SYNTHETIC INORGANIC CHEMISTRY

A LABORATORY COURSE FOR FIRST YEAR COLLEGE STUDENTS

BY

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PREFACE

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 actual 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 with the classes. 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 bodies; 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 bodies 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 result 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 Mr. J. W. Phelan, to whose efficient management of the laboratory instruction is due any success with which this course has met at this Institute.

This little book is presented for publication with the desire to offer for the consideration of those in charge of the instruction at other institutions a plan of first-year work which has quite new and perhaps advantageous features. It is hoped that it may do its part in securing recognition of the importance of synthetic or preparative work in a well-balanced course of chemical training.

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Introductory to the Student

THE following exercises are designed to illustrate the principles and methods involved in the preparation of a number of the most important chemicals. Where possible the method employed resembles that 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 large 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.

A larger number of preparations is given than it is expected that the student can accomplish in fifteen weeks with but four hours per week in the laboratory. Each student, therefore, will be assigned certain of the exercises which he is expected to thoroughly master, and which he is expected to perform *entirely independently*. But almost equal in importance is it for him to know the work which the students about him in the laboratory are performing. To this end it is important that the directions, and more especially the first sections which discuss the principles involved, be studied for each exercise, and then that the work of neighboring students actually at work upon the preparations be observed and discussed with them in the odd moments which will invariably occur when waiting for evaporations or filtrations to take place.

Directions for laboratory work: The notes for each preparation are divided into three parts:

I. Discussion of the general principles involved.

II. Directions for actual manipulation.

III. Study questions.

Part I is to be read and understood before commencing work in the laboratory.

Part II, being the working directions, is to be kept at hand while carrying out the manipulations. These directions do not need to be recorded in the laboratory notebook; but it is essential, nevertheless, to keep a laboratory notebook in which to enter 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 tests for purity of materials, etc.

Part III constitutes directions for study based upon the particular preparation. This will involve: (1) laboratory experiments and direct entries in the laboratory notebook; (2) consultation of reference books, of which all that are necessary will be found upon the shelf in the laboratory; (3) original reasoning.

The answers to the questions should be written in the laboratory notebook 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.

Besides the specific study questions for each preparation there are, accompanying each group of exercises, general questions relating to the whole group; and these are to be worked out by every student. The answers to these questions are to be written on a certain prescribed kind of paper and handed in at the office, neatly bound, within the times which will be posted.

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.

ALKALI AND ALKALINE EARTH METALS

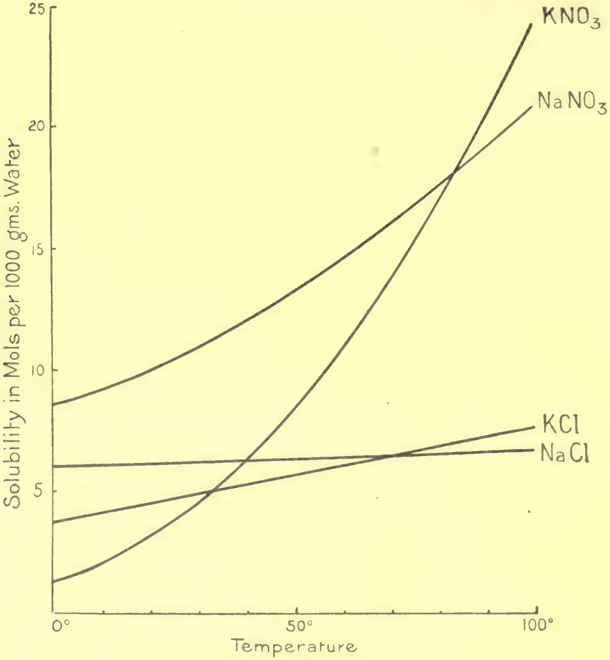
1. POTASSIUM NITRATE FROM SODIUM NITRATE AND POTASSIUM CHLORIDE

The most important source of nitrates is Chili saltpeter, sodium nitrate. This is not suited for use in explosives on account of its property of attracting moisture and rendering the explosive preparation damp. Potassium nitrate is not open to this objection, and hence large quantities of it are prepared, using sodium nitrate as a source of the nitrate radical.

When two ionizable salts are dissolved in water the resulting solution will contain, besides the undissociated molecules and the ions of these two salts, also the undissociated molecules of the two new salts which form by the interaction of the ions present. Which of these four salts will crystallize first out of solution depends upon their relative solubility. Thus if sodium nitrate and potassium chloride are dissolved together in water the resulting solution will contain Na^+, K^+, NO_3^-, and Cl^--ions, together with undissociated molecules of $NaNO_3$, $NaCl$, KNO_3, KCl. The solubility of some salts varies very much with the temperature, while that of other salts varies very little. This is seen from the following table and diagram, and practical use is made of these facts by crystallizing successively the two different salts at different temperatures.

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



Procedure. — Dissolve 100 grams of sodium nitrate and 88 grams of potassium chloride in 200 cc. of water and evaporate in a porcelain dish to half that volume. Without letting the liquor cool, separate it from the crystals which have formed during the evaporation. This is best accomplished with the aid of a suction bottle fitted with a 4-inch funnel, in which is placed a perforated porcelain filter plate covered with a disk of filter paper (Instructions). The liquid is poured through the filter and then the crystals are thrown upon the plate and pressed with a spatula, while applying gentle suction in order to remove as much as possible of the liquid clinging to them. This device is known as a Witt filter. Pour the filtrate into a beaker and set it aside to cool; then examine the crystals left on the filter and convince yourself that they consist in the main of sodium chloride. (Examine with a low power glass. The crystals should be cubical. Compare the taste with that of pure sodium chloride and that of pure potassium nitrate.) By means of running tap water cool the filtrate to about 10°, and then separate the crystals of potassium nitrate from the liquid in the same manner as above. The filtrate from these crystals is saturated with both sodium chloride and potassium nitrate, and the larger part of the latter should be saved. Evaporate the solution in a smaller dish until a considerable quantity of sodium chloride crystallizes from the boiling liquid. Filter hot, as above, and crystallize potassium nitrate from the filtrate by cooling. Unite this crop of potassium nitrate crystals with the first. Test a very small portion of them for sodium chloride by dissolving about 0.1 gram in 2 cc. of water and adding a drop of silver nitrate solution. They are not pure and must be purified. Weigh roughly the crystals while still moist, and dissolve them in from half to three quarters of their weight of water. Cool and separate the crystals from the mother liquor. The latter should now contain nearly all of the sodium chloride which was mixed with the first crop of crystals. Test as above to see if this crop is free from sodium chloride. If not, repeat the recrystallization as many times as is necessary to get a perfectly pure product. A little of this should when dissolved give no turbidity with silver nitrate solution, and when held in the flame on a platinum wire should color it the violet color of potassium, with none of the yellow sodium color. Dry the preparation on an unglazed porcelain plate, stopper it in a test tube or a small bottle, and label it neatly.

Questions

1. If potassium nitrate had been very much less soluble, would it have been more easy to purify it from sodium chloride? Explain why.

2. Describe at least two instances from your previous work in which use has been made of differences in solubility in preparing a salt from two others which furnish the positive and negative radicals, respectively.

2. CAUSTIC POTASH FROM WOOD ASHES

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 per cent. 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 derived by the Leblanc Process from potassium salts found in deposits in the earth, principally at Stassfurt, Germany.

Potassium carbonate being the principal 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 potassium hydroxide or *caustic potash* from potassium carbonate the solution of the latter is treated with milk of lime (calcium hydroxide). With this it interacts, yielding insoluble calcium carbonate and soluble potassium hydroxide,

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + 2KOH.$$

Procedure. — Tie a piece of cloth over the mouth of a thistle tube and insert it beneath the surface of a layer of sand, one-half inch deep, in the bottom of a tall 2-liter bottle. Mix 1 kilogram of wood ashes with 800 cc. of hot water in a pail, and transfer the moist mass to the bottle. Pour 200 cc. more of hot water over the surface of the ashes. Connect the thistle tube with a siphon and draw off as much liquid as possible, perhaps 200 cc., using suction and drawing the liquid into a suction bottle if it does not otherwise run rapidly enough. Commence evaporating this liquid in an 8-inch evaporating dish; then pour 300 cc. of hot water on top of the ashes and stir around the surface layer. Again draw off about 300 cc. of liquid and add it to that in the evaporating dish, and repeat the operation until the liquid drawn off is nearly colorless. Not more than 2 to 2½ liters need be drawn off in all. When the liquid is all evaporated remove the dry residue to an iron dish and heat it strongly with a Bunsen burner to destroy the tarry matter. More than a moderate red heat should not be exceeded, as it is not desirable to fuse the salt, but the heating should be continued until the ash is white or at most contains only black specks of completely charred carbon. When cooled, weigh the material; assuming it to consist wholly of potassium carbonate, calculate the amount of quicklime (calcium oxide) necessary to react with it according to the equation,

$$CaO + H_2O + K_2CO_3 = 2KOH + CaCO_3.$$

Slake 20 per cent. more than that amount of lime by covering it in a porcelain dish with water and quickly pouring off the excess of water. If the lime is of suitable quality it will soon grow hot and crumble to a powder, $Ca(OH)_2$. Take sufficient water to make ten times the weight of the crude potash. Stir up the slaked lime with half of it, thus making milk of lime. Dissolve the potash in the other half, bring it to boiling, and add the milk of lime with stirring. Let the mixture boil for 15 minutes and then filter, using a suction bottle (Witt filter, see Exercise 1). Measure the volume of the solution of caustic potash obtained and preserve it in a 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 (36.5 grams per liter), 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 KOH obtained from the wood ashes. Preserve the solution in a bottle labeled with the number of cubic centimeters of the solution, with its strength in mols per liter of potassium hydroxide, and with the actual amount in grams of the potassium hydroxide.

Questions

1. The calcium hydroxide used in causticizing the potash is a slightly soluble solid suspended in water, its solubility being 1.7 grams per liter. Explain how, in spite of its limited solubility, the required amount can enter into reaction.

2. Explain why the caustic potash solution obtained contains practically no calcium ions, even in case an excess of calcium hydroxide may have been used for causticizing.

3. Analyses of the crude potash obtained from various grades of wood ashes have given results which fall within the limits given in the table:

K_2CO_3 . . .	38–78 per cent.
Na_2CO_3 . . .	0–12 per cent.
K_2SO_4 . . .	13.5–40.5 per cent.
KCl . . .	0.9–10.0 per cent.
Insoluble matter .	0.1–9.2 per cent.

What substances other than KOH would you expect then to be present in the caustic potash solution which you have prepared? Look up the solubility of calcium sulphate and calcium hydroxide, and decide whether, in the presence of a large amount of potassium hydroxide, milk of lime would react with a small amount of potassium sulphate according to the equation:

$$K_2SO_4 + Ca(OH)_2 = CaSO_4 + 2KOH.$$

4. If a solid substance crystallizes from the caustic potash solution after it has stood, decide what it is by consulting the table in Question 3 and a solubility table.

3. SODIUM CARBONATE BY THE AMMONIA PROCESS

The principle employed in the manufacture of sodium carbonate from sodium chloride by the Solvay Process is exceedingly simple. It depends primarily upon the fact that sodium acid carbonate is but sparingly soluble in water; this compound is produced by the interaction of sodium chloride, in a saturated salt solution, with ammonium acid carbonate,

$$(1)\ NaCl + NH_4HCO_3 \rightleftharpoons \mathbf{NaHCO_3} + NH_4Cl.$$

Since ammonia and salts of ammonium are very much more expensive than sodium carbonate, it is evident that the process can be of no commercial value unless ammonia can be recovered and used again. This is accomplished in fact by treating the mother liquor, after separation from the sodium bicarbonate, with calcium hydroxide,

$$(2)\ Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O.$$

In practice the process is usually carried out as follows:

A nearly saturated salt solution is purified of iron, magnesia, lime, etc., which would otherwise get into the final product; there is then passed into it ammonia gas until it has absorbed 60 to 70 grams of NH_3 per liter, whereupon carbon dioxide is passed in until it has reacted with the ammonia to form ammonium bicarbonate,

$$NH_4OH + CO_2 = NH_4HCO_3,$$

which in turn reacts with the salt according to (1). Extensive precautions necessarily have to be observed that practically no ammonia escape during the process, so that the entire amount may be used over and over again. It is also essential that as little carbon dioxide shall be wasted as possible. Thus the carbon dioxide is utilized which is produced in converting limestone into quicklime,

$$CaCO_3 \rightarrow CaO + CO_2,$$

and in converting sodium bicarbonate into sodium carbonate,

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

Procedure. — To 50 cc. of concentrated ammonium hydroxide (sp. gr. 0.90) add 150 cc. of water. Place in a flask and add 60 grams of table salt free from lumps. Shake until the salt is nearly or quite dissolved and filter the solution if it is not perfectly clear. Pass a delivery tube through one hole of a double-bored, tightly fitting stopper placed in a 300 cc. flask. Provide a plug for the other hole. Let the tube dip into the solution which is placed in the flask, and pass in carbon dioxide gas from a Kipp generator until all the air has been displaced from the flask; then close the flask and allow the gas to pass in as fast as it will be absorbed. Occasionally, as the action seems to slacken, loosen the plug for a moment. Shake the flask frequently. It will take several hours for the solution to absorb sufficient carbon dioxide, and it may be left over night connected with the generator. When no more gas can be absorbed pour the mixture from the flask upon a Witt filter (see Exercise 1), in which the perforated plate is covered with a disk of filter paper (Instructions). Apply suction to remove the liquid from the sodium bicarbonate. Wash it three times with 15 cc. of ice water, sucking free from liquid each time. Spread on a porous plate and leave until it ceases to smell of ammonia. Test the preparation for chlorides, of which it should not contain more than a trace.

Questions

1. Describe how you tested the preparation for chlorides and explain the reason for each step.

2. How would you prepare sodium carbonate from the sodium bicarbonate?

3. What products beside sodium carbonate are obtained from the Leblanc Soda Process?

4. Why cannot potassium carbonate be prepared from potassium chloride by the ammonia process? (Look up the solubility of potassium bicarbonate.) What process may be used to obtain potassium carbonate from this source?

4. CHEMICALLY PURE SODIUM CHLORIDE FROM ROCK SALT

Common rock salt may contain other than sodium chloride up to 10 per cent. 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.

Procedure. — Dissolve 25 grams of rock salt in 75 cc. of water, hastening the action with gentle heating. To the solution add about 1 gram of sodium carbonate dissolved in a few cubic centimeters of water. Stir, let settle, and add a few drops more of sodium carbonate solution, and if no fresh precipitate is produced in the clear part of the solution no more need be added; otherwise enough more must be added to produce this result. Filter the solution, using a Witt filter (see Exercise 1). Prepare pure gaseous hydrochloric acid as follows: Place 50 grams of dry rock salt in a round-bottom liter flask provided with a rubber stopper with two holes, through which pass a thistle tube reaching to the bottom of the flask, and an exit tube just coming through the stopper. Provide a wash bottle for the gas as follows: A 300 cc. bottle is provided with a stopper with three holes. Through one passes a glass tube reaching to the bottom for entrance of the gas; through another a thistle tube reaching to the bottom for use as a safety tube; and through the third an exit tube just coming through the stopper. Pour into the bottle enough concentrated hydrochloric acid (sp. gr. 1.2) to come up three-quarters of an inch on the two lower tubes. Connect the exit tube with a 2-inch filter funnel for delivering the gas into the sodium chloride solution. Use entirely glass tubing, and, where connections must be made with rubber, bring the ends of the glass tubes close together. Before commencing to use this apparatus it must be approved by an instructor. Pour the sodium chloride solution into a beaker of 3 inches diameter, and insert the mouth of the funnel below the surface of the liquid. Pour gradually 95 cc. of concentrated sulphuric acid into the generating flask, and when the first action has ceased warm very gently. There will be a great deal of frothing, but the froth should at no time be allowed to get over into the wash bottle.[1] When hydrochloric acid gas ceases to be generated, separate the precipitated sodium chloride from the mother liquor by pouring it upon a Witt filter. Suck the moisture from the crystals. 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 succes-

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[1] The melted sodium acid sulphate left in the generating flask is very hot and must not be poured into the sink. It may be poured into some *dry* receptacle specially provided, or it may be allowed to cool slowly and solidify in the flask and then be dissolved out with water.

sive portions of 10 cc. of hydrochloric acid solution of 1.12 sp. gr. until the washings show no further test for sulphates. Then transfer the crystals to a porcelain dish and heat gently, while stirring, until all decrepitation ceases.

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 Mass Law, should one expect the solubility of sodium chloride to be lessened by the presence of hydrochloric acid? [It may be stated that another effect also comes into play here which likewise tends to lessen the solubility of sodium chloride.]

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.

5. AMMONIUM BROMIDE

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

$$NH_4OH + HBr = NH_4Br + H_2O.$$

Since, however, hydrobromic acid is a more expensive material than uncombined bromine, the latter would have the preference as a source of bromine, provided it yielded as satisfactory a product. Chlorine or bromine reacts as follows upon a cold solution of *sodium* hydroxide, as, for example, in the manufacture of bleaching liquors,

$$Br_2 + 2NaOH = NaBr + NaBrO + H_2O,$$

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

$$3NaBrO + 2NH_4OH = 3NaBr + 5H_2O + N_2.$$

Thus the action of bromine upon ammonium hydroxide yields only ammonium bromide and nitrogen gas, because even if the primary effect were to yield bromide and hypobromite in equal quantities, as is the case if sodium hydroxide is used, the ammonium hypobromite would immediately react with fresh ammonia in the same manner as does sodium hypobromite.

Procedure. — Place 55 cc. of concentrated ammonia (sp. gr. 0.90), together with 50 cc. of water, in a flask, which should be set in a pan of ice water. Put 15.8 cc. of bromine in a small separatory funnel, and add it a drop at a time to the ammonia, rotating the flask after each drop until the yellow color produced by the bromine has completely disappeared. Do not allow the contents of the flask to become heated at any time, as a dangerously explosive compound might in that case be formed. As soon as a permanent yellow color is produced, stop adding bromine and add at once a few drops of ammonia until the solution has again become colorless. Place the solution in an evaporating dish on top of a beaker of boiling water, and let the salt crystallize as the water evaporates. When only a little liquid remains, separate the crystals from it in a funnel, and dry them on a porcelain plate.

Questions

1. What products would be formed if bromine were added to a solution of sodium hydroxide instead of ammonium hydroxide, (1) if the solution were kept cold? (2) if it were heated?

2. *Experiment.* — Add about 10 drops of bromine to 10 cc. of a cold 10 per cent. 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. Write the equation showing the complete reaction between bromine and ammonia. What fraction of the entire amount of ammonia used is lost through formation of nitrogen gas?

4. Why cannot hydrobromic acid be prepared from potassium bromide by a method analogous to that used in the manufacture of hydrochloric acid (recall first term's experiments)?

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.

6. If bromine, or more especially chlorine, were allowed to act upon a neutral solution of ammonium bromide or chloride, what exceedingly dangerous compound would result? This compound is not likely to be formed in a solution containing free ammonia.

6. BARIUM HYDROXIDE FROM BARITE

One of the most important sources of barium is the mineral barite, $BaSO_4$. By reduction with charcoal this can be converted into barium sulphide,

$$BaSO_4 + 4C = BaS + 4CO,$$

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

$$BaS + \mathbf{CuO} + H_2O = Ba(OH)_2 + \mathbf{CuS}.$$

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,

$$CuO + H_2O \rightleftharpoons Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^-.$$

Therefore, since copper sulphide is a far more insoluble body than copper oxide, it follows that the few Cu^{++}-ions from the latter unite with the S^{--}-ions from the barium 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 all of the copper oxide or the barium sulphide is exhausted.

If, as frequently proves to be the case in carrying out this process, more copper oxide is taken than is required by the equation, the excess dissolves to a slight extent in the hot concentrated solution of barium hydroxide, because with the latter it can form an unstable, deep blue colored, soluble compound. When such a solution is cooled, barium hydroxide, which is but little soluble in cold water, crystallizes out, whereupon the unstable compound of copper breaks down and gives a dirty blue-green precipitate of copper hydroxide, which contaminates the crystals. To hold the copper in solution at this point, the following procedure directs to add ammonia to the solution.

Procedure. — Mix thoroughly 50 grams of powdered barite and 14 grams of powdered charcoal. Pack the mixture into a Hessian crucible and cover it with a layer of powdered charcoal. Cover the crucible and heat it for one-half hour in a gas furnace. Powder the mass when cool and suspend in 200 cc. of water in a porcelain evaporating dish. Heat to boiling and add powdered copper scale 20 to 30 grams, with constant stirring, until a small test portion of the filtered liquid gives no test for a soluble sulphide with lead acetate. Add water to make up for any lost by evaporation. Filter while hot, using a Witt filter and letting the bulk of the residue remain in the evaporating dish; immediately stir the residue with 50 cc. of hot water and then pour through the same filter, adding to the first filtrate. As the liquid cools, barium hydroxide crystallizes out. It is necessary, therefore, to have everything ready, including hot wash water, before commencing to filter and to work rapidly in order that the filter may not become clogged by the crystals. If the solution is at all blue at this point, remove the filter funnel, add 5 cc. of concentrated ammonium hydroxide, and stopper the flask again. Let the filtrate cool gradually in the suction bottle and finally cool to 0° in ice water. Then shake up the crystals with the liquid and pour the entire mass into a Witt filter, suck the crystals dry from adhering liquid as much as possible in 10 seconds, spread them on an unglazed plate, and press them with filter paper to dry still further. Let them stand on the plate until dry — not longer than necessary — and then stopper them tightly in a sample bottle.

Questions

1. What constituent of the atmosphere must be excluded from the solution while crystallizing and as much as possible 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 barium chloride be prepared from barium sulphide?

4. Give some other method by which barium hydroxide could be obtained from barium sulphide without the use of copper oxide.

5. Starting with the mineral barium carbonate, how might barium hydroxide be prepared? Barium oxide? Barium chloride?

6. Give the reason why barium sulphate should be insoluble in dilute hydrochloric acid while barium carbonate is soluble (find the reason in the relative strength of the acids).

7. STRONTIUM CHLORIDE FROM CELESTITE

Celestite, strontium sulphate, might be reduced with charcoal by the same process as was employed in the reduction of barium sulphate, and the strontium sulphide so obtained could be converted into strontium chloride by treatment with hydrochloric acid. For the sake of illustrating another method, however, a process will be employed for decomposing the strontium sulphate which does not require the use of a furnace.

The method consists in first converting the sulphate into the carbonate by boiling it with a concentrated solution of sodium carbonate, and then of 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 principle of mass action, 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,

$$\mathbf{SrSO_4} + Na_2CO_3 \rightleftharpoons \mathbf{SrCO_3} + Na_2SO_4,$$

and, if strontium carbonate were boiled with a solution of sodium sulphate, the solid would be converted into the sulphate. It is easy to deduce that if the ratio of the concentration of the ions in solution $\frac{\text{conc } CO_3^{--}}{\text{conc } SO_4^{--}}$ is greater than $\frac{1}{74}$, solid strontium sulphate will be converted into solid carbonate.

Procedure. — Take 25 grams of 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 200 cc. of water, add 30 grams of anhydrous sodium carbonate, and boil for 30 minutes with frequent stirring. Separate the solid matter left from the solution as follows:[1] Transfer the liquid and solid residue to a tall jar or beaker, rinsing it all in with the aid of 200 cc. additional of pure water. Let settle for 5 minutes, and siphon off as much of the liquid as possible without disturbing the powder at the bottom. Stir up thoroughly with 400 cc. of water, again let settle, and draw off the liquid. Repeat this operation twice again, when the residue will be washed sufficiently free from sodium sulphate. Then add about 50 cc. of water, warm, and add hydrochloric acid, drop by drop, until no more effervescence takes place. The liquid will probably still be somewhat cloudy. Filter until perfectly clear, and evaporate in a porcelain dish over a moderate sized free

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[1] This cannot be accomplished satisfactorily by means of a filter because of the nature of the solid powder, which will so clog up the pores of the filter that the liquid will barely run through.

flame until, on blowing on the surface of the liquid, a thin crystal scum will appear. Then remove the flame, add 5 cc. more of pure water and let cool, stirring so that a uniform crystalline meal will be obtained instead of a cake. When perfectly cold, remove the mass to a Witt filter and drain off all the liquid with suction. Remove the crystals to a porous plate and let them dry for a few hours, but not too long, as they are somewhat efflorescent. Evaporate the mother liquor from the first crystallization until again a scum will appear on blowing on the surface. Then add 3 cc. of pure water and let crystallize as before. If this crop of crystals when drained is pure white, add it to the first crop.

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. Could barium sulphate be converted into the carbonate with equal ease by boiling with sodium carbonate? Find the reason for the answer in the relative solubility of the substances.

GENERAL QUESTIONS. I

ALKALI AND ALKALINE EARTH METALS

1. Can potassium carbonate be converted into potassium oxide by heating? Can calcium carbonate into calcium oxide? Which metal is thus indicated as being the more strongly basic? Make a similar comparison for the hydroxides of these metals.

2. Compare in a similar manner the decomposition produced by heat upon the nitrates of sodium, potassium, ammonium, calcium, strontium, barium.

3. How can the oxides of sodium, potassium, calcium, and barium be prepared, starting with either the hydroxides, carbonates, or nitrates? What oxides are obtained by burning these metals in the air? What relation do sodium peroxide and barium peroxide bear to hydrogen peroxide?

4. In its compounds the group ammonium, NH_4, behaves similarly to the metals of the alkali group. Is it possible for ammonium to be isolated and then show any of the metallic properties of these elements?

Experiment. — Cool 25 cc. of a saturated ammonium chloride solution with ice. Add a small lump of sodium amalgam (1 to 2 grams). What is formed? After the reaction appears to be ended, remove the metallic lump to a beaker of pure water and observe what gradual change takes place.

Does this experiment show whether sodium or ammonium possesses the greater electrolytic solution tension?

How does ammonium amalgam react with water? Compare the action with that of sodium amalgam on water, and with that of pure sodium on water.

State how and to what extent ammonium possesses the metallic properties of an alkali metal.

5. How can ammonia be liberated from its compounds? How can this process be made use of to show the presence or absence of an ammonium salt in any given sample of material? Explain the chemical reaction involved in the test.

6. What are the colors imparted to a flame by the salts of the alkali and alkaline earth metals? *Experiment.* — Dip a platinum wire in solutions of the salts of these metals (the chlorides give the best results) and hold the wire in the Bunsen flame.

7. How does the solubility of the hydroxides vary in the series, Mg, Ca, Sr, Ba? *Experiment.* — To some mag-

nesium chloride solution add (*a*) some ammonium hydroxide; (*b*) some ammonium chloride and then some ammonium hydroxide. Explain the difference in the results. (How does the presence of ammonium chloride influence the extent of the dissociation of NH_4OH?)

ELEMENTS OF GROUP III

8. BORIC ACID

In this preparation, borax, the sodium salt of tetraboric acid, is chosen as the source of boron. While boron is decidedly a non-metal, yet its acid-forming characteristics are not highly developed. Its acids, therefore, having a low degree of ionization, are readily displaced by strong acids from solutions of their salts. Thus tetraboric acid would be set free from borax by hydrochloric acid; but since this is capable in aqueous solution of combining with water, and since normal boric acid (H_3BO_3) is but slightly soluble, it is this body which crystallizes from the solution.

Procedure. — Dissolve 100 grams of borax in 300 cc. of boiling water. Add hydrochloric acid (about 41 cc. of conc. acid 1.2 sp. gr.) to the hot solution until a strip of blue litmus paper is colored bright red. Allow to cool, when normal boric acid will crystallize out. Filter off the crystals, using a Witt filter, and purify them by recrystallization, dissolving in 300 cc. of hot water. Allow to cool slowly, shaking or stirring occasionally to prevent the crystals from caking together.

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 ½ 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 molecules of HCl have been added to one molecule of borax.

4. How can chloride of boron be prepared? How does this substance behave when treated with water? How would it behave if boron were a strongly metallic element?

9. ALUM FROM CRYOLITE

(BY-PRODUCT: SODIUM CARBONATE)

A characteristic series of compounds of the trivalent metals are the alums, of which the potassium aluminum, or common alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, 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 or chemical nature 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, $3NaF.AlF_3$ 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 a suspension of milk of lime ($Ca(OH)_2$), 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,

$$3NaF.AlF_3 + 3Ca(OH)_2 = 3CaF_2 + Na_3AlO_3 + 3H_2O.$$

By removing the insoluble residue left by this reaction 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 in accomplishing the separation. 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 crystals, 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; for example, hydrofluosilicic acid (H_2SiF_6).

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,

$$2Na_3AlO_3 + 3H_2O + 3CO_2 = 3Na_2CO_3 + \mathbf{2H_3AlO_3}.$$

This precipitated aluminic acid, H_3AlO_3 (or, as more frequently named, aluminum hydroxide, $Al(OH)_3$), 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.

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

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

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 15–20° about one-half of the alum will separate out, but ordinarily in the form of a mass of very minute crystals. In order to obtain large crystals during the cooling, three precautions are necessary: (1) A few minute 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 minute 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 glass plate 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.

Procedure. — Slake 46 grams of quicklime and then mix in a large casserole with 250 cc. of water to make milk of lime. Stir into this 50 grams of finely powdered cryolite, and heat to boiling while stirring constantly. 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 1½ 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 from a Kipp generator until all of the alumina 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 solution settle until the precipitate occupies less than one-sixth of the entire volume. Siphon off the clear liquid and evaporate it to dryness in a porcelain dish. Powder and preserve the sodium carbonate so obtained. 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 30 cc. of concentrated sulphuric acid, and warm, if necessary, to effect complete solution. Add 42 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°, 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.

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 proportion 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.)

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* electrolyte.

3. *Experiment.* — Add a solution of sodium hydroxide, drop by drop, to 5 cc. of a solution of aluminum chloride, continuing until a considerable amount is added after the first effect is observed. Preserve the contents of the tube.

Repeat, using a solution of ammonium hydroxide instead of one of sodium hydroxide.

To the tube saved from the first part of this experiment add a solution of ammonium chloride.

Show how the difference in the degree of dissociation of the two bases accounts for the difference in the first two cases. State how it may also explain the result in the third case.

10. ALUMINUM SULPHIDE

This compound cannot be prepared in the wet way for the reason that it is decomposed by water. It is, however, readily prepared by the action of metallic aluminum upon lead sulphide at a high temperature.

Procedure. — Mix 133 grams of finely powdered galena (lead sulphide ore) with 10 grams of granulated aluminum.

Place in a small uncovered Hessian crucible, and heat as strongly as possible in a gas furnace until the charge in the crucible commences to react and a bright glow extends throughout the whole mass. Leave two or three minutes longer in the furnace at a white heat in order that the reaction may be entirely completed and that the charge may become quite liquid (a thin solid crust of aluminum oxide may form on the surface). Then pour into a dry,[1] clean iron pan; when cool detach the brittle aluminum sulphide from the lead button and stopper the sulphide tightly in a test tube. The lead may be put in a box provided for scrap lead.

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? What are the free acid and base into which the salt is resolved by the action of water? State the specific nature of both the acid and the base, which makes this reaction possible, instead of the reverse reaction (neutralization), which is the common one between an acid and a base.

GENERAL QUESTIONS. II

ELEMENTS OF THE THIRD GROUP OF THE PERIODIC SYSTEM

1. Boron and aluminum are the only members of the third group of the periodic system of the elements which are of common occurrence or of great importance. Turn to a table of the periodic system. From what you know of the regularities of this system what should you predict would be the valence of scandium, lanthanum, indium, thallium?

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[1] If the iron pan should chance to be moist, the heat of the charge would cause the formation of steam with explosive rapidity, thus throwing about the red-hot material.

Write the symbols of the sulphates of these elements. Find out from a text-book what chlorides of thallium are known to exist. Which one is characteristic of the position of thallium in the third family? Is it of common occurrence for an element to display different valences? Does this occur in the alkali or alkaline earth groups?

2. Give the formulæ of normal boric and aluminic acids; of the meta acids; of the anhydrides; and of the sodium salts of tetraboric acid, aluminic acid, and metaluminic acid.

3. *Experiment.* — Prepare in a test tube a solution of sodium aluminate. How? Add to this hydrochloric acid, drop by drop, until a precipitate forms. What is it? Then add more hydrochloric acid until the precipitate redissolves. Is it during this last action to be considered as an acid or a base? Define "amphoteric substance."

4. What is produced in the solution when dry boron chloride is treated with water? *Experiment.* — Test the behavior of a solution of aluminum chloride with litmus. Evaporate the solution to dryness. What is left? Explain. How may dry boron and aluminum chlorides be prepared?

5. Compare the hydroxides of sodium, potassium, magnesium, barium, boron, and aluminum as regards (*a*) solubility; (*b*) tendency to dissociate to form either bases or acids.

6. All of the alums are isomorphous. What is isomorphism? Give the name and symbol of at least two alums which contain neither aluminum nor potassium.

7. It is not possible to prepare an alum from boron in which this element plays the part of aluminum in common alum. With what other properties of boron are you familiar which would lead you to conclude that this would be the case?

11. 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 becomes 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 is given free access of air. Since, however, this method would be too time-consuming to apply on a small scale, nitric acid will be employed instead of air as the oxidizing agent.

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO.$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Procedure. — Heat 50 grams of 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 300 cc. of dilute (1 : 4) sulphuric acid and 125 cc. of dilute nitric acid (sp. gr. 1.2). Warm in the hood over a Bunsen flame 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 crystals from the mother liquor by use of a Witt filter. Evaporate the mother liquor somewhat, and obtain a second crop of crystals, throwing away the mother liquor from this crystallization. Dissolve all of the crystals by heating in their own weight of water; set the solution away to cool slowly, and after several hours remove the crystals which have formed and evaporate the remaining solution to obtain another crop of crystals.

Questions

1. Explain why copper will not dissolve in dilute sulphuric acid (see Solution Tension).

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. The quantities of sulphuric and nitric acid used were considerably in excess of what is theoretically necessary to react with the given amount of copper. Give reasons why the final product is not likely to be contaminated with copper nitrate or nitric acid or with free sulphuric acid.

4. How can copper sulphate be obtained from copper sulphide on a commercial scale?

5. If, as is probably the case, the copper used for this preparation contained small amounts of iron, a considerable part of the iron would appear in the final crystals of blue vitriol. In what condition would it occur there? Explain why the product cannot be freed from it by recrystallization. (*Suggestion.* — Do the vitriols form an isomorphous series like the alums?)

12. 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. Therefore the readiest means of preparing a cuprous salt, is to first prepare the cupric salt and then partially reduce it.

If metallic copper and cupric chloride be made to react, the former will act as a reducing agent, the latter as an oxidizing agent, and both will pass into the "ous" state of oxidation:

$$Cu + CuCl_2 = 2CuCl.$$

Cuprous chloride is soluble in a concentrated solution of hydrochloric acid with formation of a complex compound; the latter, however, is broken up on dilution with water, and insoluble cuprous chloride is precipitated. 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:

$$2CuCl + 2HCl + O = H_2O + 2CuCl_2,$$

or

$$2CuCl + H_2O + O = 2Cu{<}{\begin{matrix}Cl\\OH\end{matrix}}$$

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 much more slowly.

Procedure. — Dissolve 43 grams of crystallized cupric chloride with 100 cc. of water and 100 cc. of concentrated hydrochloric acid (1.2); add 25 grams of clean copper turnings (or copper wire may be used); and heat to boiling in an Erlenmeyer flask, with a small funnel placed in the mouth, until the green color has disappeared. If then a few drops of the solution added to a test tube of water impart no blue color to it, the reaction is complete. Pour the liquid into a tall beaker containing at least a liter of water. Allow the white precipitate to settle, decant off the clear solution, and stir up the precipitate with 200 cc. of very dilute hydrochloric acid. Again let settle, collect the precipitate on a Witt filter, and wash it first with very dilute hydrochloric acid, then successively with two portions of 15 cc. each of alcohol, and two portions of 15 cc. each of ether. During the above treatment the precipitate should be kept out of contact with the air as much as possible, by keeping it covered with liquid all the time until it is freed from water by means of the alcohol and ether. After the ether has drained off, break up the caked cuprous chloride and leave it in a warm and dry place until the adhering ether has completely evaporated. Pulverize, and stopper tightly in a dry test tube. The product should be white. If it is discolored it must be dissolved in concentrated hydrochloric acid, poured into water, and washed as before.

Questions

1. Does copper resemble silver more when in the cupric or the cuprous condition?

2. *Experiment.* — Expose a little cuprous chloride covered with water to the sunlight. What property is observed in which cuprous chloride is like silver chloride?

3. *Experiment.* — Place 2 to 3 grams of cuprous chloride in the bottom of a dry test tube. Have a stopper fitted to the tube, then fill it completely with ammonia water (sp. gr. 0.96) 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 pour quickly its contents into a bottle of about 200 cc. capacity, and immediately cork the latter air-tight. Shake the bottle vigorously for 3 minutes, then place the mouth under water and open the cork. From its quantity, infer what gas is absorbed out of the air in the bottle. What is the change in the condition of the copper salt which causes its change in color? Formulate the reaction.

13. AMMONIUM AND COPPER SULPHATE

$(NH_4)_2SO_4.CuSO_4.6H_2O$

One example of the formation of a *double salt* has already been illustrated in the preparation of alum, in which there separates from a solution containing the two simple salts K_2SO_4 and $Al_2(SO_4)_3$, not a mixture of the crystals of each salt, but only a single kind of crystals which are entirely different in nature from those of the two simple salts.

The present preparation illustrates the formation of another double salt. An equal number of mols of copper sulphate and ammonium sulphate are each dissolved in water, and on mixing the solutions there are produced crystals of the formula $(NH_4)_2SO_4.CuSO_4.6H_2O$.

Whether or not a double salt will separate from a mixed solution, such as this one, depends upon the solubility relations existing among the various compounds capable of formation. In this case the double salt is considerably less soluble than either of the simple salts. On the other hand, if saturated solutions of *sodium* sulphate and copper sulphate are mixed, no double salt will separate, but, on evaporation, a mixture of the crystals of the two simple salts will be obtained. Thus it appears that the double sulphate of sodium and copper is more soluble than the simple salts.

Procedure. — Dissolve 33 grams of ammonium sulphate in 60 cc. of water and 62 grams of blue vitriol in 100 cc. of water. It will be necessary to heat, and this should be done in flasks to avoid loss of water by evaporation. Add a few drops of dilute sulphuric acid to each. Mix the two solutions while nearly at the boiling temperature in a 6-inch evaporating dish; allow it to stand uncovered until the temperature has fallen to about 75°. Then drop in several very small crystals of ammonium and copper sulphate to serve as nuclei for the crystallization (see Alum); set the dish on the middle of a towel laid on a sheet of asbestos; cover the dish with a plate of glass or another sheet of asbestos and fold the ends of the towel up over the top, so that the solution may cool very slowly. Leave until the next day to crystallize. Pour off the mother liquor. Leave the crystals on an unglazed plate until dry and then bottle. Evaporate the mother liquor to just one-half its volume, and set to crystallize in a smaller dish in precisely the same manner as the first time. Throw away the mother liquor from this crystallization, dry the crystals and add them to the first crop.

Questions

1. *Experiment.* — Dissolve a little of the salt in water. What ions does the solution contain? Make the ordinary tests for copper and sulphate ions. Does the double salt exist as such in solution?

2. Compare this double salt with the double cyanide of silver and potassium with regard to its tendency to dissociate. *Experiment.* — Make a little of the latter salt by adding to 1 cc. of silver nitrate solution just enough potassium cyanide solution to redissolve the precipitate

which at first forms. Then in this solution of potassium silver cyanide test for simple silver ions by adding a little sodium chloride solution (not hydrochloric acid).

3. Find out by experiment whether the double salt $K_2SO_4.CuSO_4.6H_2O$, analogous to $(NH_4)_2SO_4.CuSO_4.6H_2O$, can be prepared.

14. AMMONIO-COPPER SULPHATE

$CuSO_4.4NH_3.H_2O$

The copper and ammonium sulphate of the last preparation was produced by the combination of two simple salts and is therefore a so-called double salt. Ammonio-copper sulphate, on the other hand, is prepared from only one simple salt, copper sulphate, which in crystallizing is caused to unite with four molecules of free ammonia and one molecule of water, much in the same way as copper sulphate unites with five molecules of water when it crystallizes as blue vitriol. The molecules of ammonia would appear to be bound to the copper atom of the salt rather than to the sulphate radical, because when the salt is dissolved in water the four ammonia molecules remain in combination with the copper, giving the complex ion $Cu(NH_3)_4^{++}$, while the sulphate radical gives only the ordinary SO_4^{--}-ion. Thus we might say that this salt is the sulphate of the ammonio-copper complex.

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 only by slow diffusion is to insure the formation of large, well-defined crystals.

Procedure. — Dissolve 25 grams of finely pulverized blue vitriol in 84 cc. of dilute ammonium hydroxide (sp. gr. 0.96). Place 125 cc. of alcohol in a medium-sized common bottle.

Fill the stem of a small separatory funnel with water. Insert to the bottom of the alcohol, and run in 20 cc. of water to form a layer beneath the alcohol to separate it 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 mixing the layers. Set the bottle away for at least a week; at the end of that time remove the crystals from the liquid, dry them with filter paper, and stopper them at once in a sample bottle.

Questions

1. *Experiments.* — (*a*) What is the reaction between Cu^{++} and OH^--ions? Add sodium hydroxide solution, drop by drop, to a solution of copper sulphate until it is present in large excess. Save the solution.

(*b*) When ammonium hydroxide is added instead of sodium hydroxide, explain what successive reactions occur.

(*c*) Add ammonium chloride to the solution saved from (*a*) and explain the results.

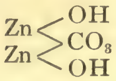
(*d*) To 5 cc. of copper sulphate solution add 10 cc. of a 10 per cent. solution of tartaric acid; then add sodium hydroxide solution, as in (*a*), and compare the results with those in (*a*) and (*b*), but do not attempt to ascribe a definite formula to the complex compound formed.

2. *Experiments.* — (*a*) To 1 cc. of silver nitrate solution add sodium hydroxide until present in large excess.

(*b*) Repeat, using ammonium hydroxide instead of sodium hydroxide, and adding the reagent at first only a single drop at a time. Finally, after an excess of 5 cc. of ammonium hydroxide is present, test the solution with a little potassium chloride for the presence of silver ions. Compare the results with those in Experiment 1.

15. 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 can 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 the former two when the ions necessary to its formation are brought together. The simplest formula for the basic carbonate is



$$\begin{array}{lcl} & & \mathrm{OH} \\ \mathrm{Zn} & < & \\ & & \mathrm{CO_3} \\ \mathrm{Zn} & < & \\ & & \mathrm{OH} \end{array}$$

but the precipitate may be of very 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.

Procedure. — Dissolve 50 grams of crystallized zinc sulphate (white vitriol) in 1.5 liters of hot water in a common 2-liter bottle, and add slowly, with stirring, a solution of 19 grams of anhydrous sodium carbonate in 250 cc. of hot water. Let the precipitate settle somewhat, and test, by adding a few drops more of sodium carbonate to the clear part of the solution, whether all the zinc has been precipitated. Let settle as much as possible (in 30 minutes perhaps to one-third or one-fourth of the bulk of the liquid).

Draw off the clear solution and then fill up the bottle with hot water, and stir thoroughly. Again let settle and draw off the clear solution, and repeat this operation until it is calculated that the remaining gelatinous precipitate contains less than 1 per cent. of the soluble salts present in the original solution. Remove the precipitate to a porcelain dish, and leave it on the steam table until it is quite dry. Pulverize the lumps, and heat in a small porcelain dish over a free flame until all the carbon dioxide has been driven off and the remaining zinc oxide is yellow when hot and pure white when cold.

Questions

1. Why could not the precipitate of basic zinc carbonate have been advantageously freed from the solution by means of filtration?

2. What test can you apply to prove that the zinc carbonate has been entirely converted into the oxide? Make the test.

3. Which is the more strongly basic, calcium oxide or zinc oxide? Which, then, could be more readily decomposed by heat, calcium carbonate or zinc carbonate?

4. *Experiment.* — To some solution of zinc sulphate add a solution of sodium hydroxide, drop by drop, until the precipitate first formed redissolves. How is zinc hydroxide similar to aluminium hydroxide in respect to its behavior towards strong acids and strong bases?

5. *Experiment.* — Knead up to a stiff paste about a gram of zinc oxide with a few drops of very concentrated zinc chloride solution, mold into a lump, and observe its condition at the end of half an hour. What chemical change occurs when this mixture hardens? Compare it with the change which occurs when plaster of Paris "sets."

Add a few drops of the concentrated zinc chloride solution to a tube of water. What is the precipitate?

16. MERCUROUS NITRATE

$HgNO_3.H_2O$

Like copper, mercury will dissolve in nitric acid, an oxide of mercury first being produced in consequence of the oxidizing action of nitric acid, and this oxide immediately reacting with the acid to form a salt. Mercury is capable of forming two oxides, Hg_2O and HgO, and two series of salts derived from these oxides in which the metal displays the valence I and II, respectively. In order to obtain the salt corresponding to the lower oxide, it is only necessary to keep an excess of mercury present throughout the action and not to allow the nitric acid to act too violently.

Procedure. — Treat 25 grams of mercury in a flask at the hood with 20 cc. of dilute nitric acid (sp. gr. 1.2), 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 upon an unglazed porcelain plate, and stopper them in a test tube as soon as dry.

Questions

1. Test the preparation for *mercuric* salt. Warm 0.5 gram of the preparation gently in about 10 cc. of water. It will not dissolve to give a clear solution. Note the character of the residue. Add nitric acid, drop by drop, until a clear solution is obtained. By adding dilute hydrochloric acid, drop by drop, all of the mercurous salt can be precipitated, leaving any mercuric salt in solution. Filter; test the filtrate for mercuric salt by means of hydrogen sulphide. Judge from the amount of the precipitate the quantity of mercuric salt, if any.

2. Explain why mercurous nitrate does not dissolve completely in pure water and what is the character of the residue. How do a few drops of nitric acid aid in the solution?

3. Explain the use of hydrochloric acid in separating mercuric from mercurous salt.

17. 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 which contains an excess of nitric acid is evaporated, it becomes a thick, heavy sirup, which by further driving off of nitric acid and water becomes a pasty mass, due to formation of small crystals of basic nitrate, $Hg{<}\begin{matrix}NO_3\\OH\end{matrix}$. If the materials taken for the preparation of this salt are pure, the product can contain no other foreign matter than an excess of nitric acid; consequently, in view of the difficulty of obtaining good crystals, it is convenient to preserve the salt in this pasty condition.

Procedure. — Heat 25 grams of mercury in a flask with 48 cc. of dilute nitric acid (sp. gr. 1.2) 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 dish 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 a small, wide-mouth sample bottle, which has previously been weighed; let it cool and stopper it.

Questions

1. To prepare a solution of this salt for use as a laboratory reagent, explain why it is necessary to add a small quantity of nitric acid. (Compare with Questions 1 and 2 under Mercurous Nitrate.)

2. *Experiment.* — 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?

18. 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 can 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 with the formation of a complex soluble compound. While by a consideration of the Mass Law one would predict that an excess of either ion would cause a decrease in the solubility of the salt $Hg(SCN)_2$, another factor nevertheless comes into play, namely, the tendency of the molecule $Hg(SCN)_2$ to combine either with Hg^{++} or SCN^--ions to form complex ions, which under the conditions given are capable of remaining in solution. Similar phenomena are not of infrequent occurrence where a given amount of a reagent will cause a precipitate, while an excess will cause the precipitate to redissolve. For instance, carbon dioxide gas, if passed into a solution of calcium hydroxide, causes a white precipitate, but more of the gas causes the precipitate to redissolve. 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 body 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 mercury vapor, which is poisonous.

Procedure. — Dissolve the mercuric nitrate obtained in the last preparation 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 25 grams of potassium sulphocyanate in 500 cc. of water until a red color appears and persists after stirring. Collect the precipitate on a Witt filter, and dry it upon an unglazed plate.

The dried salt may be made into the so-called Pharaoh's serpent eggs by kneading it with 1.5 grams of dextrine dissolved in 5 cc. of water to obtain a stiff paste, molding this into small cones or pellets, and allowing them to dry.

Questions

1. Observations made in the course of this preparation are sufficient to decide whether ferric sulphocyanate, $Fe(SCN)_3$, is an ionized or un-ionized body. Explain.

2. Refer back to Question 1 under Potassium Nitrate and state why the product in this preparation can be obtained free from other bodies with so much less manipulation than with potassium nitrate.

3. Find out what is the degree of dissociation of the soluble halides of mercury, *i. e.*, $HgCl_2$, $Hg(CN)_2$. Do these salts form in this respect any exception to the general rule regarding the ionization of salts?

4. 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.

GENERAL QUESTIONS. III

HEAVY METALS OF THE FIRST TWO GROUPS OF THE PERIODIC SYSTEM

1. What effect does metallic copper have upon a solution of a silver salt? Metallic silver upon the solution of a gold salt? Explain.

2. Starting with an alloy of silver and copper, devise a process for obtaining the two metals separately in the metallic condition.

3. Compare copper and silver hydroxides with regard to their strength as bases. How do they compare with the hydroxides of the alkali metals?

4. *Experiment.* — Dissolve 5 grams of copper sulphate crystals in 50 cc. of water, add 5 grams of tartaric acid, also dissolved in 50 cc. of water, and then add sodium hydroxide until the solution has turned to a clear, deep blue. To this add a solution of grape sugar and warm until all the copper has precipitated. What is the precipitate? Treat a little of it with dilute sulphuric acid and warm for a moment. Explain how one-half of the copper in the precipitate is oxidized at the expense of the other half, which is reduced, and write the equation for the reaction.

5. *Experiment.* — Add a little of a solution of a cupric salt to some potassium iodide solution. Test a drop of the resulting liquid for the presence of free iodine. What is the precipitate? Write the reaction.

6. Compare the chlorides of copper, silver, and gold (copper and gold each possess two chlorides) with regard to their solubility and the valence of the metal.

7. What justification, in the light of the compounds which they form, is there for placing copper, silver, and gold in the same family in the periodic classification?

8. *Experiment.* — To 5 cc. of a 10 per cent. zinc sulphate solution add 10 cc. of water, then saturate with hydrogen sulphide. Filter off the precipitate and test for zinc ions in the filtrate. How?

To a second similarly diluted portion of zinc sulphate solution add 2 cc. of dilute sulphuric acid (1 : 4) and again saturate with hydrogen sulphide.

To a third similar portion of zinc sulphate solution add 2 grams of sodium acetate and dissolve; saturate with hydrogen sulphide, filter, and test the filtrate for zinc ions. Explain the cause of the differences observed.

9. *Experiment.* — Dilute 5 cc. of cadmium nitrate solution with 25 cc. of water and saturate with hydrogen

sulphide. Filter, and test the filtrate for cadmium ions. How?

Repeat, adding dilute hydrochloric acid (sp. gr. 1.12) instead of water to the cadmium nitrate solution. Explain the cause of the difference.

10. Repeat the second part of Experiment 9, using mercuric nitrate instead of cadmium nitrate.

How does the solubility product compare among zinc sulphide, cadmium sulphide, and mercuric sulphide?

11. Given an alloy of zinc, cadmium, and mercury, how might one proceed to obtain the three separately in the metallic condition?

12. Compare the chlorides of zinc, cadmium, and mercury (mercury has two chlorides) as regards their solubility and the valence of the metal.

13. In which of their compounds do zinc, cadmium, and mercury most resemble each other, and thus justify their position in the same family in the periodic classification?

14. In what important respects do these metals differ from the alkaline earth metals which form the other family in the second group of the elements?

ELEMENTS OF GROUP IV

19. STANNOUS CHLORIDE ($SnCl_2.2H_2O$)

This salt can be prepared by the action of hydrochloric acid upon metallic tin. Since, however, the action would be exceedingly slow, it may be hastened by the addition of a very small quantity of nitric acid, which will oxidize 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 will be 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, under the influence of the oxygen of the air, oxidized quite readily to stannic; to prevent this happening during the evaporation of the solution, an excess of metallic tin is kept in the liquid.

Procedure. — Place 100 grams of feathered tin in a large casserole, cover with 175 cc. of concentrated hydrochloric acid (sp. gr. 1.2), and add (at the hood) 25 cc. of dilute nitric acid (sp. gr. 1.2), 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. Cool to 70°, add 15 cc. of concentrated hydrochloric acid to the solution, and if necessary a little water to keep any salt from crystallizing during the filtration. (The specific gravity of the liquid should be about 1.90 — measured hot — at this point.) Filter before the liquid cools, using a Witt filter in which a felt made of asbestos fibers (Instructions) is used instead of a disk of filter paper. Evaporate the filtrate in a 6-inch evaporating dish over a very small flame, not allowing the temperature at any time to rise above 70°, until the specific gravity of the liquid (measured hot) is 2.00. Set aside to crystallize over night in as cool a place as possible. Collect the crystals on a Witt filter (using a paper disk), dry them on a porous plate, and evaporate the mother liquor at 70° to obtain a second crop of crystals after the same manner as the first.

NOTE. — The product should be obtained in the form of a pure white crystalline meal. Great care must be observed not to allow the temperature to rise above 70° during the final concentration, nor to carry it further than to a specific gravity of 2.00. Otherwise difficulty will be experienced in obtaining a satisfactory crystallization. The salt is much less soluble at 0° than at room temperature, hence the crystallization should take place at as low a temperature as possible.

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.

Experiment. — 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 will, if it occurs, indicate the presence of ammonium salt, and why?

2. *Experiment.* — 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. *Experiment.* — To a cold solution of stannous chloride add sodium hydroxide until it has redissolved the precipitate first formed. Write the reaction. Save the solution.

4. *Experiment.* — Heat one-half of the solution saved from Experiment 3 for a few minutes. Pour the other half over a little bismuth hydroxide on a filter paper. (The latter can be precipitated for the occasion.) Explain the action in both cases, and compare it with the action of stannous chloride on mercuric chloride. (See Experiment 2 under Mercuric Nitrate.)

5. In preparing a solution of stannous chloride for a laboratory reagent, what is the necessity of adding free hydrochloric acid and of placing a piece of metallic tin in the bottle?

20. 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, and also, since it absorbs heat by its volatilization, it prevents the temperature from rising too high. 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.

Procedure. — Stannous Sulphide. Dissolve 50 grams of commercial stannous chloride in 1.5 liters of hot water in a 2-liter bottle, acidulating sufficiently with hydrochloric acid to prevent the precipitation of a basic salt (about 15 cc. of acid of 1.12 sp. gr.). Pass hydrogen sulphide into the solution until all the tin has been precipitated as stannous sulphide. Wash the precipitate free from acid by allowing to settle and draining off the clear liquid several times. Then dry the wet precipitate in a dish on the steam table, and powder the product.

Stannic Sulphide. — Grind together thoroughly 20 grams of the stannous sulphide just prepared, 10 grams of sulphur, and 8 grams of ammonium chloride. Bring the mixture into a small flask and place it on a sand bath, forcing it down as much as possible into the sand. Cover the mouth of the flask with an inverted test tube or small beaker, and protect the sides with asbestos paper. Heat the sand bath for 2 hours, at first rather moderately, and finally so that the bottom of the iron pan is a bright red in the center. Cool, break the flask, and preserve the layer of stannic sulphide which is found at the bottom.

Questions

1. *Experiment.* — Prepare a little stannic sulphide by precipitation with hydrogen sulphide from a solution of stannic chloride. Compare this with the stannic sulphide prepared above as regards its solubility in hydrochloric acid.

21. STANNIC CHLORIDE (ANHYDROUS)

Anhydrous stannic chloride, $SnCl_4$, is a mobile and volatile colorless liquid with a boiling point at 114°. It fumes very strongly in the air; with water in moderate amount it forms crystalline compounds, but with more water it dissolves to a clear solution. It is prepared by the action of dry chlorine gas upon metallic tin.

Apparatus. — This preparation is only to be attempted if four consecutive hours are available in the laboratory, and even then, the apparatus should be assembled as much as possible at a previous exercise.

Arrange a chlorine generator, the gas from which 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 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, but do not allow this action to become too violent. 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 a flask whose neck has been drawn down so that it can be readily sealed off. During the distillation the flask should not be open to the air, but should be connected by a tube to the absorbing bottles already used. When the liquid is all distilled, seal the neck of the flask 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. Compare the physical properties of the tetrachlorides of carbon, silicon, tin, and lead.

How do these substances behave in presence of water, and what information does this give as to the metallic character of the four elements?

22. 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 ($Pb(NO_3)_2$). In it lead appears in its usual state of oxidation, which corresponds to that of the oxide PbO; indeed, the salt is actually prepared by treating this oxide (litharge) with nitric acid.

A saturated solution contains for each 100 grams of water the given number of grams of lead nitrate

Temperature	0°	10°	18°	25°	50°	100°
$Pb(NO_3)_2$	36	44	51	56	79	127

Procedure. — Take 100 grams of litharge. 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 which is thus formed. Proceed to prepare lead nitrate, striving to obtain good crystals of as large a size as possible.

23. LEAD DIOXIDE

(BY-PRODUCT: LEAD CHLORIDE)

As already stated, the most frequently occurring and the most stable compounds of lead are those derived from the oxide PbO. Under certain conditions, however, this oxide, or any salt derived from it, may be converted into the higher oxide PbO_2. Thus if a solution of lead acetate is made strongly alkaline and is then treated with an oxidizing agent, such as chlorine, the dioxide results. On account of the disagreeableness of using chlorine gas in the laboratory, bleaching powder, which exerts practically the same oxidizing action, will be substituted for it. By the process outlined, however, it is not possible to oxidize the entire amount of the lead, but the precipitate obtained by using bleaching powder will contain both $Pb(OH)_2$ and $Pb(OH)_4$, as well as $Ca(OH)_2$. If the precipitate is treated with dilute nitric acid, all but the plumbic hydroxide will dissolve, and this when collected and dried yields the dioxide PbO_2. That part of the lead which is dissolved by the nitric acid may be saved as a by-product by causing it to form the nearly insoluble lead chloride.

Procedure. — Dissolve 100 grams of lead acetate in a common 2-liter bottle with 200 c.c. of hot water, and add 110 cc. of a 20 per cent. solution of sodium hydroxide. Rub up 60 grams of bleaching powder with a pestle with enough water to form a thin paste, stir it thoroughly into the solution in the bottle, and then bring the temperature up to 50° to 60° by setting in a pail of hot water, and keep it at this temperature several minutes while stirring. Fill the bottle to near the top with water, stir, and let settle. Draw off the clear liquid, stir up the mud in the bottom with fresh water, and repeat the operation until it is calculated that the mud remaining contains less than 1 per cent. of the soluble salts at first present. Then add to it 150 cc. of dilute nitric acid (sp. gr. 1.2). Remove to a porcelain dish, boil until the residue is deep brown or almost black, pour back into the bottle, and stir up with 1 liter of water. Let settle, draw off the clear liquid, which contains a considerable amount of lead nitrate, and preserve it. Again stir up the residue with 1 liter of water, let settle, and add the clear liquid to that already saved. Continue to wash the residue of lead dioxide in the same way until it is free from nitric acid, but discard the washings. Remove the wet lead dioxide to a dish and dry it on the steam table. Pulverize the lumps and preserve the product in the form of a powder.

To the 2 liters of washings saved as directed above, add 200 cc. of concentrated hydrochloric acid, cool the solution to about 10°, and collect the precipitated lead chloride on a Witt filter.

Questions

1. *Experiment.* — Add sodium hydroxide to a solution of a lead salt, and observe with what readiness the precipitate redissolves in an excess of the reagent.

Give reactions, and compare $Pb(OH)_2$ with $Al(OH)_3$ as regards the strength of their acidic properties.

2. Write the reaction between sodium plumbite and chlorine in the production of lead dioxide; between sodium plumbite and bleaching powder.

3. Show the relation among ortho-plumbic acid, meta-plumbic acid, and lead dioxide. Give the symbol of sodium meta-plumbate; of calcium ortho-plumbate.

4. In view of the following experiment, why could not lead dioxide have been prepared equally well by treating a solution of lead chloride, containing also free hydrochloric acid, with chlorine? *Experiment.* — Drop a grain of lead dioxide the size of a pinhead into $\frac{1}{2}$ cc. of hydrochloric acid, and warm until dissolved. What odor is observed? Cool the liquid and observe the character of the precipitate.

5. Compare the reaction of lead dioxide and of lead monoxide upon hydrochloric acid.

6. Compare the action of lead dioxide upon hydrochloric acid with that of manganese dioxide.

7. Why should not lead dioxide and manganese dioxide dissolve in nitric acid as well as in hydrochloric acid?

GENERAL QUESTIONS. IV

ELEMENTS OF THE FOURTH GROUP OF THE PERIODIC SYSTEM

1. Of the elements of the fourth group only four need be given especial consideration, namely, carbon, silicon, tin, and lead. Give the symbols of the dioxides of each

and state their most important physical properties. Which elements are base-forming and which acid-forming?

2. *Experiment.* — Add sodium hydroxide, at first slowly and finally in excess, to solutions of stannous chloride, stannic chloride, and lead acetate. Discuss the amphoteric character of $Sn(OH)_2$, $Sn(OH)_4$, and $Pb(OH)_2$.

3. *Experiment.* — Heat a small piece of tin in a casserole with some nitric acid. What is the body formed? Wash off the excess of nitric acid by decantation. Warm the white powder a few minutes with some sodium hydroxide solution. If it does not dissolve readily, how can you prove whether any has gone into solution? If any has, what is the soluble compound which it forms?

4. *Experiment.* — Prepare a little precipitated stannic sulphide. Treat portions of it with sodium sulphide and ammonium sulphide, respectively. What is the soluble compound formed, and what relation does it bear to the sodium stannate formed in 2 and 3?

5. By means of what oxidizing agents can a stannous compound be converted into a stannic? By what means can a stannic compound be reduced to a stannous?

6. Under what conditions can lead in the plumbous condition be oxidized to the plumbic condition? Is this as easily accomplished as with tin? Under what conditions does lead dioxide act as an oxidizing agent? (See Experiment 4 under Lead Dioxide.)

24. 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 phosphorus 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,

$$H_3PO_3 + 2AgNO_3 + H_2O = 2HNO_3 + 2Ag + H_3PO_4.$$

Procedure. — Place 275 cc. of nitric acid of sp. gr. 1.2 in a 2-liter, round-bottom flask. Weigh out 30 grams of red phosphorus, and at the hood add 10 grams to the nitric acid in the flask. Warm by placing the flask in a pail of hot water just until red vapors begin to appear; then stand the flask on a wooden ring, and place a large funnel in its neck to condense and allow to drip back at least a part of the vapors. After the action has nearly ceased, add a little more of the phosphorus and again wait until action has almost stopped, and so on until all of the phosphorus is used. When the action following the last addition of phosphorus has somewhat moderated, add 20 cc. of concentrated nitric acid (sp. gr. 1.42). Boil the solution in a casserole until it is considerably concentrated and a rather violent reaction is observed to take place with evolution of red fumes. When this action has ceased, the remaining solution is poured into a flask, diluted to about a liter with water, saturated with hydrogen sulphide gas, stoppered, and allowed to stand over night. If the next morning the contents of the flask smell strongly of hydrogen sulphide, the precipitate of arsenic sulphide is filtered off; if not, the solution is again treated with hydrogen sulphide in the same manner as before. Evaporate the filtrate until its temperature has risen to 125°. Test a few drops for phosphorous acid by diluting with a little water, adding some silver nitrate, and warming. If any is found add 20 cc. of nitric acid to the solution and warm it. Transfer the solution to a small casserole and evaporate it over a very 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 with silicic acid. Pour the liquid while still warm into a previously weighed small glass-stoppered bottle, and stopper it tightly. When cool introduce a small crystal of phosphoric acid to induce crystallization of the mass.

NOTE. — If no crystallized phosphoric acid is obtainable the sirupy acid obtained above can be made to crystallize spontaneously if it is placed in a vacuum desiccator over concentrated sulphuric acid and allowed to remain for a considerable time.

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 symbols. Why cannot the anhydride be prepared by heating orthophosphoric acid? For what practical purpose is phosphoric anhydride used?

3. Compare the acid strength of phosphoric acid with that of other common acids. Do all three hydrogen ions dissociate with equal readiness?

4. Give the symbols 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 is added to a solution of phosphoric acid or a phosphate, which is made strongly ammoniacal. This precipitate constitutes one of the most important tests for phosphoric acid.

6. Give an example of how phosphorous acid may behave as a reducing agent.

25. ARSENIC ACID $(H_3AsO_4)_2.H_2O$

Arsenic acid in its properties shows a striking similarity to phosphoric acid; and even the method of its preparation is similar, in that use is made of the oxidizing action of nitric acid. Instead of starting with uncombined arsenic, however, use is made of arsenious oxide, As_2O_3, a product which condenses in the flues wherever ores which contain arsenic are roasted. By the nitric acid this is oxidized to the higher oxide, As_2O_5, which, with water, yields arsenic acid, H_3AsO_4. From the salts which arsenic acid forms, it is known to be, like phosphoric acid, a tribasic acid, that is, one which yields three hydrogen ions; yet on crystallizing, two molecules of this arsenic acid take on one additional molecule of water to give $(H_3AsO_4)_2H_2O$.

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 concentrated nitric acid; warm sufficiently to keep up a vigorous but not violent action until red fumes cease coming off, and finally evaporate, holding the casserole in the hand and rotating it all the while until the residue is just dry. When cool enough add 60 cc. of water, and heat until the residue is completely dissolved.[1] Evaporate until the liquid is of a thin, sirupy consistency while hot (until its volume is 34 to 36 cc.). Place in a small beaker and cool to room temperature. Drop a small crystal of arsenic acid into the solution, and crystallization should proceed quite rapidly. Break up the mass of crystals; place the moist product in a closed vessel which contains some calcium chloride and let it remain until the adhering liquid has evaporated; then preserve in a tightly stoppered bottle.

Questions

1. Give the reaction of nitric acid upon arsenious oxide.

2. Compare the strength of arsenic acid with that of phosphoric acid; with that of arsenious acid.

3. *Experiment.* — To a solution of arsenic acid (0.1 gram in 10 cc. of water) add magnesium chloride and then ammonia until strongly alkaline. Compare with 5 under Phosphoric Acid.

4. *Experiment.* — Add a little potassium iodide solution to some arsenic acid solution, and warm gently. Is iodine set free? Give the reaction.

Prepare a faintly alkaline solution of arsenious acid as

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[1] If complete solution does not take place after heating for some minutes, either the oxidation of the arsenious oxide has not been complete or else the residue has been heated too strongly. Test for arsenious acid according to the directions in Experiment 5. If any is found it must be oxidized by the addition of more nitric acid, and the liquid must again be evaporated to dryness.

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 reaction. It is, so far as the state of oxidation of the arsenic is concerned, 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.

5. *Experiment.* — Test for arsenious acid in your preparation: Dissolve a small crystal of the arsenic acid in a few centimeters of water; add sodium bicarbonate until no more effervescence occurs, and then a considerable quantity in addition. 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 which was in the sample.

26. ANTIMONY TRICHLORIDE FROM STIBNITE

(BY-PRODUCT: ANTIMONY OXYCHLORIDE)

Native antimony sulphide (stibnite) dissolves quite readily in hydrochloric acid, yielding antimony trichloride,

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S,$$

although towards the end the reaction may be hastened by the addition of a very little potassium chlorate.

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.

The salt antimony trichloride hydrolyzes with a moderate amount of water, giving a precipitate according to the reactions,

$$SbCl_3 + 2H_2O = SbCl(OH)_2 + 2HCl,$$
$$SbCl(OH)_2 = SbOCl + H_2O;$$

with more water a further hydrolysis takes place:

$$4SbOCl + H_2O = Sb_4O_5Cl_2 + 2HCl.$$

The product obtained in this preparation by mixing the next to the last distillates with a considerable amount of water has the latter composition. This compound, however, if repeatedly boiled with fresh portions of water may be made to undergo complete hydrolysis, leaving finally only Sb_2O_3.

Procedure. — Treat 150 grams of powdered stibnite in an 8-inch dish at the hood with 750 cc. of commercial hydrochloric acid (sp. gr. 1.2), heating gradually, and keeping at the boiling temperature for 20 minutes, when the flame may be removed and 5 grams of potassium chlorate added, a small crystal at a time. Finally, heat for 5 minutes more. Pour the solution through a filter of asbestos felt, rinsing the residue on to the filter with a few cubic centimeters additional of hydrochloric acid and draining it with suction. 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. 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 used 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 without 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, and draw off as much of the water as possible. Drain the precipitate on a Witt filter, and spread it on an unglazed plate to dry.

Questions

1. *Experiment.* — Prepare a solution of antimony trichloride. How can the formation of a precipitate be avoided? Pass hydrogen sulphide into this solution. What is the precipitate? How could it be converted into a product like stibnite?

2. How would the reactions of phosphorus and arsenic trichlorides with water differ from that of antimony trichloride? Is hydrolysis more or less complete in these cases? Why, then, is there no precipitate?

27. SODIUM SULPHANTIMONATE $Na_3SbS_4 \cdot 9H_2O$

The oxides of arsenic and antimony, and more particularly the higher oxides, are acidic in nature; thus with basic oxides they will form salts:

$$3Na_2O + As_2O_3 = 2Na_3AsO_3;$$
$$3Na_2O + As_2O_5 = 2Na_3AsO_4.$$

Sulphur, in accord with its similarity to oxygen, can be substituted for 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 "sulph" or "sulpho" is inserted. Thus sulpho-salts are produced in the same manner as the oxy-salts above:

$$3Na_2S + As_2S_3 = 2Na_3AsS_3;$$
$$3Na_2S + As_2S_5 = 2Na_3AsS_4.$$

The sulpho-salts of arsenic, antimony, and stannic tin are particularly characteristic of these metals. They are easily produced, and all are soluble. They are stable in neutral or basic solutions, but are decomposed by acids, because the anions of the salts combine with hydrogen ions to produce the very weak sulpho-acids, which, being unstable, decompose at once into the sulphides of the metals and hydrogen sulphide:

$$6H^+ + 2AsS_3^{---} \rightarrow 2H_3AsS_3 \rightarrow 3H_2S + \mathbf{As_2S_3};$$
$$6H^+ + 2AsS_4^{---} \rightarrow 2H_3AsS_4 \rightarrow 3H_2S + \mathbf{As_2S_5}.$$

Sodium sulphantimonate can be prepared from stibnite by the combined action of a solution of sodium sulphide and sulphur:

$$2S + Sb_2S_3 \rightarrow Sb_2S_5;$$
$$3Na_2S + Sb_2S_5 \rightarrow 2Na_3SbS_4,$$

and it crystallizes well with nine molecules of water.

Procedure.—To 50 grams of stibnite, 107 grams of crystallized sodium sulphide ($Na_2S.9H_2O$), and 10 grams of sulphur in a porcelain dish add 100 cc. of water; bring to a boil, and keep at the boiling temperature for $\frac{3}{4}$ of an hour. Filter and rinse the residue in the dish and on the filter with hot water, bringing up the volume of the solution to 200 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. Spread the crystals on a porous plate, and stopper them tightly as soon as dry.

Questions

1. *Experiment.* — Prepare a little precipitated antimonous sulphide. How? Treat this precipitate with a solution of ammonium polysulphide, $(NH_4)_2S_x$. Discuss, with reactions, the nature of the soluble compound produced. Finally, acidify the solution with hydrochloric acid. What is the reaction?

28. 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.

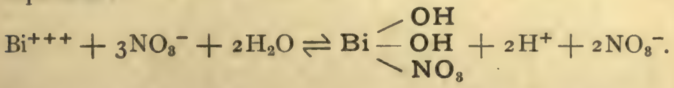
Procedure. — Dissolve 40 grams of the sodium sulphantimonate obtained in the last preparation, and dilute with 1 liter of cold water. Mix 15 cc. of concentrated sulphuric acid with 350 cc. of water, cool, and place in a 2-liter, or, better, a 3 or 4-liter common bottle. To this add slowly, and with constant 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 and draw off as much as possible of the clear liquid. Pour the gelatinous precipitate on a Witt filter. Since it will take a long time to suck out the water, it will not be desirable to keep connected constantly with the pump; but a vacuum can be once produced, and then, by closing the rubber tube with a screw cock, maintained in the flask over night. When no more water can be sucked out of the precipitate, spread the pasty mass on an unglazed plate, place it on a shelf above the steam table where the temperature will not rise above 50°, and leave, with occasional stirring, until entirely dry. Reduce to a fine powder in a mortar and preserve.

Questions

1. Write all the reactions involved in the preparation of antimony pentasulphide from stibnite.

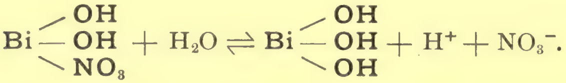
29. BISMUTH BASIC NITRATE (BISMUTH SUBNITRATE)

Although 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 of water to produce hydrolysis increases, and the basic salt of bismuth, which is only slightly soluble, separates:



$$Bi^{+++} + 3NO_3^- + 2H_2O \rightleftharpoons Bi\begin{cases} OH \\ OH \\ NO_3 \end{cases} + 2H^+ + 2NO_3^-.$$

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 about $\frac{1}{2}$ 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:



$$\mathrm{Bi}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{NO_3}\end{matrix} + H_2O \rightleftharpoons \mathrm{Bi}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{matrix} + H^+ + NO_3^-.$$

Under the conditions given 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.

Procedure. — Dissolve without heating 40 grams of crystallized bismuth nitrate, $Bi(NO_3)_3.5H_2O$, in 10 cc. of nitric acid (sp. gr. 1.2) 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.

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.

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.

GENERAL QUESTIONS. V

ELEMENTS OF THE FIFTH GROUP OF THE PERIODIC SYSTEM

1. Of Group V only those elements falling in the right-hand subcolumn need especial consideration, namely, nitrogen, phosphorus, arsenic, antimony, and bismuth. In this series we pass by a very perfect gradation from nitrogen, a pronounced non-metal, to bismuth, a quite pronounced metal. Compare the strength of the acids formed from the pentoxides, R_2O_5, of this series; from the trioxides, R_2O_3; of the bases from the trioxides of the last three.

2. Name the simplest hydrogen compound of each of the first four elements. 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. What is the behavior of the trichlorides of phosphorus, arsenic, antimony, and bismuth when treated with water? Show how this corresponds with the increasing metallic properties of the elements.

4. Describe the sulphides of arsenic, antimony, and bismuth which can be obtained by precipitation. Which of them will dissolve in ammonium polysulphide? Write the reaction between arsenious sulphide and ammonium polysulphide; between the resulting solution and hydrochloric acid.

HEAVY METALS OF GROUPS VI, VII, AND VIII

30. POTASSIUM BICHROMATE FROM CHROMITE

The most important source of chromium is the mineral chromite, $FeO.Cr_2O_3$ or $Fe(CrO_2)_2$. This substance, as indicated by the formula, may be regarded as a mixture 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 accomplished is by treatment at a high temperature with an alkali and an oxidizing agent. By this treatment the iron of the chromite is 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 (for example, K_2CrO_4).

In the commercial method for manufacturing chromates, atmospheric oxygen is utilized as 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 thus from other salts in the solution. Potassium bichromate, however, is much less soluble, and if this is formed by adding a sufficient amount of sulphuric acid,

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O,$$

it can be 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, however, 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 bichromate which, especially in the presence of the large amount of the other salt with the K^+-ion in common, can be very readily 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
$K_2Cr_2O_7$	5	7	12	20	26	35	55	88

Procedure. — Mix 40 grams of finely powdered chromite with 100 grams of potassium carbonate and 30 grams of potassium nitrate. Place the mixture in a cast-iron crucible, which it must on no account fill more than two-thirds full, else when melted it will run over. Heat in a gas furnace to a white heat (but using care not to reach the very highest heat, which might melt the crucible) until the melted charge has ceased to effervesce. Pour the molten mass out onto a dry[1] 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 bichromate from the mother liquor. Purify the product by recrystallization.

Questions

1. Mention at least three oxidizing agents which might have been used instead of potassium nitrate in this preparation.

2. How might the oxidation of chromic hydroxide, $Cr(OH)_3$, be accomplished in the wet way? *Experiment.* — To 5 cc. of a cold solution of a chromic salt add about 1 gram of sodium peroxide, agitate for a few moments, and then warm until effervescence ceases. Formulate the equations for the intermediate reactions in such a way as to show the state of oxidation of chromium in each compound involved, and then add the separate equations to give one for the complete reaction.

3. *Experiment.* — To a solution of potassium bichromate add potassium carbonate until no more effervescence occurs. Observe and explain any change in color. To a solution of potassium chromate add an acid and observe as

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[1] See footnote, page 33.

before. Explain fully the relation between chromates and bichromates.

31. CHROMIC ANHYDRIDE FROM POTASSIUM BICHROMATE

If a solution of potassium bichromate, $K_2Cr_2O_7$, is treated with a strong acid, such as sulphuric acid, bichromic acid, $H_2Cr_2O_7$, is thereby produced. The affinity of CrO_3 for water is not great (very much smaller than that of SO_3), and, in consequence, the dehydration of $H_2Cr_2O_7$ is very easy to accomplish; in fact, it seems very probable that in a solution containing a considerable amount of sulphuric acid a large part of the chromic acid already has changed into the form of CrO_3.

A solution, then, which is obtained by adding sulphuric acid to potassium bichromate will contain the following components: chromic acid, which, in consequence of the rather weak affinity of CrO_3 for water, may exist in the forms H_2CrO_4, $H_2Cr_2O_7$, and CrO_3; potassium acid sulphate, $KHSO_4$; and excess of sulphuric acid. If this solution is evaporated, the least soluble constituent will crystallize out first; but whether chromic anhydride or potassium acid sulphate will be the least soluble depends upon the amount of sulphuric acid present. If a large amount of sulphuric acid is added, chromic anhydride can be precipitated, but it is difficult to get it unmixed with a considerable amount of potassium acid sulphate. Thus it is better to regulate the amount of sulphuric acid so as to precipitate the greater part of the potassium salt first, then upon addition of more sulphuric acid to the filtrate the chromic anhydride can be precipitated nearly pure.

Procedure. — Cover 100 grams of potassium bichromate with 167 cc. of water; add 140 cc. of concentrated sulphuric acid; stir until the salt is dissolved and allow it to stand over night. Filter, using a large funnel with a small, perforated porcelain plate. Rinse the crystals of acid potassium sulphate with 5 cc. of water, adding the washings to the filtrate. Heat the filtrate in an 8-inch evaporating dish to 90°, and add cautiously, with constant stirring, 50 cc. of concentrated sulphuric acid. This will cause the rapid precipitation of chromic anhydride in very minute crystals which could not be filtered off. Add hot water until the precipitate just redissolves, and then evaporate until a film of crystals forms on the surface of the liquid. Cover and allow to stand over night. Collect the crystals on a perforated plate as above. Recover another crop of crystals from the mother liquor and add them to the first crop. Wash the crystals with 20 cc. of concentrated nitric acid, using small portions at a time. Drain with suction. Transfer to a porcelain dish and heat gently, with continuous stirring, until the crystals are dry and the odor of nitric acid can no longer be detected.

Questions

1. When chromic anhydride is dissolved in water, what components are produced in the solution? What salt is precipitated if lead acetate or barium acetate is added to this solution? Why is it not the bichromate which is obtained?

2. *Experiment.* — Heat a little chromic anhydride strongly on a bit of porcelain. What color change occurs? (The color of the product can be better observed if a particle is pulverized in a white mortar.) Is the product soluble in water? In hydrochloric acid? What relation does it bear to the mineral chromite?

32. CHROMIC ALUM

The preparation of potassium bichromate 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, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, 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, as already stated, very resistant to the action of acids. It yields only to the action of powerful oxidizing agents, which convert it into a chromate, and therefore potassium, or sodium, bichromates 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 bichromate it is necessary to reduce the chromium to the same 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, a body 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 noncrystallizable body. This green body 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 $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ will dissolve in 100 grams of water, and the solubility increases very rapidly with the temperature.

Procedure. — Pulverize 100 grams of potassium bichromate, and cover it in an 8-inch evaporating dish with 400 cc. of water. Add 78 cc. of concentrated sulphuric acid, and stir until the bichromate is all dissolved. Place the dish in a pan of ice water and cool to below 30°. Then add alcohol, not more than 1 to 2 cc. at a time, stirring with the stem of a thermometer between each addition, until the temperature has stopped rising, and keeping all the time well below 50°. If the temperature should start to rise rapidly, due to too large an addition of alcohol, and get above 50°, drop a piece of ice directly into the solution. When the last tinge of yellow has disappeared from the liquid and further addition of alcohol produces no heating, cool the solution to 0°, or let it stand over night, collect the crystal meal on a Witt filter, and suck it free 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 29). A saturated solution of this salt should be prepared at 35°. After freeing it of any undissolved particles of the crystal meal, warm it to 40°, and set it to crystallize, with the addition of about ten very small crystals to serve as nuclei. Dry the crystals obtained with filter paper, and stopper at once in a bottle, since they are quite efflorescent.

Questions

1. Formulate the equations for the separate reactions involved in the reduction of the bichromate, in such a way as to show the changes occurring in the state of oxidation of the chromium; but do not attempt to show what is produced by the oxidation of the alcohol.

2. Sulphur dioxide might serve as the reducing agent.

Give equations for the partial and complete reactions in this case.

3. Dissolve ½ gram of potassium bichromate in 10 cc. of water and add 10 cc. of dilute sulphuric acid. Heat to boiling, and pass in hydrogen sulphide until the color is changed completely to green. To what is the green color due? What is the precipitate? Formulate equations also for this reaction.

33. 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 Process, in which use is made of metallic aluminum as the reducing agent according to the reaction,

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr.$$

The heat produced by the oxidation of aluminum is so great that it is sufficient to effect the decomposition of the chromic oxide with still enough surplus heat to 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 Bunsen 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.

Procedure. — Mix thoroughly 300 grams of powdered chromic oxide and 100 grams of granulated aluminum (not the powder which is prepared for use as a pigment). Place the mixture in a Hessian crucible and pack it down firmly. Make a hole in the top of the charge 3 to 4 cm. deep, and fill it up with a fuse powder made from one part of granulated aluminum and ten parts of barium peroxide. Put some dry sand in the bottom of a pail; on this place the crucible and fill in around it with sand. Place the whole under the hood at a distance from any woodwork. Finally, heap up the fuse powder a little on top of the charge, insert in it a strip of magnesium ribbon, and when all is ready ignite the end of the ribbon with a Bunsen 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.

34. POTASSIUM PERMANGANATE FROM MANGANESE DIOXIDE

Manganese dioxide although under many conditions a powerful oxidizing agent, yet under certain conditions may itself be oxidized. Thus when melted with a basic flux it has a tendency to take on another atom of oxygen, and thus to form the trioxide, MnO_3. Since this trioxide is acidic it at once combines with the base to form a salt, and it is therefore evident why the oxidation should take place more readily in presence of a base.

The manganate thus formed can be dissolved in water, and is fairly stable in the solution so long as it contains also an excess of base. In presence, however, of an acid, even so weak an acid as carbonic acid, the salt is unstable and decomposes spontaneously, part of it going into a permanganate, the salt of the higher oxide of manganese, Mn_2O_7, at the expense of the other portion of the manganate, which is reduced again to manganese dioxide.

Thus the solution obtained from the fusion of manganese dioxide with the basic flux will hold in suspension, after the excess of base has been neutralized with carbon dioxide, a precipitate of MnO_2, besides any of the original MnO_2 not affected by the fusion. The precipitated manganese dioxide (or hydrated manganese dioxide, $MnO_2.2H_2O$) is very fine and of a colloidal nature, so that it will completely clog a filter; and therefore the only successful means of removing it from the solution is by sedimentation. The crystals of $KMnO_4$ obtained from the decanted liquid will be sure to contain appreciable amounts of manganese dioxide. Therefore the crystals first obtained must be purified by re-solution, filtration, and recrystallization.

Procedure. — Melt in a sheet-iron crucible 50 grams of potassium hydroxide and 25 grams of potassium chlorate; lower the flame and stir with an iron spatula, adding 50 grams finely powdered manganese dioxide. Heat again at a dull red heat, stirring until the mass has become dry and hard. Powder the substance after cooling, and bring it into a porcelain dish with 1¼ liters of hot water. Lead carbon dioxide into the boiling solution until a drop of it on a piece of white porcelain shows a clear red color. Decant the liquid into a tall beaker, leaving the heavier part of the sludge behind. Let settle for some time, and then very carefully, so as not to stir up the light precipitate, pour the liquid into a clean evaporating dish, and evaporate the solution until crystals will form quickly on cooling a few drops on a piece of cold porcelain. Let stand 24 hours, separate the crystals, and obtain another crop of crystals from the mother liquor.

Redissolve all the crystals in boiling water, filter through an asbestos filter and recrystallize, protecting carefully from the dust.

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? Reaction?

5. Does it frequently happen that, with an element which can exist in several states of oxidation, a compound derived from one oxide is stable in an alkaline solution but unstable in an acid solution, while in the latter solution the compound derived from another oxide is the stable one? What other preparation besides the present one illustrates this point?

35. 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 Exercise 33. 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_2O_3.

Procedure. — Place 1 kilogram of finely powdered pyrolusite in a Hessian 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 place it in a pail of sand, as in the preparation of chromium. 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 little fuse powder and a magnesium ribbon (see Chromium), 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?

36. FERROUS AMMONIUM SULPHATE

$FeSO_4.(NH_4)_2SO_4.6H_2O$

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, $FeSO_4.7H_2O$, 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 much less easily oxidized by contact with the air.

Procedure. — Prepare crystallized ferrous ammonium sulphate from equimolal quantities of crystallized ferrous sulphate and ammonium sulphate, using 70 grams of the former and 33 grams of the latter. Observe the same general directions as given for Copper and Ammonium Sulphate (page 39), but taking into account the solubilities given in the following table:

A saturated solution contains for each 100 grams of water the given number of grams of the anhydrous salt.

Temperature	0°	10°	20°	30°	40°	50°	70°	90°
$FeSO_4$	16	21	26	33	44	48	56	43
$(NH_4)_2SO_4$	71	73	75	78	81	84	92	99
$FeSO_4.(NH_4)_2SO_4$	12	17	22	28	33	40	52	. .

Questions

1. Dissolve a little of the preparation in water and test it with potassium ferrocyanide. If the precipitate is white or only a pale blue, of what does it consist? If it is deep blue, what is shown?

37. 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,

$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, 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.

Procedure. — Heat together 100 grams of crystallized ferrous sulphate, 100 cc. of water, and 12 cc. of concentrated sulphuric acid until the salt is dissolved. While the solution is boiling, add concentrated nitric acid, a little at a time, until the iron is completely oxidized to ferric sulphate and a few drops of the solution diluted with a few cubic centimeters of water give no blue precipitate with potassium ferricyanide. Evaporate the solution until it is thick and sticky and most of the excess of nitric acid has been driven off. Dissolve this in water, making up to a volume of 125 cc.; heat to boiling and add 25 grams of ammonium sulphate dissolved in 100 cc. of hot water. Allow the solution to cool slowly and crystallize. Collect the crystals in a funnel; wash with a very little water and allow to dry on an unglazed plate. Obtain a second crop of crystals from the mother liquor.

Questions

1. Write the reaction involved in 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?

2. Write the reaction involved in 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 ferrocya-

nide, potassium ferricyanide, and potassium sulphocyanate. Tabulate the results. These constitute the standard tests for ferrous and ferric salts.

GENERAL QUESTIONS. VI

HEAVY METALS OF THE SIXTH, SEVENTH, AND EIGHTH GROUPS OF THE PERIODIC SYSTEM

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. Give the symbols and names of salts derived from each of the three oxides of chromium, CrO, Cr_2O_3, CrO_3. Which is the most stable oxide, and which gives the most stable series of salts? In which of its compounds does chromium most resemble sulphur? iron and aluminum? nickel, cobalt, copper, and zinc?

3. Give the symbols 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?

4. *Experiment.* — Acidify a solution of potassium bichromate with sulphuric acid and treat with sulphur dioxide (sulphurous acid). Formulate equations for the separate parts of the reaction in such a way as to show the state of oxidation of chromium in each compound involved, and then add the separate equations to give one for the complete reaction.

5. *Experiment.* — Repeat Experiment 4, substituting potassium permanganate for potassium bichromate and hydrogen sulphide for sulphur dioxide and give reactions.

6. Write the reactions for the oxidation of a ferrous salt by (*a*) nitric acid; (*b*) bromine; (*c*) potassium permanganate. Write the reactions for the reduction of a ferric salt by (*d*) hydrogen sulphide; (*e*) sulphur dioxide; (*f*) stannous chloride.

7. Is it possible to prepare any compound of iron which corresponds to a chromate or a manganate? If so, how?

8. Explain the relation between a chromate and a bichromate. (See Experiment 3 under Potassium Bichromate.)