4 \cdot 9H_2O$ from preceding preparation, 48 grams = $\frac{1}{10}$ F.W.

6-n H_2SO_4 , 108 cc.

Apparatus: large common bottle, 2 liters or larger.

5-inch funnel and plain 10-inch filter.

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, with barium chloride, the test for a sulphate. After the last washing let settle for some time, draw off as much as possible of the clear liquid, and transfer the slime to a large plain filter (Note 4 (c); do not omit to reënforce the point of the filter) to drain for 12 hours or longer. Without removing the pasty antimony sulphide from the filter, open out the latter 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 test tube.

QUESTIONS

1. Write equations for all reactions involved in the preparation of antimony pentasulphide from stibnite.

PREPARATION 54

METALLIC ANTIMONY

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 latter 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 a slag; but the slag is made more fusible by the admixture of sodium sulphate as directed, 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 slag furthermore covers the surface of the metal and hinders its volatilization and oxidation.

Materials: stibnite, Sb_2S_3 , 112 grams. = $\frac{1}{3}$ F.W.
iron filings, 48 grams.
anhydrous sodium sulphate, 12 grams.
powdered charcoal, 2 grams.

Apparatus: clay crucible of 250 cc. capacity.
gas furnace.
iron stirrer, use old file gripped with furnace tongs.

Procedure: Mix the stibnite, iron filings, sodium sulphate, and charcoal, and place the mixture in a clay crucible. Cover the crucible tightly, and heat it in the gas furnace for one hour at a bright red heat. The temperature should not be high enough to volatilize the antimony, which would in that case escape as a white smoke consisting of antimony oxide, yet the slag of iron sulphide must be completely softened, although it should not melt to a thin liquid. After about half an hour test the conditions by removing the cover a moment and stirring the slag to see whether it is in the proper semi-fluid condition. After the reaction is complete, allow the crucible to cool, break it and separate the regulus of antimony from the slag.

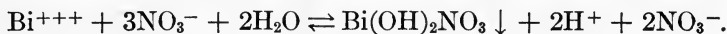
QUESTIONS

1. Warm a piece of metallic antimony with hydrochloric acid. Where does antimony stand in the electromotive series?
2. Boil $\frac{1}{2}$ gram of powdered antimony in a small casserole with 6-n HNO_3 . Describe the reaction and the product and write equations.

PREPARATION 55

BISMUTH BASIC NITRATE (BISMUTH SUBNITRATE)

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:



On pouring a solution of bismuth nitrate into a considerable quantity of cold water the basic nitrate, according to the above formula, is precipitated. 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:



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, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 42 grams = $\frac{1}{10}$ F.W.
6-n HNO_3 , 10 cc.
 Na_2CO_3 solution.

Apparatus: small beaker.
2-liter common bottle.
suction filter.

Procedure: Dissolve without heating the crystallized bismuth nitrate, in 10 cc. of 6-n 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 at the steam table, and preserve it as a powder in a cork-stoppered test tube.

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 test tube.

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 Chap. III the section on the Ionization of Polybasic Acids, p. 102.

in Chap. IV, Preps. 7, 14, and Exps. 15, 25.

in Chap. VIII, Exps. 12, 13.

1. Oxidation Products of the Metals. Treat $\frac{1}{2}$ 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 $\text{Bi}(\text{NO}_3)_3$ 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 $\text{Bi}(\text{OH})_3$.

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 ammonium polysulphide ($(\text{NH}_4)_2\text{S}$ 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.

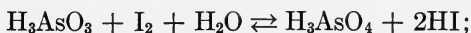
Review the discussion of thio- or sulpho-salts under Prep. 52. The trisulphides As_2S_3 and Sb_2S_3 are oxidized by the free sulphur to the pentasulphides, As_2S_5 and Sb_2S_5 , which react with the $(\text{NH}_4)_2\text{S}$ to form the soluble thio-salts, Na_3AsS_4 and Na_3SbS_4 .

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 to 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 Prep. 49, 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 Exp. 15, Chap. IV, 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 Exp. 3 under Prep. 50. Arsenious acid reduces iodine to hydriodic acid in a solution containing sodium bicarbonate, the latter neutralizing the acid produced:



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 bismuth 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 grape sugar solution, continue to boil and note a black precipitate.

(b) Again suspend about 2 milligrams bismuth subnitrate in 10 cc. boiling water. Pour through a filter leaving the white $\text{Bi}(\text{OH})_3$, 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 shaking 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.

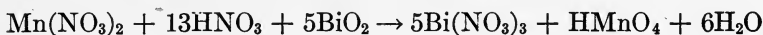


Sugar may be tested for in urine by an adaptation of the reaction in (a); its presence indicates diabetes.

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 $\text{Mn}(\text{NO}_3)_2$ or MnSO_4 solution (but not MnCl_2) to 5 cc. of cold 6-n HNO_3 . Add about $\frac{1}{10}$ 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.



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 symbol 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 bismuth. 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.

4. How do the trisulphides of arsenic and antimony behave when treated with a solution of ammonium sulphide, $(\text{NH}_4)_2\text{S}$? With a solution of ammonium polysulphide, $(\text{NH}_4)_2\text{S}_x$? How does the solution obtained with ammonium 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 extremely 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 unknown element which should come below manganese, ruthenium, rhodium, palladium, silver, and cadmium. In the middle of the next long period come tungsten, another unknown element which should resemble manganese, 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 show none of the group characteristics, but show the general base-forming properties of the heavy metals.

In the Group VII, manganese, the only 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.

In the 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 of the members are heavy metals. The Zero Group, which comprises the inert gases, helium, neon, argon, krypton, and xenon, may be regarded as bearing the same relation to Group VIII as Family B of an ordinary group bears to Family A. If this view is a correct one, the divergence in properties between the families is in this case at a maximum.

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 56

POTASSIUM DICHROMATE FROM CHROMITE

The most important source of chromium is the mineral chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ or $\text{Fe}(\text{CrO}_2)_2$. This substance, as indicated by the formula, may be regarded as a compound of ferrous oxide and chromic oxide, or as a salt, chromite of iron, 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 hexavalent condition (CrO_3), at the same time combining with the alkali to form a chromate (K_2CrO_4).

In the commercial method for manufacturing chromates, atmospheric oxygen is the oxidizing agent. The chromite is mixed with potassium carbonate and calcium carbonate, the latter to give porosity, and then heated for a considerable time in a furnace with free access of air. The chromium trioxide, CrO_3 , produced by the oxidation reacts with the potassium carbonate, displacing carbon dioxide and giving potassium chromate, K_2CrO_4 . After cooling, the contents of the furnace are treated with a solution of sodium sulphate; the potassium chromate dissolves, the iron oxide is insoluble, and the calcium oxide (from heating the carbonate) reacts with the sodium sulphate to form insoluble calcium sulphate. From the solution potassium chromate could be crystallized but for the fact that it is very soluble in water and

could not be separated from the other salts. Potassium dichromate, however, is much less soluble, and it may be formed by adding sulphuric acid,



and obtained pure by crystallization.

On account of the difficulty of carrying out the above process on a laboratory scale, the following less economical procedure is given in which the mineral is heated with considerably more than the quantity of potassium carbonate theoretically required, in order to give a more liquid melt, and with potassium nitrate for the oxidizing agent. The solution obtained by extracting this melt with water contains so much potassium carbonate that it would be very difficult to separate the also very soluble potassium chromate from it by crystallization. If acetic acid is added until the solution reacts slightly acid, the potassium carbonate is converted into the very soluble acetate, and the chromate is changed to the only moderately soluble potassium dichromate which, especially in the presence of the large amount of the other salt with the K^+ -ion in common, can be crystallized out.

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
$\text{K}_2\text{Cr}_2\text{O}_7$	5	7	12	20	26	35	55	88

Materials: finely powdered chromite, $\text{Fe}(\text{CrO}_2)_2$, 37 grams = $\frac{1}{8}$ F.W.; unless very pure mineral is available better results will be obtained by using 25 grams of artificially prepared chromic oxide, Cr_2O_3 .
 anhydrous potassium carbonate, K_2CO_3 , 92 grams.
 potassium nitrate, 28 grams.
 glacial acetic acid.

Apparatus: cast iron crucible of 350 cc. capacity.
 gas furnace.
 8-inch evaporating dish.

Procedure: Mix the chromite, potassium carbonate, and potassium nitrate in the cast iron crucible which must be on no account

more than two-thirds filled with the dry mixture. Heat in the gas furnace to a yellow heat until the melted charge has ceased to effervesce, but use great caution not to melt the crucible nor to let the melted charge overflow. Pour the molten mass out onto a dry iron plate. When cool crack it up and dissolve it, together with what still adheres to the crucible, in boiling water. Filter the solution, and extract the residue with a little more boiling water and pour through the same filter. Add glacial acetic acid (cautiously) to the filtrate until it has become acid. Boil down the solution to 300 cc., or to even a less volume if no solid salt begins to separate. Add 25 cc. more of glacial acetic acid, let stand for some time, and finally cool to 0° before separating the crystal meal of potassium dichromate from the mother liquor. Purify the product by recrystallization, and put it up in a cork-stoppered test tube.

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 salt solution (CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$) 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 Exp. 3 add 6-n 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 57

POTASSIUM CHROMATE FROM POTASSIUM DICHROMATE

Dissolve 49 grams of potassium dichromate in water and add the calculated amount of potassium carbonate dissolved in water. Crystallize the product from the solution (see solubility table on page 286).

Answer the questions given under Potassium Dichromate.

PREPARATION 58

CHROMIC ANHYDRIDE, CrO_3

When a chromate or a dichromate is treated with a strong acid, chromic acid is formed in the solution. The affinity of chromic anhydride for water is far less than that of sulphuric anhydride for water; and chromic acid, therefore, instead of existing in solution entirely in the form H_2CrO_4 , is broken down to a great extent into $\text{H}_2\text{Cr}_2\text{O}_7$ (*i.e.*, $\text{H}_2\text{O} \cdot 2\text{CrO}_3$) and even to CrO_3 . Especially in the presence of a large amount of sulphuric acid, the last form is produced so freely that it crystallizes out in the shape of red needles.

Materials: sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, 100 grams = $\frac{1}{4}$ F.W.

36-n H_2SO_4 , 400 cc.

Apparatus: 8-inch evaporating dish.

glass plate to cover the 8-inch dish.

suction filter with glass marble.

unglazed porcelain plate.

glass-stoppered sample bottle.

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 onto 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 a glass spatula, 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 transfer the product to an unglazed porcelain plate, place the latter on an iron ring and heat it by playing under it the burner held in one hand while with the other hand the crystals are continually stirred. Continue this operation, being very careful not to overheat, until nitric acid vapors cease to be given off. Transfer the product at once to a dry, previously weighed, glass-stoppered bottle.

QUESTIONS

1. Dissolve $\frac{1}{2}$ 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 to better observe its color. What is the residue?

PREPARATION 59

AMMONIUM DICHROMATE, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

This salt is prepared by crystallization from a solution of chromic anhydride to which the calculated amount of NH_4OH is added. It is of particular interest because one radical is an oxidizing agent and the other a reducing agent, in consequence of which if the dry salt is heated a little, a self-propagating reaction which is rather spectacular takes place.

Materials: chromic anhydride, CrO_3 , 50 grams = $\frac{1}{2}$ F.W.
14-n NH_4OH , 36 cc.

Apparatus: 300 cc. flask.
4-inch crystallizing dish.

Procedure: Dissolve the chromic anhydride in 100 cc. water in a flask. Add the NH_4OH cautiously so as not to volatilize am-

monia, and leave the solution to crystallize in a 4-inch dish. After getting one crop of crystals evaporate the mother liquor somewhat and obtain more crystals. Dry the product on paper towels at room temperature and preserve it in a 2-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. Suggest a method of preparing ammonium chromate, $(\text{NH}_4)_2\text{CrO}_4$.

PREPARATION 60

CHROMIC ALUM

The preparation of potassium dichromate illustrated how chromic oxide, Cr_2O_3 , as it exists in nature as a constituent of the mineral chromite, can be oxidized to a chromate in which chromium exists as CrO_3 . For the preparation of chromic alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, it might seem as if chromite should yield chromic sulphate directly on treatment with sulphuric acid. This is, however, impossible, because the natural material is very resistant to the action of acids. It yields only to the action of alkaline oxidizing agents, which convert it 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 aldehyde, $\text{C}_2\text{H}_4\text{O}$, 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. Care must, however, be exercised not to allow the temperature of its

solution to rise above 50° during the preparation, for when heated beyond this point it undergoes a change into a green non-crystallizable substance. This green substance is not stable at the ordinary temperature, and after cooling it will change slowly back into the ordinary crystallizable chromic alum; but so slowly, however, that if once it is formed the preparation is practically spoiled.

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 = $\frac{1}{3}$ F.W.
36-n H_2SO_4 , 76 cc.
alcohol, 63 cc.

Apparatus: 8-inch evaporating dish.
thermometer.

Procedure: Pulverize 98 grams of potassium dichromate, and cover it in an 8-inch evaporating dish with 400 cc. of water. Add 76 cc. of concentrated sulphuric acid, and stir until the salt is all dissolved. Adding the sulphuric acid should produce enough heat to dissolve the dichromate, but if it is necessary heat the mixture a little more. Be sure that the last trace of solid is dissolved. Allow the solution to cool to 40° ; then add alcohol, a drop at a time, while stirring constantly with the stem of a thermometer until the temperature commences to rise. Then place the dish in a pan of ice and water and add alcohol, 63 cc. in all, at first very slowly, endeavoring to keep the temperature between 35° and 45° , and finally more rapidly. Keep the temperature at all times below 50° , and if it should start to rise suddenly, due to too large an addition of alcohol, and get as high as 50° , drop a piece of ice directly into the solution. Finally, let the solution cool completely in the bath of ice water, or, still better, let it stand over night. Collect the crystal meal on a suction filter and free it from liquid. Recrystallize so as to obtain large, well-shaped crystals, following a similar procedure and observing the same precautions as with common alum (see page 181). A saturated solution of this salt should be prepared at 35° (Note 7, p. 12). After freeing it of any undissolved particles of the crystal meal, warm it to 45° , and set it to crystallize, with the addition of about ten very small

crystals to serve as nuclei. Dry the crystals by leaving them wrapped in paper towels over night (Note 9(b), p. 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.

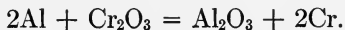
2. Sulphur dioxide might serve as the reducing agent. Write equations for the reaction in steps and add the equations.

3. Describe the effect observed when hydrogen sulphide is passed into a hot acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$. Write equation in one line marking with Roman numerals the valences of sulphur and chromium and showing that the algebraic sum of the valence changes is zero. (See Exps. 10 and 23, Chap. IV.)

PREPARATION 61

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 aluminothermic process, in which use is made of metallic aluminum as the reducing agent according to the reaction,



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 produce a temperature high enough to melt the metallic chromium. 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.

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.

Apparatus: clay crucible of 600 cc. capacity.
gas furnace.
iron pan.
pail of sand.

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 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 hot sand and place the latter under the hood at a distance from any woodwork. Start the reaction by igniting the end of the magnesium ribbon with a gas flame. It is advisable for the operator to wear colored glasses while watching the reaction, and to keep at a little distance to be out of the way of flying sparks. When the crucible has cooled, break it and separate the regulus of metallic chromium from the slag of fused aluminum oxide.

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 62

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 in 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, $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons 3\text{HCl} + \text{Fe}(\text{OH})_3$. In the presence of manganous carbonate the small amount of free acid thus formed is continuously used up according to the reaction, $\text{MnCO}_3 + 2\text{HCl} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{CO}_2$. Thus the reaction of hydrolysis is enabled to run to completion. The remaining solution, which is almost absolutely neutral and entirely free from iron salts, yields crystallized manganous chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, upon evaporation.

Materials: waste liquor from chlorine generator, 500 cc.
sodium carbonate.

Apparatus: 6-inch evaporating dish.
8-inch evaporating dish.

Procedure: Boil 500 cc. of waste manganese liquor in a 6-inch evaporating 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 1,000 cc. of water; without filtering the solution, take one-tenth of it, dilute this portion to 1,000 cc., and add a solution of sodium carbonate to it until all of the manganese is precipitated as carbonate (test for complete precipitation). Transfer the precipitate to a tall, common bottle and wash it by decantation at least four times. Add the slime of manganous carbonate to the remaining nine-tenths of the manganous chloride solution, and boil the mixture in a casserole until a few drops of the filtered liquid give no red color when tested with KSCN. Filter the solution and evaporate it in an 8-inch dish 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 of 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 purpose of the test with potassium sulphocyanate.
2. 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?
3. 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.
4. 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 pass in 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.

5. Explain how facts involved in the foregoing preparation show that $\text{Mn}(\text{OH})_2$ is more strongly basic than $\text{Fe}(\text{OH})_3$.

PREPARATION 63

POTASSIUM PERMANGANATE

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 so long as a considerable excess of potassium hydroxide is present; but in presence of an acid — even so 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:



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, it 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, 50 grams.
potassium chlorate, 25 grams.
carbon dioxide.
shredded asbestos for filter.

Apparatus: 8 cm. sheet iron crucible.
furnace glove.
iron stirrer (old file with wooden handle).
tongs.
suction filter and glass marble.

Procedure: Grind 50 grams of pyrolusite to as fine a powder as possible (the finer it is ground, the more successful the preparation). Place 50 grams of potassium hydroxide and 25 grams of potassium chlorate in an 8 cm. 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 with a thick glove and with the other hand the crucible should be held firmly by means of long iron tongs. After all of 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. Boil the solution in the dish, and at the same time pass in carbon dioxide until the green color of the manganate has entirely changed to the violet-red color of the permanganate. Test the color by touching a drop of the solution on a stirring rod to a piece of filter paper. If the spot is violet with no trace of green and only a fleck of brown manganese dioxide in the center, the change to permanganate is complete. Remove the lamp; let the sludge settle in the dish for 5 minutes; then pour the solution through an asbestos filter (see Note 4(d) on page 8), being careful to avoid stirring up the sludge until the very last, since the slimy precipitate of manganese dioxide would so clog

the filter as to nearly stop the flow. 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 a 6-inch dish, and allow it to cool slowly in a place protected from the 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 through asbestos, and obtain a second crop of crystals. 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 1-ounce glass-stoppered bottle.

QUESTIONS

1. Name and give the symbols 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 64

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 Prep. 61. 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 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.

Procedure: Place the pyrolusite in a crucible and heat 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; start the reaction with a fuse powder made of 10 grams barium peroxide and 1 gram of aluminum, and a magnesium ribbon (see Prep. 61), and then add fresh portions of the charge rapidly but without allowing the reaction to become too violent. 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 65

FERROUS AMMONIUM SULPHATE $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

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 only be preserved free from ferric salt 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, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, can be preserved fairly well without becoming oxidized; but the double ferrous and ammonium sulphate is not only more easily prepared on account of the readiness with which it crystallizes, but it is also less easily oxidized by contact with the air.

Materials: crystallized ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 70 grams = $\frac{1}{4}$ F.W.
ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, 33 grams.

Apparatus: beakers, filter, and crystallizing dish.

Procedure: Prepare crystallized ferrous ammonium sulphate from ferrous sulphate and ammonium sulphate. In crystallizing the product, observe the solubilities given in the following table, and make use of suggestions given in Note 8, page 13 and under Alum, page 181:

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
$(\text{NH}_4)_2\text{SO}_4$	71	73	75	78	81	84	92	99
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$. . .	12	17	22	28	33	40	52	..

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.

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.

PREPARATION 66

FERRIC AMMONIUM ALUM

In this preparation ferrous sulphate is converted into ferric sulphate under the oxidizing action of nitric acid in the presence of the amount of sulphuric acid theoretically necessary to form

this salt. By the addition of ammonium sulphate the double salt, ferric ammonium sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, crystallizes, this being one of the isomorphous series of alums (see Alum).

At 25° , 100 grams of water dissolve 44 grams of the anhydrous or 124 grams of the hydrated ferric ammonium sulphate.

Materials: crystallized ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 93 grams = $\frac{1}{3}$ F.W.

ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, 22 grams.

36-n H_2SO_4 , 12 cc.

6-n HNO_3 ,

Apparatus: 500 cc. casserole.

6-inch evaporating dish with a watch glass or glass plate for a cover.

Procedure: Place the ferrous sulphate and 100 cc. of cold water in the casserole, add the 12 cc. of 36-n H_2SO_4 , warm to about 50° and let the salt at least partially dissolve. Add 20 cc. 6-n HNO_3 and keep the mixture at about 50° until the salt is entirely dissolved. Then heat the solution to boiling and add 6-n HNO_3 , 1 cc. at a time, until further addition produces no further reaction. The solution should now be of a deep brownish yellow color but perfectly clear and should give no test for ferrous salt. Test by adding about 2 drops to 100 cc. of water and adding $\frac{1}{2}$ cc. of $\text{K}_3\text{Fe}(\text{CN})_6$. No intense blue color should be produced, although there may be a brown or yellow color. If a deep blue color or precipitate does show the presence of ferrous salt add more HNO_3 and boil until the iron is completely oxidized. Evaporate the solution carefully to expel the greater part of the excess of nitric acid. Keep the casserole in the hand, rotating the solution to keep the sides of the vessel wet with the liquid. It is very important not to superheat any dry salt caked on the side of the dish. When the solution begins to get thick and sticky stop heating, add water to make a volume of 115 cc., heat to boiling and dissolve the ammonium sulphate in the hot solution. Filter the liquid if it is not entirely clear, and set it to crystallize in a 6-inch evaporating dish, covering the latter and wrapping it with a towel so that it may cool slowly. Large clear crystals should be obtained. Pick them out by hand, rinse them quickly in a dish of cold water and dry them on paper towels. Obtain if possible a second crop of crystals from the mother liquor. Preserve the product in a 10-ounce cork-stoppered bottle.

QUESTIONS

1. Write the equation for the oxidation of ferrous sulphate as carried out in this preparation.

If an unacidified solution of ferrous sulphate is oxidized by the oxygen of the air, what products are formed? Equation?

2. Write the equation for the test for ferrous salt with potassium ferricyanide.

3. *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.

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 Exps. 10 and 23 in Chap. IV.

1. Stability of Carbonates of Metals in Divalent State. Test the stability of nickel carbonate, NiCO_3 , by heating 1 gram of it gently in a test tube while shaking it over a flame. Test the gas evolved for carbon dioxide; and compare the action of the remaining solid, when treated with hydrochloric acid, with that of the original carbonate. The carbonates of divalent iron, cobalt, manganese, and chromium are all of approximately the same degree of stability as nickel carbonate, so that this one experiment may be taken as typical of this class of carbonates.

2. To Show Whether the Carbonate of a Trivalent Metal Can Exist. Dissolve 2 grams of ferric alum in 10 cc. of water (this gives a trivalent iron salt in a solution that contains no free acid). Add 2-n Na_2CO_3 slowly until no more action takes

place. What is the gas evolved? What is the precipitate? In this experiment the ions Fe^{+++} and CO_3^{--} are brought together; the other ions, Na^+ and SO_4^{--} , could not react together to give any visible effect. If, therefore, ferric carbonate were stable in contact with water, it would either form a precipitate if it were insoluble, or if it were soluble it would simply stay in solution and no effect would be observable. The gas given off shows that the carbonate is unstable. Write the equation for the reaction. None of the carbonates of the metals of this chapter, when they are in the trivalent condition, are any more stable than ferric carbonate. A salt of chromium, such as chromic alum, might be used instead of ferric alum in the above experiment.

3. Oxidation of a Divalent Oxide. Heat $\frac{1}{2}$ gram of cobalt carbonate, CoCO_3 , in an open porcelain dish, holding the dish with tongs and keeping it rotating in the flame, but not allowing the porcelain to even approach a visible red heat. Heat until the color of the cobalt carbonate has completely changed. Like nickel carbonate, cobalt carbonate is decomposed by heat into cobaltous oxide, CoO , and carbon dioxide. If the cobaltous oxide is readily oxidized by the oxygen of the air, it may at once be changed into Co_2O_3 or Co_3O_4 . To test for this, treat a little of the product with hydrochloric acid in a test tube. A clear solution is obtained, deep blue when hot and concentrated, pink when cold and dilute, and chlorine is given off. The solution shows the properties that cobaltous chloride, CoCl_2 , is known to possess. Therefore the conclusion is that a higher oxide corresponding to CoCl_3 ($\text{Co}_3\text{O}_4 = \text{CoO} \cdot \text{Co}_2\text{O}_3$) was present and that the chloride formed by metathesis was unstable and decomposed into CoCl_2 and free chlorine.

Note. In Exp. 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 normal solutions of (a) CrCl_3 , (b) MnCl_2 , (c) FeCl_2 , (d) FeCl_3 , (e) CoCl_2 , (f) NiCl_2 , or of the sulphates or nitrates of the same metals. Add 10 cc. of water to each tube and 6-n NaOH until the solution is alkaline in each case.

(a) A light green precipitate ($\text{Cr}(\text{OH})_3$) appears in the first tube, but it redissolves in an excess of the reagent, and again precipitates when the solution is heated. Chromic hydroxide is amphoteric and dissolves in NaOH to form sodium chromite, Na_3CrO_3 , or

meta-chromite, NaCrO_2 , but the acidic properties of $\text{Cr}(\text{OH})_3$ are so weak that the chromite is completely hydrolyzed by boiling water.

(b) A light buff colored precipitate ($\text{Mn}(\text{OH})_2$) appears in the second tube. It does not redissolve in excess of reagent, but, on the surface of the liquid in contact with air, it turns dark brown. Manganous hydroxide is solely basic; it is easily oxidized by the air to $\text{Mn}(\text{OH})_3$.

(c) A light greenish gray precipitate appears in the third tube. It does not redissolve in excess of reagent, but at the surface of the liquid it turns reddish brown. Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is solely basic; it is oxidized by air to ferric hydroxide, $\text{Fe}(\text{OH})_3$.

(d) A reddish brown precipitate ($\text{Fe}(\text{OH})_3$) is formed in the fourth tube. It is unchanged by excess of reagent.

(e) A precipitate which finally becomes a light brown tinged with purple, insoluble in excess of reagent, is formed in the fifth tube.

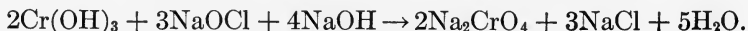
(f) An apple green precipitate insoluble in excess of reagent is formed in the sixth tube.

Save the six tubes containing the precipitates for Exp. 5.

5. Action of Alkaline Oxidizing Agents on the Hydroxides. Sodium hypochlorite is formed by passing chlorine into NaOH . Therefore the use of NaOCl as a reagent is equivalent to using chlorine. This reagent is made by stirring bleaching powder and an excess of sodium carbonate with water and filtering.

Shake each of the tubes (a)-(f) from Exp. 4 to uniformly suspend the precipitate of hydroxide, pour 2 cc. of each suspension into a fresh test tube, and to each add about 10 cc. of the NaOCl reagent. Observe the effect for a minute and then warm the tube.

(a) The precipitate dissolves and a yellow solution is formed.



(b) The light colored precipitate turns dark brown.



Collect the dark brown precipitate and save it for Exp. 6.

(c) The light greenish gray precipitate turns reddish brown.



(d) The reddish brown $\text{Fe}(\text{OH})_3$ is not altered.

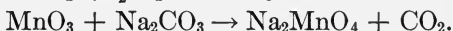
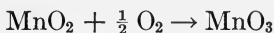
(e) The light colored precipitate turns black.



(f) The apple green precipitate turns black.



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 the precipitate of MnO_2 reserved from Exp. 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. The oxygen of the air oxidizes manganese to the trioxide in alkaline fusion.



(b) Repeat (a) using $\text{Cr}(\text{OH})_3$ instead of MnO_2 . A yellow bead is obtained, the chromium being oxidized to yellow chromate, Na_2CrO_4 .

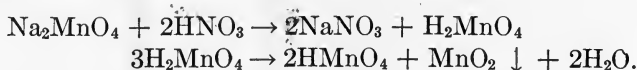
(c) Prepare a somewhat larger amount of sodium manganate as follows: Melt a mixture of 5 grams sodium hydroxide, 1 gram of potassium nitrate and 0.1 gram of manganese dioxide in a small iron crucible and heat it until it ceases to foam and the crucible is dull red. Cool the crucible and treat the contents 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 Exp. 7 (a).

(d) Repeat (c) using iron oxide instead of manganese dioxide. The solution of the melt is red, having almost the same shade and intensity of color as permanganate.

In strongly oxidizing alkaline fusion, iron is oxidized to ferrate (Na_2FeO_4), which gives the intense red color. This is an unusual compound of iron, it is formed only under exceptional conditions, and it is very unstable. If any pink color was observed in Exp. 5 (d) it was due to the formation of a trace of ferrate.

7. Permanganate. (a) Add 6-n HNO_3 , drop by drop, to the solution of Na_2MnO_4 reserved from Exp. 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; there is a very small dark brown precipitate found in the bottom. Reserve the solution for (b).



The salts of manganic acid, H_2MnO_4 , can exist in alkaline solution, but the free manganic acid decomposes at once. The second of the equations represents an interesting case of oxidation and reduction. Manganese is the only element whose valence changes.



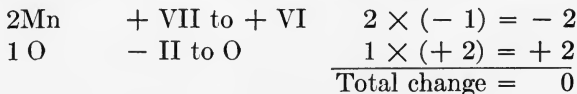
the sum of the valences of the manganese being the same, namely 18, on each side of the equation.

(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.



The equation is written ionically in order to show that OH^- -ions are used up as the reaction progresses, thus explaining why presence of alkali favors the change of permanganate to manganate. Note that the anions of the two salts have exactly the same composition except for the difference of one negative electron.

The oxidation and reduction changes add up as follows:



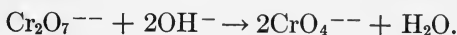
(c) To 1 drop of $\text{Mn}(\text{NO}_3)_2$ solution and 10 cc. 6-n HNO_3 in a test tube add 1 gram of lead dioxide and boil. Let the surplus of lead dioxide settle and note that the clear solution has the intense permanganate color.

Write the equation and show that the algebraic sum of the valence changes of lead and manganese is zero. Compare the action of lead dioxide with that of bismuth dioxide in Chap. X, Exp. 5.

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 $\text{Cr}_2\text{O}_7^{--}$ ion. The changes take place according to the reversible reaction.



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 VI, 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.



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 $\text{K}_2\text{Cr}_2\text{O}_7$ with HCl . For both of these cases write equations according to the *oxide method* as outlined in Question 1, under Prep. 60. 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-normal 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-normal, use commercial *glacial* acetic acid, about 99.5%, of sp. gr. 1.055

6-normal, mix 350 cc. of *glacial* acetic acid with 650 cc. of water.

Hydrochloric acid

12-normal, use commercial concentrated HCl of sp. gr. 1.19

6-normal, mix 12-normal HCl with an equal volume of water

Nitric acid

16-normal, use commercial concentrated HNO₃ of sp. gr. 1.42

6-normal, mix 380 cc. of 16-normal HNO₃ with 620 cc. of water

Sulphuric acid

36-normal, commercial 96% H₂SO₄ of sp. gr. 1.84

6-normal, pour 1 volume of the 96% H₂SO₄ into 5 volumes of water

Ammonium hydroxide

15-normal, use commercial concentrated NH₄OH of sp. gr. 0.90

6-normal, mix 400 cc. of 15-normal NH₄OH with 600 cc. of water

Sodium hydroxide

6-normal, add to 250 grams of NaOH enough water to make the volume 1000 cc.

Salts

1-normal, all salts solutions on the reagent shelves unless otherwise labelled are understood to be 1-normal

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	Cd.....	+0.43	As.....	—
Na.....	+2.7	Fe(Fe ⁺⁺).....	+0.42	Bi.....	—
Ba.....	+2.7	Co.....	+0.23	Sb.....	—
Ca.....	+2.2	Ni.....	+0.23	Hg(Hg ⁺).....	-0.74
Mg.....	+1.8	Sn(Sn ⁺⁺).....	+0.15	Ag.....	-0.80
Al.....	+1.3	Pb.....	+0.13	Pd.....	—
Mn.....	+1.1	H ₂	+0.00	Pt.....	—
Zn.....	+0.8	Cu(Cu ⁺⁺).....	-0.32	Au.....	—

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	-1.10		

PERIODIC CLASSIFICATION OF THE ELEMENTS

The atomic weights are placed next to the symbols of the elements.

The figures in parentheses are the atomic numbers of the elements.

	Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Series	A B A	E ₂ O	EO	E ₂ O ₃	EO ₂ EH ₄	E ₂ O ₃ EH ₃	EO ₃ EH ₂	E ₂ O ₇ EH	
1	Helium (8) He 4.00	Hydrogen (1) H 1.008 Lithium (3) Li 6.94	Beryllium (4) Be 9.1	Boron (5) B 10.9	Carbon (6) C 12.005	Nitrogen (7) N 14.008	Oxygen (8) O 16.00	Fluorine (9) F 19.0	
2	Neon (10) Ne 20.2	Sodium (11) Na 23.00	Magnesium (12) Mg 24.32	Aluminum (13) Al 27.0	Silicon (14) Si 28.1	Phosphorus (15) P 31.04	Sulphur (16) S 32.06	Chlorine (17) Cl 35.46	
3	Argon (18) Ar 39.9	Potassium (19) K 39.10	Calcium (20) Ca 40.07	Scandium (21) Sc 45.1	Titanium (22) Ti 48.1	Vanadium (23) V 51.0	Chromium (24) Cr 52.0	Manganese (25) Mn 54.93	Iron (26) Fe 55.84 Cobalt (27) Co 58.97 Nickel (28) Ni 58.68
4		Copper (29) Cu 63.57	Zinc (30) Zn 65.37	Gallium (31) Ga 70.1	Germanium (32) Ge 72.5	Arsenic (33) As 74.96	Selenium (34) Se 79.2	Bromine (35) Br 79.92	
5	Krypton (36) Kr 83.92	Rubidium (37) Rb 85.45	Strontium (38) Sr 87.63	Yttrium (39) Yt 89.83	Zirconium (40) Zr 90.6	Columbium (41) Cb 93.1	Molybdenum (42) Mo 96.0		Ruthenium (44) Rhodium (45) Palladium (46) Ru 101.7 Rh 102.9 Pd 106.7
6	Xenon (54) Xe 130.2	Silver (47) Ag 107.88	Cadmium (48) Cd 112.40	Indium (49) In 114.5	Tin (50) Sn 118.7	Antimony (51) Sb 120.2	Tellurium (52) Te 127.5	Iodine (53) I 126.92	
7		Cesium (55) Cs 132.91	Barium (56) Ba 137.37	Lanthanum (57) La 139.0	Cerium (58) Ce 140.25				
8		Francium (87) Fr (87)	Gadolinium (64) Gd (64)	Ne (60) Sa (67) Eu (63)	Dy (62) Er (68) Tantalum (73)				
9		Gold (79) Au 197.2	Mercury (80) Hg 200.6	Tl 204.0	Lead (82)				
10	Nitron (88) Nt 222.4		Radium (88) Ra 226.0	Actinium (89) Ac (89)	Thorium (90) Th 232.15	Uranium (92) U _{x3} (91)			Osmium (76) Iridium (77) Platinum (78) Os 190.9 Ir 183.1 Pt 196.2

PERIODIC CLASSIFICATION OF THE ELEMENTS ACCORDING TO THEIR ATOMIC NUMBERS AND THE ARRANGEMENT OF THEIR ELECTRONS

Atomic Number. The periodic classification of the elements was originally made by Mendelejeff on the basis of atomic weights. But the increments in atomic weight between successive elements are not uniform and in the cases of argon, cobalt, and tellurium a heavier element has to be placed in the classification before one of smaller atomic weight in order to bring these elements where they obviously belong in virtue of their chemical properties.

Another property of the elements however has been discovered, which seems to be more fundamental even than the atomic weight in determining the progressive recurrence of chemical properties. This property has come to be known as *atomic number*. It is determined from the characteristic lines of the X-ray spectra of the elements, and it is found that the reciprocal of the square root of the vibration frequency of the characteristic X-ray of an element always differs from that of the element of next lower atomic number by a constant quantity. The atomic number is therefore a strictly additive property; furthermore, when the elements are arranged in the order of their atomic numbers, argon, cobalt, and tellurium fall in the places corresponding to their chemical properties. Giving hydrogen the atomic number 1, the known elements satisfy all of the atomic numbers up to and including uranium 92, with the exception of 43, 61, 75, 85 and 87. It is not unreasonable to suppose that elements having these atomic numbers exist and may some day be discovered.

Theory of the Structure of the Atom. An atom is believed to be complex and to consist of a positively charged nucleus surrounded by negative electrons, the number of which in the electrically neutral atom is exactly equal to the number of positive charges of the nucleus. The charge on the nucleus is an even multiple of the charge of a hydrogen ion, and this charge, measured in terms of that of the hydrogen ion as a unit, is equal to the atomic number. Confirmation of this view is given by measuring the scattering effect on a beam of alpha rays passing through the elementary substances.

According to a theory proposed by Lewis and extended by Langmuir, the most stable configuration of electrons is possessed

by the atoms of the inert gases helium, neon, argon, krypton, xenon and nitron. A somewhat less, but still very stable configuration, is possessed by the beta forms of nickel, palladium, erbium, and platinum (shown in the table as $Ni\beta$, $Pd\beta$, $Er\beta$, $Pt\beta$).

The configuration of the atoms of the inert gases is so stable, that the atoms can neither part with any of their exterior electrons, nor take on added ones. These elements, do not form any compounds and thus do not exhibit any valence.

The atoms of all the other elements are less stable and seek to acquire the configuration of the stable atoms of the inert gases, or of the stable forms of nickel, palladium, erbium, or platinum. This can be accomplished only by losing some of the exterior electrons or acquiring extra electrons to complete the outer shell of the stable atoms. But this upsets the electrical neutrality of the whole atom and makes it positive if electrons have been lost, and negative, if electrons have been acquired. According to the theory, this tendency to change the number of exterior electrons in reverting to some one of the stable forms of atoms is the origin of valence and the cause of chemical combination.

Let us choose for illustration the element carbon, atomic number 6. If its atom loses four electrons it acquires the stable form of helium, atomic number 2, of which the nuclear charge is 2 and the number of external electrons is two. But the carbon atom with a nuclear charge of 6 and only two electrons will have now a surplus of four positive charges, and therefore a positive valence of four, as in carbon tetrachloride.

If the carbon atom takes on four extra electrons it acquires the stable form of neon, atomic number 10. But the carbon atom with a nuclear charge of only 6 and ten external electrons has a surplus of four negative charges, and therefore a negative valence of four as in methane, CH_4 .

The table on the next page shows the elements arranged in periods, each of which begins with an inert gas, and ends with the next inert gas. Secondary periods within the complete periods are shown, and these arise from the tendency of its atoms to revert to the beta form of the initial element of the secondary period.

The elements which come midway in the longer periods would have to lose or gain a large number of electrons to acquire the stable form of the inert gases. It is not surprising that this should

TABLE OF SOLUBILITIES¹

In the following tables are given data which should be useful in connection with the preparations and questions in this book.

The formulas given 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, and it has often been difficult to decide which one to place in the table.

In the second column the behavior of the crystallized salt when it is exposed to the air of the laboratory is indicated: **s** = **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**; **CO₂** = **absorbs carbon dioxide and falls to a white powder**; **Ox** = **compound is oxidized, especially in presence of moisture**.

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.

¹ Much of the data in this table has been obtained from Seidell, Solubilities of Inorganic and Organic Substances.

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	SOLUBILITY IN WATER.			F. W. per liter of solution at laboratory temperature.
			Grams anhydrous salt per 100 grams water in a saturated solution at	0°	25°	
Aluminum:						
	chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	d		(15°) 70		4
	nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	d		very soluble		
	sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$...	s	31	38	89	0.8
Ammonium:						
	acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	d		very soluble		
	bromide, NH_4Br	s	(10°) 66	(30°) 81	(100°) 128	6
	(bi) carbonate, NH_4HCO_3	s	12	24		2.7
	chloride, NH_4Cl	s	29	39	77	5
	nitrate, NH_4NO_3	d	118	214	871	11
Antimony:						
	chloride, SbCl_3	d	} hydrolyzes with water to insoluble basic salt;			
	sulphate, $\text{Sb}_2(\text{SO}_4)_3$	d	} very soluble in acids			
	sulphide, Sb_2S_3	s	insoluble; soluble in concentrated acids			
Arsenic:						
	sulphide, As_2S_3	s	insoluble in water or acids; soluble in alkalies			
Barium:						
	bromide, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$	s	98	106	149	2.5
	carbonate, BaCO_3	s		0.0023		0.00011
	chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	s	32	37	59	1.7
	chromate, BaCrO_4	s		0.0004		0.000015
	hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	CO_2	(0°) 1.7	(25°) 4.7	(80°) 101	0.2
	iodate, $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	s	0.008	0.03	0.2	0.001
	iodide, $\text{BaI}_2 \cdot 6\text{H}_2\text{O}$	d	170	213	272	3
	nitrate, $\text{Ba}(\text{NO}_3)_2$	s, d	5	10	34	0.3
	sulphate, BaSO_4	s		0.00023		0.000010
	sulphite, BaSO_3	s	(20°) 0.020	(80°) 0.002		0.001
	sulphide, $\text{BaS} \cdot 6\text{H}_2\text{O}$	Ox	very soluble; hydrolyzes to $\text{Ba}(\text{SH})_2$ and $\text{Ba}(\text{OH})_2$			
Bismuth:						
	chloride, BiCl_3	d	} hydrolyzes with water to insoluble basic salt;			
	nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	d	} insoluble basic salt;			
	sulphate, $\text{Bi}_2(\text{SO}_4)_3$	d	} very soluble in acids			
	sulphide, Bi_2S_3	s	insoluble in acids or alkalies			
Cadmium:						
	chloride, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	e	(0°) 90	(18°) 110	(100°) 147	5
	nitrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	d	(0°) 110	(18°) 127	(60°) 326	4.3
	sulphate, $\text{CdSO}_4 \cdot 2\frac{1}{3}\text{H}_2\text{O}$	e	(0°) 76	(40°) 79	(100°) 61	2
	sulphide, CdS	s	insoluble; soluble in concentrated acids			

Salt.	Formula of crystallized salt.	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°	
Calcium:						
	acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$. . .	e	37	34	30	1.9
	carbonate, CaCO_3	s		0.0013		0.00013
	chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	d	60	88	159	5.2
	chlorate, $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$	d		(18°) 178		5.3
	chromate, $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$	e	11	12	3	0.8
	fluoride, CaF_2	s		0.0016		0.0002
	hydroxide, $\text{Ca}(\text{OH})_2$	CO_2	0.19	0.16	0.08	0.02
	nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	d		(18°) 122		5.2
	oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	s		0.0007		0.00004
	sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	s	0.18	0.21	0.16	0.015
	sulphite, CaSO_3			0.004		0.0003
Chromium:						
	chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	d		130		8
	nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$			very soluble; melts 36.5°		
	sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	s, e		120		4
Cobalt:						
	carbonate, CoCO_3	s	insoluble; soluble in acids			
	chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	s	42	53	104	3
	nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	d	(0°) 84	(91°) 340		4.3
	sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	s	26	39	83	2
	sulphide, CoS	s	insoluble in water or dilute acids			
Copper:						
	carbonate, CuCO_3	s	insoluble; soluble in acids			
	chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	s, d	71	79	108	5.0
	nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	e { melts 38°	82	150	275	4.8
	sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	s, e	14	23	75	1.2
	sulphide, CuS	s	insoluble in water or acids			
Hydrogen:						
	arsenic acid, $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	d	very soluble; melts 35.5°			
	benzoic acid, $\text{HC}_7\text{H}_5\text{O}_2$	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, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	s	(0°) 3.5	(25°) 11.4	(70°) 64	0.9
	phosphoric acid, H_3PO_4	d	very soluble; melts 37°			

Salt	Formula of crystallized salt.	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°	
Iron:						
chloride	(ous), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.. (ic), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	d d	(15°) 67	(80°) 100		
carbonate	(ous), FeCO_3	s	insoluble; soluble in acids			
nitrate	(ous), $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ic), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Ox d	(18°) 82			
sulphate	(ous), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (ic), $\text{Fe}_2(\text{SO}_4)_3$	e, Ox d	(0°) 16	(30°) 33	(90°) 43	2
sulphide		s	very soluble insoluble; soluble in acids			
Lead:						
acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	s		50	200	1.5
bromide	PbBr_2	s	0.5	1.0	4.8	0.02
carbonate	PbCO_3	s		0.0001		0.000003
chloride	PbCl_2	s	0.7	1.1	3.3	0.05
hydroxide	$\text{Pb}(\text{OH})_2$			0.01		0.0004
iodide	PbI_2	s	0.04	0.08	0.44	0.002
nitrate	$\text{Pb}(\text{NO}_3)_2$	s	38	59	132	1.4
sulphate	PbSO_4	s		0.004		0.00013
sulphide	PbS	s	insoluble; soluble in concentrated strong acids			
Lithium:						
carbonate	Li_2CO_3	s	1.5	1.3	0.7	0.17
bicarbonate	LiHCO_3	s		(13°) 5.5		0.8
chloride	LiCl	d	67	82	128	13.3
hydroxide	$\text{LiOH} \cdot \text{H}_2\text{O}$	CO_2	12.7	12.9	17.5	5.0
nitrate	$\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$	d	(0°) 54	(30°) 138	(70°) 176	7.3
sulphate	Li_2SO_4	s	35	34	30	2.8
Magnesium:						
carbonate	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	s		0.2		0.01
chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	d	53	57	73	5.1
hydroxide	$\text{Mg}(\text{OH})_2$	CO_2		0.001		0.0002
nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	d	(0°) 67		(40°) 85	4.0
sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	e	27	39	74	2.8
Manganese:						
carbonate	MnCO_3	s	insoluble; soluble in acids			
chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	e, d	63	77	115	5
nitrate	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	d	(0°) 102	(25°) 166	(35.5) 331	5
sulphate	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	s, e	53	65	32	4
sulphide	MnS	Ox	insoluble; soluble in dilute acids			
Mercury:						
chloride	(ous), HgCl (ic), HgCl_2	s s		0.0002		0.00001
			3.7	7.4	61	0.2

Salt.	Formula of crystallized salt.	Behavior when exposed to atmosphere.	SOLUBILITY IN WATER.			F. W. per liter of solution at laboratory temperature.
			Grams anhydrous salt per 100 grams water in a saturated solution at	0°	25°	
Mercury:						
	iodide (ic), $\text{HgI}_2 \dots \dots \dots$	s		0.005		0.0001
	nitrate (ous), $\text{HgNO}_3 \cdot \text{H}_2\text{O} \dots$ (ic), $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	s, e d	} very soluble in a little water } much water ppts. basic salt } very soluble in HNO_3			
	sulphate (ous), $\text{Hg}_2\text{SO}_4 \dots$	s		0.006		0.0001
	sulphide (ic), $\text{HgS} \dots \dots \dots$	s	insoluble; insoluble in concentrated acids			
Nickel:						
	carbonate, $\text{NiCO}_3 \dots \dots \dots$	s	insoluble; soluble in acids			
	chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} \dots \dots \dots$	s, d	54	67	88	4
	nitrate, $\text{NiNO}_3 \cdot 6\text{H}_2\text{O} \dots \dots \dots$	s, d	(0°) 80	(20°) 96	(95°) 233	6
	sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \dots \dots \dots$	e	(0°) 27	(30°) 43	(99°) 77	2
	sulphide, $\text{NiS} \dots \dots \dots$	s	insoluble in water or dilute acids			
Potassium:						
	acetate, $\text{KC}_2\text{H}_3\text{O}_2 \dots \dots \dots$	d	(5°) 188	(14°) 230	(62°) 492	25
	bromate, $\text{KBrO}_3 \dots \dots \dots$	s	3.1	8.0	50	0.38
	bromide, $\text{KBr} \dots \dots \dots$	s	54	68	104	4.6
	carbonate, $\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O} \dots \dots \dots$	d	89	113	156	5.9
	(bi) carbonate, $\text{KHCO}_3 \dots \dots \dots$	s	(0°) 22	(25°) 36	(60°) 60	2.8
	chlorate, $\text{KClO}_3 \dots \dots \dots$	s	3.1	8.2	56	0.52
	chloride, $\text{KCl} \dots \dots \dots$	s	28	36	57	3.9
	chromate, $\text{K}_2\text{CrO}_4 \dots \dots \dots$	s	59	64	79	2.7
	(di) chromate, $\text{K}_2\text{Cr}_2\text{O}_7 \dots \dots \dots$	s	5	16	89	0.4
	fluoride, $\text{KF} \cdot 2\text{H}_2\text{O} \dots \dots \dots$	d		(18°) 92		12.4
	hydroxide, $\text{KOH} \cdot 2\text{H}_2\text{O} \dots \dots \dots$	d	97	119	178	18
	iodate, $\text{KIO}_3 \dots \dots \dots$	s	4.7	9.9	32	0.35
	iodide, $\text{KI} \dots \dots \dots$	s	128	148	208	6.0
	manganate, $\text{K}_2\text{MnO}_4 \dots \dots \dots$	d	very soluble			
	nitrate, $\text{KNO}_3 \dots \dots \dots$	s	13	37	246	2.6
	oxalate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \dots \dots \dots$	s		38		1.6
	perchlorate, $\text{KClO}_4 \dots \dots \dots$	s		1.9	20	0.11
	permanganate, $\text{KMnO}_4 \dots \dots \dots$	s	(0°) 2.8	(25°) 8.0	(65°) 25	0.33
	sulphate, $\text{K}_2\text{SO}_4 \dots \dots \dots$	s	7	12	24	0.62
	(bi) sulphate, $\text{KHSO}_4 \dots \dots \dots$	s	(0°) 36	(20°) 51	(100°) 122	3.5
	sulphide, $\text{K}_2\text{S} \cdot 5\text{H}_2\text{O} \dots \dots \dots$	d	very soluble			
	sulphite, $\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O} \dots \dots \dots$	d	very soluble			
Silver:						
	acetate, $\text{AgC}_2\text{H}_3\text{O}_2 \dots \dots \dots$	s	(0°) 0.7	(25°) 1.1	(80°) 2.5	0.06
	bromate, $\text{AgBrO}_3 \dots \dots \dots$	s		0.19		0.008
	bromide, $\text{AgBr} \dots \dots \dots$	s		0.00001		0.000006
	carbonate, $\text{Ag}_2\text{CO}_3 \dots \dots \dots$	s		0.003		0.0031
	chlorate, $\text{AgClO}_3 \dots \dots \dots$	s		15		0.6
	chloride, $\text{AgCl} \dots \dots \dots$	s		0.0002		0.00001

Salt.	Formula of crystallized salt.	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°	
Silver:						
chromate, Ag_2CrO_4		s		0.002		0.00015
fluoride, AgF		d		(16°) 182		13.5
iodate, AgIO_3		s		0.005		0.00014
iodide, AgI		s		0.0000003		0.00000001
nitrate, AgNO_3		s	122	257	952	8.4
oxide, Ag_2O , dissolves as AgOH		s		0.0025		0.0002
perchlorate, AgClO_4		d		very soluble		
sulphate, Ag_2SO_4		s	(18°) 0.73	(100°) 1.5		0.024
sulphide, Ag_2S		s	insoluble in water or acids			
Sodium:						
acetate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$		s, e	(0°) 34	(25°) 53	(40°) 65	6
(tetra) borate (borax), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$		s	(5°) 1.3	(30°) 3.9	(100°) 53	0.15
bromide, $\text{NaBr} \cdot 2\text{H}_2\text{O}$		s	73	87	118	6.9
carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$		e	7.0	28	46	1.8
(bi) carbonate, NaHCO_3		s	(0°) 6.9	(25°) 10	(60°) 16	1.1
chlorate, NaClO_3		s	82	105	233	6.4
chloride, NaCl		s	36	36	40	5.4
chromate, $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$		e	(0°) 32	(21°) 90	(100°) 126	3.3
(di) chromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$		d	(0°) 163	(98°) 433		5.0
fluoride, NaF		s		(21°) 4.2		1.1
hydroxide, $\text{NaOH} \cdot \text{H}_2\text{O}$		d	42	114	348	21
iodide, $\text{NaI} \cdot 2\text{H}_2\text{O}$		e, d	159	184	302	8.1
nitrate, NaNO_3		s	73	92	178	7.4
oxalate, $\text{Na}_2\text{C}_2\text{O}_4$		s	(15°) 3.2	(100°) 6.3		0.24
permanganate, $\text{NaMnO}_4 \cdot 3\text{H}_2\text{O}$		d	very soluble			
sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		e	(0°) 5.0	(32.75°) 50.65	(100°) 43	1.2
(bi) sulphate, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$		d	(25°) 29	(100°) 50		
sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$		{ Ox d, e	very soluble			
sulphite, $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$		e	(0°) 14	(20°) 27	(40°) 50	2
thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$		s, e	(10°) 60	(25°) 76	(45°) 124	5
Strontium:						
carbonate, SrCO_3		s		0.001		0.00007
chloride, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$		e	44	56	101	3.0
hydroxide, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$		CO_2	0.4	1.0	32	0.06
nitrate, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$		e	40	79	101	2.7
sulphate, SrSO_4		s		0.01		0.0006
Tin:						
chloride (ous) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$		{ S Ox	(0°) 84	(15°) 270		7

Salt.	Formula of crystallized salt.	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°	
Zinc:						
carbonate, $ZnCO_3$		s		0.004?		0.0003?
chloride, $ZnCl_2 \cdot 3H_2O$		d	208	432	615	9.2
nitrate, $Zn(NO_3)_2 \cdot 6H_2O$		d	95	127		4.7
sulphate, $ZnSO_4 \cdot 7H_2O$		e	42	58	81	3.1
sulphide, ZnS		s	insoluble; soluble in acids			

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