This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

[redacted]

Frank Peter Sheehan

William Potter

A LABORATORY MANUAL OF GENERAL CHEMISTRY

William Shakespeare

William Shakespeare

[redacted]

THE MACMILLAN COMPANY
NEW YORK · BOSTON · CHICAGO · DALLAS
ATLANTA · SAN FRANCISCO

MACMILLAN & CO., Limited
LONDON · BOMBAY · CALCUTTA
MELBOURNE

THE MACMILLAN CO. OF CANADA, Ltd.
TORONTO

[redacted]

A LABORATORY MANUAL

OF

GENERAL CHEMISTRY

BY

WILLIAM J.ay HALE
ASSOCIATE PROFESSOR OF GENERAL CHEMISTRY
IN THE UNIVERSITY OF MICHIGAN

New York
THE MACMILLAN COMPANY
1917

Set up and electrotyped. Published August, 1917.

Norwood Press
J. S. Cushing Co. — Berwick & Smith Co.
Norwood, Mass., U.S.A.

[redacted]

PREFACE

In experimental general chemistry we find but few laboratory manuals which make any pretense to a general systematic study of the elements. Whatever criticism they may have received must lie primarily in the lack of correlation of the experimental work, for the fact remains that modern chemistry demands a thorough and rigorous training in experimental general chemistry as a prerequisite for all other courses in the science.

The aim of this manual is to present experimental general chemistry in a complete and detailed form and at the same time to lay great emphasis upon the correlation of all results. The study of the metals, for example, has suffered lamentably by reason of this lack of correlation and otherwise unsatisfactory treatment accorded in our manuals. Though the detailed study of the metals seems to have been left largely to the subject of qualitative analysis, there certainly need be no barrier between that subject and general chemistry. As a matter of fact, the reactions which form the basis of group separations in the former are among the most elementary of those studied in the latter. The classification, for example, of sulphides, chlorides, and carbonates finds especial attention in the study of general chemistry. The application, therefore, of these elementary principles in the simple recognition of compounds even when mixed with other compounds, but in the absence of any complicating factors, should be made a necessary training in experimental general chemistry. Those characteristic reactions which serve to typify each of the analytical groups attain all the

[redacted]

greater importance when the student, through his study of the elements in their regular order as presented in the periodic system, gradually comes upon the means of effecting actual separations. Beyond the separation of metals into the main groups the elementary student need not proceed.

A special chapter has been introduced for the study of negative radicals. A differentiation is here made between the reactions of a few special reagents upon compounds before and after heating.

Finally, the highly objectionable method of recording in the laboratory those observations which are only to be transferred later to a "so-called" notebook is now eliminated. A student who but once engaged in this indefensible practice is far too prone in later years to record weighings and other data on scraps of paper. When such useless records seem to attain a reasonable degree of satisfaction to his untrained mind he may actually transfer them to a more desirable location, but neither to the credit of the location nor the student. This manual is so constructed that all questions under each heading are consecutively numbered. These same numbers appear also upon the opposite or blank pages and indicate positions for the records. Upon the form and accuracy of these records the student himself must expect the proper estimate of his scientific ability.

For the interest and care with which the manuscript has been read by Professor William G. Smeaton of this laboratory and for his many valuable suggestions the author wishes to express his gratitude and appreciation.

WILLIAM J. HALE.

ANN ARBOR,
July, 1917.

[redacted]

CONTENTS

GENERAL DIRECTIONS

EACH student should read these notes at the beginning of the course and constantly refer to them, especially when they are called into consideration in later experiments.

Note 1. Acids spilt upon the clothing should be neutralized at once with ammonium hydroxide solution and the spot then washed with warm water.

Note 2. Cuts must be washed well in running water, and then with hydrogen peroxide solution. Dress with gauze soaked in boric acid solution.

Note 3. Burns, caused by heat or by the action of corrosive chemicals, are to be covered with a paste of sodium hydrogen carbonate and water for a short time, and afterwards dressed with gauze soaked in boric acid solution, or a mixture made up of 40 parts phenol, 200 glycerol, and 800 water.

Note 4. The blank pages in this Manual serve for the record of all experiments. Whenever an italicized number occurs in the text this same number appears on the blank page opposite and indicates where the answer or observation must be entered. The italicized number itself may be looked upon as a question mark in that all of these numbers call for answers.

Note 5. The answers to all questions must be made as brief as possible. Each equation, when called for, should be written upon a single line. In all equations indicate the color and physical state of products found.

Note 6. Constant use of a text on General Inorganic Chemistry will be found necessary in framing the answers herein to be recorded. Where further reading is required of a student the letter R appears and carries with it a number which designates its order in the table inside of the rear cover of this volume. The pages, therefore, which are to be read, in any particular edition of the text adopted, must be given out by the instructor, and entered in order in the blank spaces by the student.

Note 7. All weighings excepting those marked [Balance] are to be made upon the rough laboratory scales. When the finer balance is to be used the experiment itself is marked [Quantitative] and the student, unless already provided, will need to draw from the dispensing stand or storeroom a set of weights for temporary use.

Note 8. The expression [Storeroom] indicates that the apparatus in question is to be drawn out on a temporary order.

Note 9. The expression [Hood] indicates that a particular operation is accompanied by dangerous fumes and must not be performed in the open laboratory but transferred to a position under a desk-ventilator or in a laboratory hood.

Note 10. The chemicals are distributed between two side-shelves and accordingly divided into two sets, one consisting of solids in small bottles and the other of liquids. Both are arranged alphabetically according to the scientific names.

Note 11. A few special chemicals which are to be procured of the instructor are marked [Special].

Note 12. In procuring chemicals from the side-shelves do not, under any conditions, remove the bottles to your desk. Take with you, instead, a watch glass for solids, or a test-tube for liquids, and convey these materials to your desk. Never take more than a gram or two of a solid or two or three cubic centimeters of a liquid unless otherwise specified. Do not return unused chemicals to the bottles, but throw them into the waste jars.

Note 13. Distilled water is to be employed in your wash bottles and for making solutions for all of the experiments.

Note 14. All students are to work independently excepting where otherwise directed.

Note 15. In the study of any particular reaction it is customary, first, to observe if the action proceeds in the cold (shaking when dealing with liquid mixtures, and rubbing when dealing with solids, will be found of service). If, however, no action occurs in the cold then the application of a gentle heat is tried.

Note 16. When heating a substance in a test-tube use a test-tube holder to support the tube, or, if this is not provided, use a strip of folded filter paper. (Wrap a piece of filter paper around a pencil, withdraw the pencil, and flatten out the cylinder of paper. Then fold the strip of paper once around the test-tube close to its mouth and clasp the two ends of the paper between thumb and forefinger, but close up to the test-tube itself.)

Note 17. Condensed moisture from an object heated in a test-tube is often likely to collect in droplets and run down the side of the tube and crack it. Always heat an object at first cautiously, and continually move the tube backward and forward over the flame during this heating. The walls of the tube thus become warmed and do not lend themselves well to the collection of moisture. If too great a quantity of water is given off it is often well to heat the tube while held in a horizontal position.

Note 18. Whenever a dropping funnel is required, and none is at hand, a substitute may be made by attaching a straight piece of glass tubing to an ordinary funnel by means of a short rubber tubing and placing a pinch clamp upon this rubber connection to regulate the flow of liquid from the funnel.

Note 19. In order to dry test-tubes and beakers quickly it is advisable to warm them slightly over a Bunsen flame and then blow air from the laboratory supply into the vessels, allowing the tube connected with this air supply to reach to the bottom of the vessels.

LABORATORY MANUAL

OF

GENERAL CHEMISTRY

CHAPTER I

MANIPULATION

CHECK the apparatus found in desk with reference to the list likewise provided. Record any missing articles upon a separate slip provided by instructor; then, after his approval, sign name and desk number upon slip and return it to the storeroom.

A list of apparatus supplied to the student, as well as special apparatus on hand in the storeroom, will be found in Appendix VII.

1. Bunsen Burner

a. Attach the Bunsen burner to a gas connection by means of a rubber tubing. Turn on the gas and light the burner with its air holes at base closed. Hold a cool porcelain dish in this luminous flame for a moment. The black deposit is carbon. Repeat, holding the dish about 5 cm. above the flame.

b. Gradually open the air holes at base of burner and observe the effect of intake of air upon the flame (*1*). Hold the cool porcelain dish in this nonluminous flame (*2*). To what does the luminous flame owe its luminosity (*3*)?

c. Study the structure of the nonluminous flame. By use of a platinum wire determine which regions are relatively hotter and which regions cooler. Insert one end (the lower) of a piece of glass tubing into the inner cone of the flame and test for the presence of unburnt gas in this region by applying a lighted match at the upper end of the glass tubing (*4*). Draw a diagram of flame, shading the hotter portions (*5*).

d. Procure from the side-shelf a very small quantity of borax (sodium tetraborate) and a few minute particles of manganese dioxide. Heat your platinum wire and insert the hot end into the borax, then bring this adhering borax into the nonluminous flame. The borax melts and loses water, assuming a spheroidal form. Now bring this hot borax bead in contact with one minute particle of manganese dioxide and again reheat in the hotter portions of the flame. Observe the color of bead when cold. Anything more than the merest trace of manganese dioxide will give an opaque bead, which is undesirable and therefore to be discarded (*6*).

e. Reduce the supply of air to the flame, by partially closing the air holes at base of burner, until a small luminous region appears at the tip of inner cone of unburnt gas. Now hold the colored borax bead steadily in this inner luminous region of the flame for five or six minutes. Withdraw and observe effect of this heating in presence of carbon (*7*).

This inner luminous region is termed the reducing flame. Reheat the borax bead in the outer edge, or oxidizing portion, of the same flame (*8*).

(*1*)
(*2*)
(*3*)

(*4*)
(*5*)

(*6*)

(*7*)

(*8*)

2. Glass Tubing. [Blast-Lamp Table]

a. Select a piece of wide soft-glass tubing and make a test-tube out of it.

b. Cut off 8–10 cm. of glass tubing by making a slight scratch upon the tubing with a triangular file. Hold the tubing in the two hands and apply pressure by the thumbs from beneath the scratch while at the same time each hand exerts a slight pulling force from each side of the scratch.

Fire-polish all edges of freshly cut tubing by heating these edges in the Bunsen flame to point of softening. The rough particles are thus fused together.

c. Bend a small piece of glass tubing by holding the tubing lengthwise in a flat luminous flame. Use here the fish-tail burner provided at the blast-lamp table or place a " wing-top " (if in desk outfit) upon your Bunsen burner and use the luminous flame thus spread out. Rotate the tubing continuously during this heating to secure uniform effect and, when sufficiently soft (but not before), remove the soot-covered tubing (still straight) from the flame and bend slowly through the desired angle.

d. For the sake of comparison attempt to bend a small piece of glass tubing by heating it in the nonluminous flame without rotating; bend while still in the flame.

e. Cut off a small piece from your glass tubing (8–10 cm. in length, the piece from *b* is serviceable) and soften it at the middle by heating in the hotter portions of the Bunsen flame. As in *c* the tubing must be rotated continuously and further it must be moved about in the flame more quickly in order to avoid overheating at any one point. When the middle portion of the tubing is sufficiently soft,

quickly remove the tubing from the flame and very gently pull the ends apart until the bore at center approaches capillary dimensions. When cool cut at center, fire-polish each end carefully, and reserve the two pieces for future use.

3. Wash Bottle

a. Select a cork such that the smaller end will just enter the 500 cc. flask or special bottle provided for this purpose. Soften the cork by rolling it between some hard object and the desk or floor. By means of a cork-borer (which should be slightly less in diameter than the tubing) bore two holes through the cork in lines parallel to the axis and possibly 0.5 cm. apart. To secure the best results hold the cork in the hand and bore carefully from the narrow end of the cork, rotating both cork and borer around their axes. Clean out the cork-borer by use of the rod provided, then by means of the round file smooth the holes in the cork and enlarge them, if necessary. Bend two pieces of glass tubing to accord with the forms indicated in Fig. 1; one piece to serve as inlet for air and the second as outlet for water. The upper end of the latter piece is connected to a nozzle such as was made in **2** *e*, by means of a short piece of rubber tubing. The edges of all the pieces of glass tubing should be fire-polished.

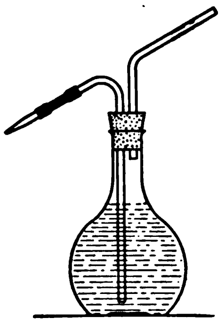


Fig. 1.

b. Test the wash bottle for air-tightness by placing in it sufficient water to cover the outlet tube. Close the inlet tube by a small cork or a piece of rubber tubing bearing a pinch clamp. Now blow a few bubbles of air through

the outlet tube to increase the pressure of the air in the flask. When the mouth is withdrawn, water will rise in this same outlet tube to some definite level. If the water in the tube gradually falls from this upper level to the level in the flask, the apparatus is not air-tight. If no defect can be found in such cases, it is better to select a new cork and bore it more carefully.

4. The Balance. [Consult Instructor]

a. A Balance must be used with the greatest care. When not in use the pans of the balance must be let down upon their supports. So, also, during the process of weighing, each addition or removal of a weight must be made when the pans are resting upon their supports. All objects to be weighed must first be carefully cleaned and dried. Chemicals are weighed only in properly selected and previously weighed beakers, watch-glasses, and similar vessels. The weights must not be handled by the fingers but only by use of the forceps provided in each box of weights. These weights are usually placed on the right-hand pan and the objects to be weighed on the left-hand pan. A check upon the result of any particular weighing is usually made by counting the value of the places made vacant in the box of weights and again by counting the value of the weights themselves upon the balance pan. The weighing thus checked is set down at once in the space reserved on the blank page of the Manual.

By means of the screw attachment in front of balance case raise the pans from their supports and allow the beam and pans to swing freely. Observe the pointer as it travels from side to side. When its swing is brought within the

field of division markings, count off the total divisions thus made in one full swing. Divide this number by two and count off this half value from either end of the pointer's swing, thus giving the true resting point or center of swing. This resting point may lie at the exact zero of the scale or slightly to its right (indicate here by the "+" sign in your weighings) or slightly to its left (indicate here by the "−" sign). This resting point, however, is never read by letting the pointer come to rest. It must always be determined while the beam is swinging freely and again determined for each weighing to be made.

b. Fit your burette with a small piece of rubber tubing (5 cm.) and a glass nozzle made as in **2** *e*. Place a pinch clamp upon the rubber tubing to regulate the withdrawal of liquid. Support the burette upon a ring-stand by means of a burette clamp. Fill the burette with distilled water, draw off a portion and insure the removal of any air from the rubber tubing and nozzle. Record the height of the water in the burette by reading on the scale the lower side of the meniscus (*1*). Now draw off in a carefully dried and weighed beaker (*2*) about 10 cc. of this water (*3*) and weigh again (*4*). Record these weighings and the volume readings in the places indicated on the page opposite, and calculate therefrom the weight of 1 cc. of water (*5*).

c. Into this weighed beaker from *b* (*4*), containing the water from the burette, pour about 10 cc. of water from a graduated cylinder (*6*) and again weigh (*7*). From the weighings and volumes here recorded calculate also the weight of 1 cc. of water (*8*). Which method of measuring volumes of liquids is more accurate (*9*)? The weight of 1 cc. of water at 4° is 1 gram.

Final reading of burette =
(*1*) Initial reading of burette =
(*3*) Vol. of water taken =

(*4*) Wt. of beaker + water =
(*2*) Wt. of dry beaker =
Wt. of water taken =
Vol. in cc. (water taken) : 1 cc. = wt. (water taken) :
(*5*) Wt. of 1 cc. water =

Initial reading of cylinder =
Final reading of cylinder =
(*6*) Vol. of water taken =

(*7*) Wt. of beaker + water + water from cylinder =
(*4*) Wt. of beaker + water =
Wt. of water taken from cylinder =
Vol. in cc. (water taken) : 1 cc. = wt. (water taken) :
(*8*) Wt. of 1 cc. of water =
(*9*)

CHAPTER II

MIXTURES AND COMPOUNDS

5. Iron and Sulphur

a. Components. Grind together in a mortar about 4 g. of sulphur and 6 g. of clean iron filings. Divide the mass into four portions, reserving one portion for use in *b.*

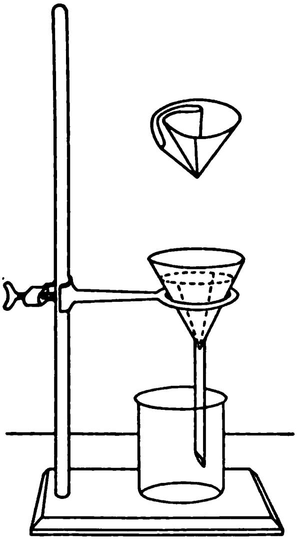


Fig. 2.

Upon one portion try the effect of a magnet (*1*).

Place the second portion in a test-tube and add 5 cc. of carbon disulphide. Shake and filter, collecting the clear filtrate in a small beaker or watch-glass and allowing it to evaporate spontaneously (Fig. 2). Do not bring the carbon disulphide near a flame, as it is readily inflammable (*2*).

Place the third portion in a test-tube and add about 10 cc. of dilute hydrochloric acid. What ingredient is seen to disappear (*3*)? What name is applied to these ingredients or parts of a mechanical mixture (*4*)?

b. Constituents. Heat the final portion of the mixture, prepared in *a*, in a small test-tube until the mass begins to

(1)

(2)

(3)

(4)

glow at the bottom. Remove the tube from the flame and observe the progress of this combustion. Is this an exothermal or endothermal reaction (*5*)?

When the action is over, strongly reheat the lower end of the test-tube for a few minutes or until that component (the sulphur), which was in excess of the amount required for the reaction, has been driven further up the tube. Why was sulphur taken in excess (*6*)? Now carefully break off the lower end of the cooled test-tube in your mortar. Discard all but the dark product and grind this latter to a powder. Divide into three portions.

Examine one portion with a magnet (*7*).

Place a second portion in a small test-tube, add a few cc. of carbon disulphide, shake and filter. Allow the filtrate to evaporate spontaneously. Is there a residue (*8*)?

Treat the last portion in a test-tube with a few cc. of dilute hydrochloric acid. Note odor (*9*).

Is there a residue left undissolved (*10*)?

The properties now identified are those of the compound — iron sulphide. Does this compound contain more or less chemical energy than the components from which it was made (*11*)?

What name do we apply to the elements which constitute a compound (*12*)?

6. Mercury and Sulphur

a. Mercuric Sulphide. Grind together in a mortar 1 to 1.5 g. of sulphur and a small globule of mercury not exceeding 0.3 cm. in diameter. Continue a vigorous grinding until no trace of the mercury can longer be observed. If this stage is not reached, a slight additional amount of sul-

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

phur should be added and the vigorous grinding continued. Is there a marked thermal change in the course of the reaction (*1*)?

Transfer the final product to a small dry test-tube and add 3 or 4 cc. of carbon disulphide to dissolve away the excess of sulphur in the mixture. Shake well (care being used to keep all flames away) and decant the carbon disulphide solution into a sink in the hood. Repeat this operation several times or until a few drops of the carbon disulphide solution fail to give a trace of sulphur upon spontaneous evaporation. Finally, by means of carbon disulphide, wash out upon a filter paper this insoluble product remaining in the test-tube. When dry divide it into two portions, reserving one portion for *b*.

Transfer one portion of the black product to a small, clean, dry test-tube and strongly heat it over the free flame. Note the odor at mouth of test-tube (*2*).

Examine the product condensing upon the walls of the test-tube by rubbing it with a glass rod (*3*).

The carbon disulphide removed all traces of free sulphur as a component in the original mixture. In what capacity must any remaining sulphur have served (*4*)?

The mortar is best cleaned by the use of a few drops each of concentrated hydrochloric acid and nitric acid.

b. Iron and Mercuric Sulphide. Place the second portion of the mercuric sulphide, prepared in *a*, in a small test-tube and add a pinch of powdered iron. Carefully heat the mixture and note if the reaction is exothermal (*5*).

What constituent of the mercuric sulphide is driven off (*6*)?

Do you detect any trace of the other constituent of mercuric sulphide in the free state (*7*)?

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

c

When the test-tube is cool, add a few drops of dilute hydrochloric acid; note the odor and compare this action with the result obtained in **5** *b* (*8*).

If the iron has replaced a constituent of mercuric sulphide, what compound is now present (*9*)?

7. Definite Proportions between Constituents of a Compound. [Quantitative] [Two Students Working Together]

a. Lead and Sulphur. Clean and dry two small porcelain crucibles and weigh them carefully [Balance]. Place about 2 g. of powdered lead in one crucible and about 3 g. in the other, and weigh the crucibles again, thus obtaining the weight of lead in each crucible. Now place each crucible, containing its known weight of lead, as recorded on opposite page, upon a clay triangle supported upon a ring-stand. Weigh out upon the laboratory scales two portions of sulphur, of approximately 1 g. each, and introduce one of these portions of sulphur into crucible designated as No. 1 and the second portion into crucible No. 2. By means of a small flame from a Bunsen burner, placed beneath each crucible, gently warm the crucibles till the sulphur melts and spreads throughout the mass; then increase the flame slowly till the mixture begins to glow, after which turn on the full flame and continue this heating until the excess of sulphur has been driven off (a point determined by the disappearance of burning sulphur and yellow vapors). Just as soon as this point is reached, remove both flames and allow the crucibles to cool. Owing to the tendency for lead sulphide to undergo further change when heated in contact with air, care must be used to discontinue the heating

(*8*)

(*9*)

		Crucible No. 1	Crucible No. 2
Wt. of crucible + lead	=		
Wt. of crucible alone	=		
Wt. of lead	=		
Wt. of crucible + lead sulphide	=		
Wt. of crucible	=		
Wt. of lead sulphide	=		
Wt. of lead sulphide	=		
Wt. of lead	=		
Wt. of sulphur	=		

Wt. lead sulphide : wt. sulphur = 100 : x

(*1*) Therefore: percentage sulphur = ______

(*2*)

Wt. of lead sulphide	=		
Wt. of sulphur	=		
Wt. of lead	=		

Wt. lead sulphide : wt. lead = 100 : x

(*3*) Therefore: percentage lead = ______

of the crucibles so soon as the last trace of free sulphur (excess) is removed.

Weigh and determine the weight of lead sulphide in each crucible. From the weights of lead and lead sulphide determine the amount of sulphur held in combination and calculate its percentage in each sample of lead sulphide. Compare the two percentage values thus obtained for sulphur in lead sulphide (*1*) (page 19).

What do these two percentage values for sulphur prove in regard to the proportions in which lead and sulphur are here combined (*2*) (page 19)?

The percentage values for lead in each sample of lead sulphide may likewise be used for the purpose of this comparison (*3*) (page 19).

[*Instructions:* In cleaning the crucibles any black spots adhering to the inside may be removed by the action of a drop or two of warm nitric acid.]

b. Copper and Sulphur. Substitute here finely powdered copper in place of the lead used in *a*, employing, however, somewhat more sulphur than in the preceding experiment. For 2 g. and 3 g. of copper use about 2 g. and 3 g. of sulphur, respectively. Proceed experimentally as in *a* and calculate the percentage of sulphur (or copper) in each sample of cuprous sulphide thus prepared. Finally relate these two percentage values for sulphur (*4*) or copper (*5*).

		Crucible No. 1	Crucible No. 2
Wt. of crucible + copper	=		
Wt. of crucible	=		
Weight of copper	=		
Wt. of crucible + copper sulphide	=		
Wt. of crucible	=		
Wt. of copper sulphide	=		
Wt. of copper sulphide	=		
Wt. of copper	=		
Wt. of sulphur	=		

Wt. copper sulphide : wt. sulphur = 100 : x

(*4*) Therefore : percentage sulphur = ____________

		Crucible No. 1	Crucible No. 2
Wt. of copper sulphide	=		
Wt. of sulphur	=		
Wt. of copper	=		

Wt. copper sulphide : wt. copper = 100 : x

(*5*) Therefore : percentage copper = ____________

CHAPTER III

OXYGEN

8. Detection

a. Heat about 1 g. of barium peroxide in a small test-tube and hold a glowing splint of pine wood in the mouth of the tube (see *Note* 17), (*1*).

Account for the difference in action of the glowing splint when in this gas and when in air; air is a mixture of four parts nitrogen (a gas which does not support this type of combustion) and one part oxygen (*2*).

b. Select a hard glass test-tube and place in it about 4 g. of powdered manganese dioxide (previously dried by warming it for a few minutes in a crucible over the free flame). Now heat the tube by means of a strong flame, using a blast-lamp if necessary, and apply the glowing splint test for the presence of oxygen (*3*).

c. Repeat *b*, using ferric oxide (*4*).

d. Catalysis. In a small test-tube, fixed in a vertical position upon a ring-stand by means of a burette clamp, heat a small quantity of potassium chlorate just to, and not beyond, its melting point and apply the glowing splint test. Care must be used to bring about the melting of the chlorate without overheating that part already melted (*5*).

Now heat the molten potassium chlorate slightly beyond its melting point and apply the glowing splint test (*6*).

Allow the molten mass to cool to point of solidification and then remelt, using care, as previously described, to avoid

(1)

(2)

(3)

(4)

(5)

(6)

overheating. Introduce into the molten mass a pinch of manganese dioxide and again apply the glowing splint test. (Ferric oxide may be substituted here for the manganese dioxide) (*7*).

Compare the effect of the manganese dioxide in this case with that of further application of heat as described in preceding paragraph (*8*).

What name is applied to substances which influence chemical reactions without themselves being affected by the reactions (*9*)?

Both manganese dioxide and ferric oxide are insoluble in water. How may we prove that the decomposition of potassium chlorate proceeded without the decomposition of the manganese dioxide or the ferric oxide (***10***)?

9. Laboratory Method of Preparation

Mix together in your mortar about 6 g. of potassium chlorate and 3 g. of powdered manganese dioxide (or ferric oxide) previously dried (see **8** *b*). Transfer this mixture to a hard glass test-tube and fit this tube with a one-hole cork and delivery tube, as shown in Fig. 3. Gently heat the lower end of the test-tube by means of a Bunsen burner, holding the burner in the hand and applying the heat to all parts of the tube adjacent to the mixture. The further end of the delivery tube is at first left immersed in the water of the pneumatic trough for a few minutes to insure the removal of air from the test-tube, and especially to indicate, through the escape of bubbles, how the operator may apply the heat and secure a uniform but not too rapid evolution of gas. After this the end of the delivery tube is brought under an inverted wide-mouthed bottle previously filled with water

(7)

(8)

(9)

(10)

and now resting upon the shelf of the pneumatic trough. The bubbles of oxygen will ascend into the bottle and completely displace the water. When thus filled with oxygen slide a glass plate close under the mouth of bottle and remove the closed bottle of gas from the trough, the plate now serving as a cover to the bottle. Fill in this manner three or four wide-mouthed bottles (250 cc.) with oxygen and reserve for 10.

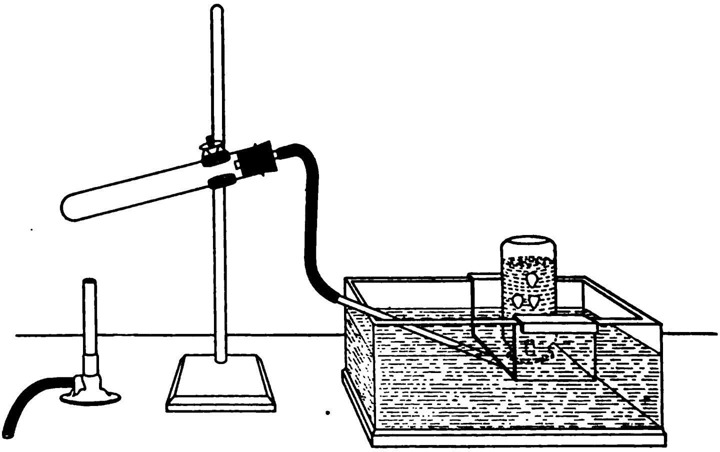


FIG. 3.

10. Properties of Oxygen

a. Insert a glowing splint of pine wood into one bottle of oxygen (*1*).

b. Into the second bottle lower a deflagrating spoon containing a pinch of sulphur previously ignited by a flame. Note odor (*2*).

(1)

(2)

c. Repeat *b*, substituting a pinch of red phosphorus for the sulphur and lowering this burning substance into the third bottle of oxygen. Of what does the smoke consist (*3*)?

d. Hold the base of your Bunsen burner in one hand and direct a small nonluminous flame downward nearly perpendicular to the top of desk. Hold a pinch of powdered iron between the fingers of the other hand and allow this substance to fall slowly into the flame (*4*).

Immediately open one of the bottles of oxygen and direct this downward-pointed flame into the mouth of the bottle. Now let a little powdered iron fall through the flame into the bottle (*5*).

Compare the two results thus obtained in low and high concentration of oxygen (*6*).

e. Into a small test-tube half filled with water drop a pinch of powdered iron; close the mouth of the tube with your thumb and invert the tube in a small beaker filled with water. Equalize the levels of water in tube and beaker and mark the height of the water in the tube by means of a label or rubber band. Set the beaker and tube aside for a day or two and again determine, by readjusting the levels of water, whether the iron (held afloat by absorbed air) has removed any oxygen from the inclosed volume of air (*7*).

Compare this result with that obtained in *d*, where the same elements unite at higher temperature and under change of concentration (*8*).

What name is usually applied to the yellow product into which the iron is converted and which slowly settles to the bottom of beaker (*9*)?

(3)

(4)

(5)

(6)

(7)

(8)

(9)

CHAPTER IV

HYDROGEN

11. Detection

[*Instructions:* In identifying the presence of hydrogen by the explosion of its mixture with air (oxygen) it must be remembered that the application of heat to the generating materials may liberate sufficient steam, or other vapors, which will displace the oxygen (*i.e.* the air) and thus interfere with the detection of hydrogen by the explosion method. When applying heat, therefore, it is well to remove the heat supply temporarily just before the tests are made.]

a. Displacement of Hydrogen from Water. Place a few cc. of water in a small test-tube and drop into the water a little metallic calcium (gran.). Apply a flame to the mouth of the tube (*1*).

Recall the action of sodium upon water [R. 1] and construct an equation for the reaction here between calcium and water (*2*).

b. Displacement of Hydrogen from Acids. Pour a few cc. of dilute sulphuric acid upon a few granules of zinc in a small test-tube. Apply a flame to the mouth of the tube (*3*).

Ascertain, by the application of heat to this tube, if the effervescence (the evolution of gas bubbles other than steam) from around the zinc is facilitated (*4*).

c. Effect of an Inactive Metal in the Presence of an Active Metal and an Acid. Into a test-tube containing a few granules of zinc and a few cc. of dilute sulphuric acid

(1)

(2)

(3)

(4)

let your platinum wire (with glass support) slide down so that the platinum wire now touches the zinc. What is the effect of this contact action upon the evolution of hydrogen (*5*)?

From what metal does hydrogen seem to come [R. 2] (*6*).

Remove the platinum wire and add a drop or two of cupric sulphate solution to the test-tube. The zinc will precipitate metallic copper from this salt in the form of a black deposit. What effect has this copper upon the interaction of zinc and the acid (*7*) ?

d. Influence of Physical State of Metal When Interacting with Acid. Place a little zinc dust in a small test-tube and add dilute sulphuric acid. Compare the action here with that in *b*, where granulated zinc was used (*8*).

e. Filter the contents of any one of the test-tubes in *b*, *c*, or *d* and evaporate the clear solution to dryness in a dish upon a sand-bath. What is the product (*9*) ?

Construct an equation to explain the formation of this product and hydrogen (*10*).

12. Comparison of Metals in Their Action upon Acids

Place a few small pieces of each one of the following eight metals in separate test-tubes: zinc (gran.), iron (pulv.), copper (disks), lead (pulv.), aluminium (gran.), magnesium (ribbon), tin (gran.), and antimony (pulv.). Dilute 20 cc. of concentrated hydrochloric acid, contained in your graduated cylinder, with an equal volume of water and pour about 5 cc. of this partially diluted acid into each test-tube. Apply a flame to the mouth of each test-tube for the detection of hydrogen. Observe the action of the acid upon these

(5)

(6)

(7)

(8)

(9)

(10)

D

[redacted]

several metals and, by a study of the effervescence, try to estimate the comparative rate at which hydrogen is evolved from this acid by the several metals. Arrange the metals in their order of decreasing activity, or ability to liberate hydrogen from acids (*1*). When hydrogen is not readily evolved in the cold, try the effect of heat, but bear in mind that steam and other vapors will now escape.

Construct equations for the reactions between hydrochloric acid and those metals which interact with it (*2*).

From this experiment what metals could you recommend as a substitute for copper in **11** *c* (*3*)?

13. Comparison of the Concentration of Acids in their Action upon Metals

a. Place a few cc. of concentrated sulphuric acid in a small test-tube and add a few granules of zinc. Compare this action with that in **11** *b*, where diluted acid was used (*1*).

What is the effect of heat upon this reaction (*2*)?

The identification of a gas by its odor may here be made [R. 3] (*3*).

b. Try also the effect of acetic acid upon zinc (gran.), both in the cold and when heated (*4*).

14. Laboratory Method for the Preparation of Hydrogen

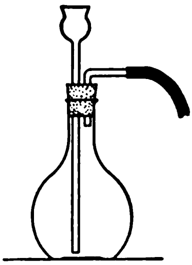


Fig. 4.

Arrange a hydrogen generator as shown in Fig. 4. A 125 cc. flask, or wide-mouthed bottle, is fitted with a two-hole cork, through which passes a safety tube, extending nearly to the bottom of the flask, and an exit tube fitted with

(*1*)

(*2*)

(*3*)

(*1*)

(*2*)

(*3*)

(*4*)

a short piece of rubber tubing. Place in the flask about 20 g. of commercial zinc (gran.) and add sufficient water to cover the bottom of the safety tube, then tightly adjust the cork and test for air-tightness as in **3** *b*. Why is commercial zinc more effective for this work than pure zinc (*1*)?

Now pour 30 to 40 cc. of dilute hydrochloric acid into the flask through the safety tube and test the issuing gas till it is found free from air.

[*Instructions:* The mixture of hydrogen with the air in the flask constitutes an explosive mixture, hence all flames must be removed from the neighborhood of the delivery tube. Collect samples of this gas from time to time by inserting the end of the delivery tube to the upper part of an inverted small test-tube, and gradually withdrawing this rubber delivery tube, thus filling the test-tube from the upper end downward to its mouth. Immediately close the mouth of the tube with the thumb and carry the closed tube (still mouth downward) to a flame and there, removing the thumb, ignite the gas at the mouth of the tube. As these tests are continued the loud reports at first are replaced finally by only slight explosions of the gases at the mouth of the tube, while the remaining gas in the test-tube burns quietly. When this stage is reached the apparatus may be considered free from air and three or four test-tubes of hydrogen are at once to be collected over the pneumatic trough and reserved for use in **15**. The apparatus is also ready for experiment **16** and after that **17**.]

15. Properties of Hydrogen

a. Bring one of the test-tubes of hydrogen, as provided in **14**, in touch mouth to mouth with a similar test-tube filled with air and show how it may be demonstrated that hydrogen is lighter than air (*1*).

b. Place an inverted test-tube of hydrogen (mouth downward) directly over and closely touching the mouth of a test-tube of air (mouth upward). Allow the two tubes to remain in this position for three or four minutes and then,

(*1*)

(*1*)

bringing both to a flame, test for the presence of hydrogen in each. Explain this from your study of diffusion among gases (*2*).

c. Holding the third test-tube of hydrogen mouth downward, slowly insert a lighted splint into the tube from below (*3*).

Is hydrogen a supporter of this combustion (*4*)?

16. Qualitative Synthesis of Water

Attach a nozzle to the open end of the rubber delivery tube of the hydrogen generator arranged in **14**. Press the end of this nozzle close against the inner walls of an inverted cold dry beaker. Account for the moisture here condensed from the unlighted gas (*1*).

Now detach the glass nozzle and, in its place, attach to the rubber delivery tube one arm of a U-tube previously filled with calcium chloride [R. 4]. To the other arm of the U-tube attach this same nozzle by means of a short piece of rubber tubing, thus bringing the U-tube between the nozzle and the hydrogen generator. Does the unlighted hydrogen, which now must pass through the U-tube, deposit moisture upon the walls of a cold dry beaker (*2*)?

What name is given to the action of calcium chloride (*3*)?

After a test has been made, as in **14**, to insure the absence of air from the gas issuing from the nozzle, ignite the hydrogen at the end of the nozzle and note the color of the flame at the moment of igniting the gas, and then later (*4*).

Hold an inverted cold dry beaker over this flame and account for the product observed (*5*).

(*2*)

(*3*)

(*4*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

[redacted]

[*Instructions:* The dry hydrogen as now delivered may be used directly in Experiment 17 unless there is another supply in the laboratory.]

17. Reduction by Means of Hydrogen

Fit each end of an open hard glass tube, 25 to 30 mm. long, with a one-hole cork bearing a short piece of glass tubing. Support this tube near one end on a ring-stand as shown in Fig. 5. Strongly heat over your Bunsen burner 1–2 g. of cupric oxide in a porcelain crucible to insure the removal of all traces of moisture. Then transfer this dried oxide to a porcelain boat and slide the boat with the oxide to the middle region of the hard glass tube. With the boat and corks in place connect one end of this tube to the laboratory supply of dry hydrogen by means of rubber tubing. If no such supply is at hand, use the hydrogen generator with the calcium chloride attachment as set up in **14**. After conducting a steady flow of the dry hydrogen through the tube for a few minutes, test the gas issuing from the further end of the tube (as in **14**) to make sure that all of the air has been driven out of the apparatus. Now apply the flame from a Bunsen burner directly under the middle portion of the tube. It is best to hold the burner in the hand and, at first, to heat the tube as gently as possible, waving the flame backward and forward beneath the boat. Later the highest heat of the burner is to be employed for three or four minutes. Do you observe any product of this reaction condensing in the cooler forward portion of the tube (*1*)?

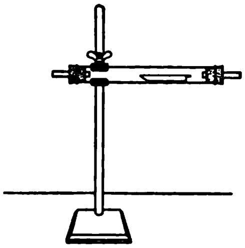


Fig. 5.

Judging by the color alone, what substance do you recognize in the boat (*2*)?

Construct an equation for this reaction between cupric oxide and hydrogen (*3*).

What name is given to this process of removing oxygen (*4*)?

How may we determine the weight of oxygen thus removed (*5*)?

How do you reconcile the action of steam upon red-hot copper (or iron) with the result here obtained [R. 5] (*6*)?

Repeat the experiment, replacing the cupric oxide with freshly heated (dried) aluminium oxide, and carefully observe all precautions as before. Do you detect any reaction in this case (*7*)?

Classify a few of the metallic oxides as to their action toward hydrogen (*8*).

What metallic oxides lose oxygen under the influence of heat alone (*9*)?

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

CHAPTER V

WATER

18. Distillation

a. [Two students working together.] Obtain from the storeroom a Liebig condenser, a 125 cc. distilling flask, and a thermometer. Arrange an apparatus as shown in Fig. 6, connecting the condenser by rubber tubing to the laboratory water supply so that cold water will pass into the outer jacket of the condenser, entering at the lower or cooler end, and passing out at the upper or warmer end. Fit the side-arm of the distilling flask into the upper or larger end of the condenser by means of a one-hole cork, and also by means of a tightly fitting one-hole cork suspend the ther-

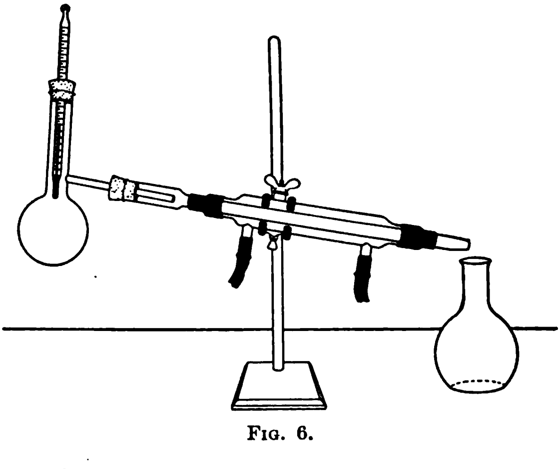


FIG. 6.

RECORD

mometer, free from contact with any part of the flask itself, in such a position that the bulb will come just below the exit tube (or side-arm). In this way almost the entire mass of mercury is kept constantly immersed in the distilling vapors. When the bulb is at a lower position the possibility of superheating interferes with the correct observation of boiling point.

Now place in the flask about 50 cc. of ordinary tap water and drop in also a crystal or two of some colored substance, such as potassium permanganate or potassium dichromate. Heat this water to boiling and continue till about 20 cc. of the distillate have been collected in a flask placed at the other end of the condenser. Does any of the colored substance pass over with the aqueous vapor (*1*)?

Note the boiling point of the water as recorded by the thermometer dipping into its vapor (*2*).

Account for variation between this value and 100° (*3*).

Is there a difference in appearance and taste between this distilled water and the ordinary water (*4*)?

b. Evaporate a few cc. of distilled water upon a clean watch-glass over a water-bath or sand-bath (*5*).

Repeat, using ordinary tap water (*6*).

What class of impurities will escape identification by this test (*7*)?

19. Filtration

a. Add a few cc. of a litmus solution to a test-tube half full of water. To the colored aqueous solution add a little powdered charcoal (about as much as could be placed on a dime) and heat the mixture to boiling. After a few minutes filter and explain the result (*1*).

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(1)

b. Repeat *a*, using 1 cc. of ammonium hydroxide solution in place of the colored litmus. Compare odor of solution before charcoal was added with the odor after filtration (*2*).

20. Chemical Action of Water

a. Test distilled water both with red and with blue litmus paper (*1*).

b. Place a pinch of calcium oxide (lime) in a test-tube, add a few cc. of distilled water, shake and test the solution with litmus paper (*2*).

c. Repeat *b*, using cupric oxide and water (*3*).

d. Ignite a piece of sulphur in a deflagrating spoon and lower the burning sulphur into a wide-mouthed bottle containing a little distilled water. After a few minutes remove the burning sulphur, close the bottle with the hand and shake, thus bringing the gaseous product in contact with the water. Now test this solution with litmus (*4*).

Classify these oxides as to their action upon water (*5*).

21. Water of Hydration

a. Select a few small crystals of barium chloride, potassium nitrate, sodium sulphate, potassium dichromate, and cupric sulphate, and warm each separately in a dry test-tube. Ascertain if moisture is driven off from these substances and is sufficiently indicative that the original substance contained water of hydration or crystallization (*1*).

Do you infer that all crystalline substances contain water of hydration (*2*)?

b. Place a little cupric sulphate (blue vitriol) in a porcelain crucible and heat gently over a Bunsen flame till only

(2)

(1)

(2)

(3)

(4)

(5)

(1)

(2)

E

the white anhydrous product remains. Remove one half of this product and dissolve it in just sufficient boiling water to effect complete solution, then set the tube aside for a day or two (*3*).

Allow the remaining portion to remain in the crucible exposed to the air of the laboratory for several hours (*4*).

c. Weigh a watch-glass upon the laboratory scales (*5*) and place in it a gram or two of cupric sulphate and weigh again (*6*). Allow the dish and its contents to stand exposed to the air of the laboratory for an hour or more and reweigh (*7*). Does the substance change in appearance and in water content (*8*)?

d. Repeat *c*, substituting sodium sulphate (Glauber's salt) for the cupric sulphate, and note change in appearance and water content (*9*).

What name is applied to this action (*10*)?

e. Repeat *c*, substituting calcium chloride for the cupric sulphate and noting results as before (*11*).

What name is applied to this action (*12*)?

f. Dip a splint of wood, or a match stick, into a solution of cobalt chloride and write with this solution upon a piece of white paper. When the writing is dry, warm the paper gently by holding it high over a Bunsen flame (*13*).

Now breathe upon the writing and explain (*14*).

g. Heat 1–2 g. of sodium chloride (salt) in a test-tube and note the decrepitation due to mechanically inclosed moisture. Does this substance contain water of hydration (*15*)?

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

CHAPTER VI

MOLECULAR WEIGHTS AND CHEMICAL FORMULÆ

22. Decomposition of Potassium Chlorate. [Quantitative]

[*Instructions:* If the percentage composition of potassium chlorate is not desired and **22** *b* is not to be performed, the student need not drive off the last traces of oxygen from the potassium chlorate, but may arrest the decomposition at any point desired. The data in **22** *a* may first be recorded at positions indicated by numbers in the text. The calculations, however, are to be made on page 55.]

a. Density and Molecular Weight of Oxygen. Arrange an apparatus as shown in Fig. 7. Use a 1-liter bottle (or your wash bottle if necessary) and through one of the two holes of a tightly fitting rubber stopper pass a piece of glass tubing such as serves for outlet tube in your wash bottle. Attach a piece of rubber tubing to the upper end of this glass tube and connect it with a glass nozzle which, in turn, should reach to the bottom of a large beaker of not less than 600 cc. capacity. A pinch clamp is placed on this rubber tubing. Through the second hole of the rubber stopper introduce a small piece of sharply bent glass tubing, and to

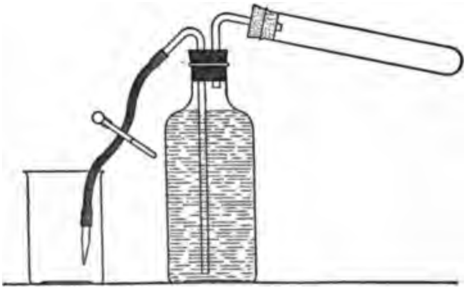


Fig. 7.

the further end of this fit a hard glass test-tube by means of a tightly fitting cork. When the apparatus is thus adjusted, fill the 1-liter bottle almost to the shoulder with water.

Powder about 2 g. of potassium chlorate and dry it for a few minutes in an oven (or by holding it in a watch-glass above a small Bunsen flame). Carefully weigh the hard glass test-tube [Balance] (*1*), and after placing in it a little less than 1.5 g. of the potassium chlorate weigh again (*2*). This hard glass test-tube, containing the known amount of potassium chlorate (*3*), is then carefully and tightly refitted to the cork on the short piece of glass tubing. Now place the beaker under the nozzle, open the clamp and blow air into the bottle through this nozzle; but before releasing the air pressure quickly close the clamp, drop the nozzle to the bottom of the beaker and then open the clamp. The increased pressure within the bottle will at once force water out through the long tube and nozzle and into the beaker. If, at this stage, the column of water is not held confined in the long outlet tube and nozzle, the apparatus is not air-tight and further operation must be delayed till the connections are reëxamined and made tight. Now raise the beaker (which should have sufficient water in it to cover the end of the nozzle) until the levels of water in beaker and bottle are the same, then close the clamp, remove the beaker, empty it and return it when dry to its proper position.

Finally open the clamp and decompose the potassium chlorate by a gentle heat. It is necessary here to move the flame backward and forward along the tube to insure slow and uniform decomposition. If the white smoke of solid particles, which forms over the molten mass, tends to escape

(*2*) Wt. of tube + potass. chlorate =
(*1*) Wt. of tube alone =
(*3*) Wt. of potass. chlorate =

(*2*) Wt. of tube + potass. chlorate =
(*13*) Wt. of tube + residue =
(*14*) Wt. of oxygen =

(*4*) Vol. of water in beaker (*i.e.* the vol. of oxygen evolved) =
(*5*) Temp. in laboratory =
(*7*) Temp. near barometer =

(*6*) Barometric reading =
(*8*) Correction for barometer at this temp. =
(*9*) Corrected barometric reading =
(*10*) Tension aq. vapor at temp. of laboratory =
(*11*) Partial pressure of the oxygen =

(*12*) Vol. oxygen at 0° and 760 mm. = x =
$x = (\quad)(\text{——})(\text{——})$

(*15*) Wt. of 1 liter of oxygen = x =
Vol. in cc. of oxygen found : 1000 cc. = wt. oxygen found : x

(*16*) Gram-molecular weight of oxygen = x =
Vol. in cc. oxygen found : 22,400 cc. = wt. oxygen found : x

(*17*) Percentage oxygen in potass. chlorate = x =
Wt. potass. chlorate : wt. oxygen found = 100 : x

from the tube check the heating until the particles have subsided. Gradually increase the heat as the reaction proceeds and continue until gas is no longer evolved, — a point determined when no additional water is driven over into the beaker. During this decomposition of the chlorate there is driven into the beaker a volume of water equal to that of the oxygen driven from the tube into the bottle. It is necessary, therefore, at all stages of the operation to keep the end of the nozzle under the surface of the water in the beaker, and also, when the action is over, to allow free communication between the water in the beaker and in the bottle (the pinch clamp therefore still open) until the gas and the water are approximately at the same temperature as the air in the laboratory.

When the apparatus has stood for a short time, raise the beaker till the levels of water in beaker and bottle are the same, close the clamp and remove the beaker with its water content. Measure the water now in the beaker by means of a graduated cylinder (*4*), and at the same time note the temperature of the laboratory (*5*) and also the barometric reading (*6*). Observe the temperature near the barometer (*7*) and, from Appendix I, find the correction (*8*) (in mm. of mercury) which must be subtracted from the barometric reading in order to obtain the corrected reading for a column of mercury at 0° (*9*). See Appendix II for the tension of aqueous vapor (in mm. of mercury) at the temperature of the laboratory (*10*) as recorded by thermometer [Storeroom], and subtract this from the corrected barometric reading to obtain the true or partial pressure of the oxygen (*11*). Reduce the observed volume of oxygen (*i.e.* the volume of water measured) to standard conditions, — 0° and 760 mm. [R. 6] (*12*).

RECORD

Now detach the hard glass test-tube with its final residue and weigh again (*13*). It is best to reheat this tube and its residue over the free flame until a constant weight is obtained (*13*). The weight of this volume of oxygen at 0° and 760 mm. (*14*) is represented by the difference in weight of the hard glass test-tube with its residue of potassium chloride (*13*) and its weight with the original quantity of potassium chlorate (*2*). The weight of one liter of oxygen at standard conditions may now easily be calculated (*15*).

Calculate the gram-molecular weight of oxygen, — *i.e.* the weight in grams of 22,400 cc. of oxygen at standard conditions (*16*).

From the weight of potassium chlorate taken (*3*) calculate also the percentage of oxygen present in this compound (*17*).

b. Formula of Potassium Chlorate. The ratio between the weights of potassium chloride (*18*) and oxygen (*14*) found in Experiment *a* will be in direct proportion to the formula-quantities of these substances in the compound potassium chlorate. With the assumption that potassium chloride has the formula KCl and, therefore, the molecular weight 74.6 (*i.e.* 39.1 + 35.5), we may calculate the formula-quantity of oxygen in the compound potassium chlorate (*19*). This formula-quantity will be a multiple of 16 (the atomic weight of oxygen) by some whole number, — a value (x) thus representing the number of atomic weights of oxygen associated with the formula-quantity KCl in the original molecular weight of $KClO_x$. The formula for potassium chlorate may now be written (*20*).

(***13***) Wt. of tube + potass. chloride =
(***1***) Wt. of tube =
(***18***) Wt. of potass. chloride =

(***19***) Formula-quantity of oxygen in chlorate = $x(16)$
Number of atomic weights of oxygen = x =
Wt. of potass. chloride : wt. of oxygen = $74.6 : x(16)$

(***20***) Formula of potass. chlorate = $KClO_x$ =

Write the equation for the decomposition of potassium chlorate into potassium chloride and oxygen (*21*).

c. Formula of Potassium Perchlorate. Weigh an open, hard glass test-tube [Balance] (*22*), place in it about 1 g. of potassium perchlorate and weigh again (*23*). Now heat this potassium perchlorate (*24*) very gently at first and thereafter more strongly, in the same manner as described for the decomposition of potassium chlorate in *a*. Cool and weigh the tube and its contents (*25*). It is well to reheat, cool, and reweigh to constant weight.

From the difference in weight between the tube containing potassium perchlorate and the same tube containing the residue of potassium chloride we find at once the weight of oxygen (*26*) that was associated with the residue of potassium chloride (*27*) in the form of a perchlorate.

Accepting the molecular weight of potassium chloride to be 74.6 (*i.e.* 39.1 + 35.5), we now calculate the formula-quantity of oxygen (*28*) in the compound potassium perchlorate. This formula-quantity will be a multiple of 16 (*i.e.* the atomic weight of oxygen) by some whole number, — a value which thus represents the number of atomic weights of oxygen (x) associated with the formula-quantity KCl in the original molecular weight of $KClO_x$, whose formula may now be written (*29*).

Write the equation for the decomposition of potassium perchlorate (*30*).

Compare the formula-quantity of oxygen in potassium perchlorate with the formula-quantity of oxygen found for potassium chlorate in *b*, and state how these values express the law of multiple proportions (*31*).

(*21*)

(*23*) Wt. of tube + potass. perchlorate =

(*22*) Wt. of tube =

(*24*) Wt. of potass. perchlorate =

(*23*) Wt. of tube + potass. perchlorate =

(*25*) Wt. of tube + potass. chloride =

(*26*) Wt. of oxygen =

(*25*) Wt. of tube + potass. chloride =

(*22*) Wt. of tube =

(*27*) Wt. of potass. chloride =

(*28*) Formula-quantity of oxygen in potass. perchlorate $= x(16)$

Number of atomic weights of oxygen $= x =$

Wt. potass. chloride : wt. oxygen $= 74.6 : x(16)$

(*29*) Formula of potass. perchlorate $= KClO_x =$

(*30*)

Form.-quant. oxygen $[x(16)]$ for potassium chlorate and perchlorate:

(*31*) $\left\{\begin{array}{l}\text{From } \mathbf{22}\,b \\ \\ \text{From } \mathbf{22}\,c\end{array}\right\}$ for one G.M.W. potass. chloride $\left\{\begin{array}{l} = \\ \\ = \end{array}\right.$

23. Composition and Formula of an Oxide of a Metal. [Quantitative]

[*Instructions:* Heated magnesium, when freely exposed to the oxygen of the air, burns most vigorously. The crucible cover retards the free access of air and thus permits slower combustion. A very small amount of nitrogen from the air will also unite with this heated magnesium [R. 7], but the error from this source is negligible in this experiment.]

a. Magnesium and Oxygen: Direct Oxidation in the Air. Clean and dry your porcelain crucible and cover; weigh them together [Balance] (*1*). Also clean a few strips of magnesium ribbon by rubbing the surface with a knife. Cut the magnesium, if necessary, into smaller pieces, 1 to 2 cm. in length, and place these small pieces in your crucible and weigh again the crucible with its cover (*2*). The weight of the magnesium (*3*) should not exceed 0.3–0.4 g. Now place the closed crucible and its contents upon a clay triangle over a Bunsen burner and apply at first a gentle heat. Gradually increase the flame until most of the magnesium is burnt to an oxide (an operation requiring 10 to 15 minutes). Now, by means of tongs, cautiously lift the cover about 1 cm. from the crucible and notice if any unburnt portion of the magnesium still glows; if so, replace the lid of the crucible and continue the heating till no further glow is detected upon a reëxamination. After this the highest heat of the flame is to be applied for a few minutes and the crucible then left to cool. Finally reweigh the crucible and its contents (*4*) and determine the weight of magnesium oxide (*5*). It is well to reheat, cool, and reweigh to constant weight.

Calculate the percentage of oxygen in the compound magnesium oxide (*6*).

(*2*) Wt. crucible + lid + magnesium =
(*1*) Wt. crucible + lid =
(*3*) Wt. magnesium =

(*4*) Wt. crucible + lid + magnesium oxide =
(*1*) Wt. crucible + lid =
(*5*) Wt. magnesium oxide =

(*5*) Wt. magnesium oxide =
(*3*) Wt. magnesium =
(*9*) Wt. oxygen =

(*6*) Wt. magnesium oxide : wt. oxygen = 100 :

Calculate the percentage of magnesium in the same compound (*7*).

If **7** *a* or **7** *b* were not performed, this experiment might be repeated, using a slightly different weight of magnesium, and the two sets of results compared. Will the percentage composition of this compound, as derived from the two sets of data, accord with the law of definite proportions (*8*)?

b. Formula of Magnesium Oxide. From the weight of oxygen (*9*), which was found to combine with the known weight of magnesium (*3*) employed in *a*, calculate the weight of magnesium that is here associated with 1 g. of oxygen in magnesium oxide (*10*).

Calculate also the weight of magnesium (*11*) associated, in this compound, with 16 g. of oxygen, — *i.e.* the equivalent of magnesium in terms of oxygen in magnesium oxide.

The formula-quantities of magnesium and oxygen, in any combination between these two elements, must be in the ratio of $(24)x : (16)y$, where x and y represent respectively certain unknown integral multiples of the atomic weights of magnesium and oxygen. Consider x as unity and thus accept one gram-atomic weight of magnesium as its formula-quantity in the compound. Determine next the weight of oxygen (*12*) actually associated in this compound with 24 g. of magnesium; the value obtained corresponds now to the formula-quantity of oxygen, 16 y, and must be a multiple of the atomic weight of oxygen by some whole number. The value of y may easily be found and the actual formula of the compound, $(Mg)_x(O)_y$, determined (*13*). This result, of course, is based upon the assumption that only one atomic weight of magnesium is present in the molecular weight of magnesium oxide.

[redacted]

(*7*) Wt. magnesium oxide : wt. magnesium = 100 :

(*8*)

(*9*)
(*3*)

(*10*) Wt. oxygen : wt. magnesium = 1 :
(*11*) Wt. oxygen : wt. magnesium = 16 :

(*12*) Wt. magnesium : wt. oxygen = 24 : 16(y)
Number of atomic weights of oxygen = y =

(*13*) Formula of magnesium oxide = $\mathrm{MgO}y$ =

c. Tin and Oxygen: Oxidation by the Action of Nitric Acid. Clean and dry your porcelain crucible (without the cover) and weigh it [Balance] (***14***). Place in the crucible a few strips of pure tin foil and weigh again (***15***). The weight of tin foil (***16***) should not exceed 1 g. Now place the crucible upon a clay triangle and pour about 2 cc. of concentrated nitric acid upon the metal and see that all of the foil is in contact with the acid. Hold your Bunsen burner in the hand and gently warm the crucible by means of a small nonluminous flame, checking the heat at any time when there appears a tendency for minute particles to spatter out from the crucible. The white product first obtained is finally heated with the full flame for 10 to 15 minutes or until the last traces of moisture and brown fumes (oxides of nitrogen) are driven off. The crucible is then cooled and weighed (***17***); it is well here to reheat and weigh again to constant weight. Determine by difference the weight of tin oxide produced (***18***).

Calculate the percentages of oxygen and tin present in this oxide of tin (***19***).

The crucible may be cleaned by use of a warm sodium hydroxide solution.

d. Formula of Stannic Oxide. From the weight of tin (***16***) and the weight of oxygen (***20***) found in combination as oxide in *c*, calculate the weight of tin here combined with 1 g. of oxygen (***21***).

Calculate the weight of tin associated with 16 g. of oxygen (one gram-atomic weight of oxygen) (***22***).

Calculate now the weight of oxygen associated here with one gram-atomic weight of tin (namely, 119 grams) (***23***).

In the formula for this compound, Sn_xO_y, consider x to

(*15*) Wt. crucible + tin =
(*14*) Wt. crucible = ______
(*16*) Wt. tin =

(*17*) Wt. crucible + oxide =
(*14*) Wt. crucible = ______
(*18*) Wt. tin oxide =

(*18*) Wt. tin oxide =
(*16*) Wt. tin = ______
(*20*) Wt. oxygen =
(*19*) Percentages =

(*21*) Wt. oxygen : wt. tin = 1 :

(*22*) Wt. oxygen : wt. tin = 16 :

(*23*) Wt. tin : wt. oxygen = 119 :

(*23*) Wt. tin : wt. oxygen = 119 : 16(y)

be unity and the ratio between the formula-quantities of these elements then becomes $(119)_1 : (16)_y$. The value just found for the weight of oxygen associated here with one gram-atomic weight of tin (119 g.) now represents the formula-quantity of the oxygen (*i.e.* $(16)_y$) in the molecular weight of this oxide. The value for y is now easily computed and the formula for the oxide can be written (*24*). It is assumed here that only one atomic weight of tin is present in one molecular weight of the oxide.

24. Composition and Formula of a Sulphide of a Metal. [Quantitative]

a. Lead Sulphide. From the data obtained in **7** *a* we may now derive the formula for this compound of lead and sulphur, Pb_xS_y, by calculating the weight of sulphur here combined with 207 g. (one gram-atomic weight) of lead (*1*). This value corresponds to the formula-quantity of sulphur ($(S)_y$ in the formula, *i.e.* $(32)_y$) in the gram-molecular weight of the compound, when we consider the formula-quantity of lead ($(Pb)_x$ or $(207)_x$) as made up only of one gram-atomic weight of this element. From this formula-quantity of sulphur we at once derive the value of y and construct the correct formula for the sulphide (*2*) based upon the assumption that only one atomic weight of lead is present in one molecular weight of the compound.

b. Cuprous Sulphide. From the data obtained in **7** *b* we may now derive the formula for this sulphide of copper, Cu_xS_y, by calculating the weight of sulphur (corresponding to the formula-quantity denoted here by $(S)_y$, *i.e.* $(32)_y$) which is here associated with 63.6 g. of copper (one gram-atomic weight) (*3*). As the formula-quantity of copper

(*24*) Formula of tin oxide = SnO_y =

(*1*)

(*2*)

(*3*)

in this compound is denoted by Cu_x we need only make x equal to unity in order to base our calculations upon one gram-atomic weight of copper. The value for y is then easily determined from the formula-quantity of sulphur (*3*) when this is referred to its equivalent $(32)_y$. In this case, however, y appears as a fraction (*4*), hence the formula Cu_1S_y must be multiplied through by some integer to clear the expression of this fraction, — the correct formula is then obtained (*5*).

25. Volume (and Weight) of Hydrogen Displaced by Metal Interacting with an Acid. [Quantitative]

a. Magnesium and Hydrochloric Acid. The same apparatus as employed in **22** *a* (Fig. 7) is here to be arranged and the same general instructions are to be followed. The hard glass test-tube, however, is now replaced by a large test-tube (of about 100 cc. capacity) and into this is slipped an ordinary 30 cc. test-tube. The large test-tube is tightly fitted by a one-hole cork to the small piece of glass tubing which leads into the 1-liter bottle. The arrangement is shown in Fig. 8.

FIG. 8.

[*Instructions:* It is well to place the 1-liter bottle at a little higher position than the beaker so that the syphoning of the water from the bottle to the beaker may proceed more easily. If one beaker is not sufficiently large to contain all of the water that is driven over, pour some of the water out of this beaker into a second beaker, but use great care to hold the end of the nozzle continually under the surface of the water in the first beaker. Tabulate records on page 75.]

(3)

(4)

(5)

Weigh out accurately [Balance] about 0.5 g. of magnesium ribbon (*1*) and introduce this to the bottom of the large test-tube. Pour into the inner test-tube about 10 cc. of concentrated hydrochloric acid and add 15 cc. or more of water nearly to fill the tube but not so much as to cause an overflow while lowering this tube into its position upon the magnesium in the large test-tube. When all is adjusted open the clamp on the rubber exit tubing just long enough to blow a quantity of air into the apparatus through the nozzle, a quantity which will be sufficient to force water into the exit tube and into the beaker when the pressure is released by opening the clamp. Equalize the levels of the water in beaker and bottle, close the clamp, empty what little water is in the beaker and return the beaker to its proper position. Finally open the clamp and slowly tilt the apparatus forward toward the beaker so that at first only a few cc. of the dilute acid (contained in the inner test-tube) may be spilled into the outer compartment upon the magnesium.

A rapid action is at once developed and, unless care is used not to spill too much acid at one time, the outer tube may even be forced off of its support. As the reaction proceeds, more and more of the dilute acid is to be transferred from the inner test-tube to the outer compartment. Finally, when all of the metal has disappeared and sufficient time has elapsed for the gas and water to have attained the temperature of the laboratory, the levels of water in beaker and bottle are again equalized, the clamp closed and the water measured in a graduated cylinder (*2*).

Observe the temperature of the laboratory in the neighborhood of the apparatus (*3*).

Read the temperature in the neighborhood of the barometer (*4*), read the barometer (*5*) and subtract from it the correction for the barometer at this temperature (*6*). Subtract the tension of aqueous vapor (*7*) at the temperature of the laboratory from the corrected barometric reading (*8*) to obtain the partial pressure of the hydrogen (*9*). Reduce the volume of hydrogen to the standard conditions, of 0° and 760 mm. (*10*), and from the weight of 22,400 cc. of hydrogen (2.016 g.) calculate the weight of this volume here obtained (*11*).

From the weight of hydrogen (*11*) thus found to be liberated by the known weight of magnesium (*1*) upon an acid, calculate what weight of magnesium is exactly equivalent to one gram-atomic weight of hydrogen (1.008 g.) (*12*). This is the equivalent of magnesium in terms of hydrogen in the compound magnesium chloride. The gram-atomic weight of magnesium is 24; how many gram-atomic weights of hydrogen are here found to be equivalent to one gram-atomic weight of magnesium (*13*)?

What is the valence of magnesium (*14*)?

b. Aluminium and Hydrochloric Acid. Substitute 0.5 g. of aluminium (gran.) for the magnesium in *a*, and follow all of the directions as described therein. Answer the same questions throughout and construct the same set of tabulations as provided in *a*.

c. Zinc and Hydrochloric Acid. Substitute here 1 g. of zinc for the magnesium used in *a* and, to hasten the reaction, drop in also a small crystal of cupric sulphate, or place your platinum wire and support in the tube so that contact action may be obtained. Tabulate observations as in Experiment *a* and answer the same questions.

[redacted]

(*1*) Wt. of magnesium =

(*2*) Vol. of hydrogen (water displaced) =

(*3*) Temp. in laboratory =

(*4*) Temp. near barometer =

(*5*) Barometric reading =

(*6*) Correction for barometer at this temp. =__________

(*8*) Corrected barometric reading =

(*7*) Tension aq. vapor at temp. in laboratory =__________

(*9*) Partial pressure of the hydrogen =

(*10*) Vol. hydrogen at 0° and 760 mm. = x =

$x = (\quad)(\text{——})(\text{——})$

(*11*) 22,400 cc. : vol. hydrogen in cc. = 2.016 :

(*12*) Wt. hydrogen : 1.008 = wt. magnesium :

(*13*)

(*14*)

26. Relation of Equivalents to Each Other

The weight of magnesium in **25** *a* which was found to replace 1.008 g. of hydrogen is called the equivalent of magnesium in terms of hydrogen in the compound magnesium chloride.

The weight of magnesium in **23** *a* which was found to combine with 16 g. of oxygen is called the equivalent of magnesium in terms of oxygen in the compound magnesium oxide.

From these two sources calculate severally the weights of hydrogen and oxygen that are equivalent to one gram-atomic weight of magnesium, 24 g. (*1*). The weights of hydrogen and oxygen here found are equivalent to each other in the compound water.

27. Percentage of Water in a Hydrate and the Corresponding Formula. [Quantitative]

Weigh [Balance] a clean dry crucible (*1*) and place in it about 1 g. of crystallized calcium sulphate (gypsum), previously powdered, and weigh again (*2*). Place the crucible, containing this known amount of calcium sulphate (*3*), upon a clay triangle, almost cover the crucible with the crucible cover and heat to redness. Cool and weigh (*4*). Reheat the crucible and its contents to redness and continue till a constant weight is obtained. The loss of weight here recorded (*5*) represents the water of hydration driven off.

Determine the percentage of water present in the original compound (*6*).

Determine, by difference, the weight of anhydrous sulphate (*7*) associated with the weight of water of hydration.

Calculate the weight of anhydrous calcium sulphate associated with 1 g. of water (*8*).

(*1*)

(*2*) Wt. crucible + gypsum =
(*1*) Wt. crucible =
(*3*) Wt. gypsum =

(*2*) Wt. crucible + gypsum =
(*4*) Wt. crucible + gypsum heated =
(*5*) Wt. water lost =

(*6*) Wt. gypsum : wt. water = 100 :

(*4*) Wt. crucible + gypsum heated =
(*1*) Wt. crucible =
(*7*) Wt. anhydrous gypsum (calcium sulphate) =
(*8*) Wt. water : wt. anhydrous gypsum = 1 :

Calculate the weight of anhydrous calcium sulphate associated with 18 g. (one gram-molecular weight) of water (*9*).

From the molecular weight of anhydrous calcium sulphate ($CaSO_4 = 40 + 32 + 64$) or 136 determine how many gram-molecular weights of water are associated in the hydrated salt with 1 gram-molecular weight of calcium sulphate (anhydrous) (*10*).

State formula of the hydrated salt, $CaSO_4 . x(H_2O)$ (*11*)?

(*9*) Wt. water : wt. anhydrous gypsum = 18 :

(*10*) Wt. anhydrous gypsum : wt. water = 136 : x(18)

(*11*)

CHAPTER VII

SOLUTION

28. Gases in Liquids

Pour about 200 cc. of distilled water into a 500 cc. flask, close the flask with a cork and shake well in order to saturate the water with air. Note the temperature of the water (*1*), the corrected barometric reading (*2*), and subtract from the latter the tension of aqueous vapor at the temperature of the laboratory (*3*) in order to obtain the true or partial pressure (*4*) of the dry gas that is here to be measured.

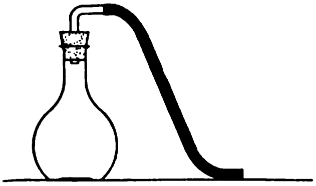


FIG. 9.

Now fit a 100 cc. flask with a one-hole cork and short glass exit tube. To this exit tube attach a piece of rubber tubing which will lead into a beaker and under an inverted small test-tube, both of which have previously been filled with tap water. See Fig. 9.

Determine the exact capacity of the 100 cc. flask by filling it close up to the cork with tap water and then measuring the volume of this water by means of a graduated cylinder (*5*). The flask is now emptied and both flask and entire exit tubing filled with the distilled water previously charged with air. Place the flask upon a ring-stand, heat the contents to boiling over a Bunsen burner and collect the liberated gas in the inverted test-tube. When no more

gas is driven over, equalize the levels of water in test-tut and beaker and mark the level of the water in the test-tub by means of a rubber band. Remove the test-tube fron the beaker, empty it and fill again with water just up to the rubber band. Measure this small volume of water and obtain directly the corresponding volume of air it represents (*6*).

Correct this volume of air for aqueous vapor present and thus obtain the volume of dry air (*7*) dissolved in the registered volume of water (*5*) in the flask at the temperature and pressure of the laboratory.

From this calculate the volume of dry air dissolved under these same conditions by 100 cc. of water (*8*).

Determine the ratio of volumes between the water and the air dissolved (*9*).

29. Liquids in Liquids

[*Instructions:* (1) Use the greatest care to keep the liquids carbon disulphide and ether far removed from flames. (2) Potassium permanganate dissolves in water to give a purple solution; the appearance, therefore, of this color may be used to indicate the presence of water.]

a. Drop one single drop of water into a small test-tube and add thereto 4 to 5 cc. of carbon disulphide. Shake the mixture and notice what becomes of the drop of water (*1*).

After settling pour out a portion of the carbon disulphide into a watch-glass, using care to prevent any minute droplets of water coming out with this liquid. Drop into the watch-glass one small crystal of potassium permanganate nd, as the carbon disulphide evaporates spontaneously, rush this crystal by pressing it with a glass rod against the

(*1*) Temp. of the water (or laboratory) =

Temp. in neighborhood of barometer =

Barometric reading =

Correction for barometer at this temp. = ________

(*2*) Corrected barometric reading =

(*3*) Tension of aq. vapor at temp. of lab. = ________

(*4*) Partial pressure of dry gas =

(*5*) Vol. water in 100 cc. flask =

(*6*) Vol. of air dissolved in this water =

(*7*) Vol. dry air $= x =$

$x = (\quad)(\quad)$

(*8*) Vol. water : 100 = air dissolved : x

(*9*)

(*1*)

dish and noticing if any water has been dissolved by the carbon disulphide (*2*).

b. Repeat *a*, using one drop of water and adding thereto 4 to 5 cc. of ether. Take care (as in *a*) to prevent tiny droplets of water being poured out with the ether upon the watch-glass. Does the ether dissolve any water (*3*)?

c. Absolute alcohol does not contain water and will not show a color with potassium permanganate. Test the alcohol in the laboratory for the presence of water (*4*).

d. Measure out exactly 10 cc. of alcohol in your graduated cylinder and pour this volume into a dry test-tube. Now fill the graduated cylinder with water just to this 10 cc. division mark and then return the 10 cc. of alcohol from the test-tube to this cylinder containing the water; add the alcohol slowly and during constant shaking. Compare the volume of the final solution with the sum of the volumes of the components (*5*).

30. Solids in Liquids

a. Select two crystals of cupric sulphate of about equal size (that of a large pea) and pulverize one of these crystals in your mortar to a fine powder. Transfer this powder to a dry test-tube and place the remaining crystal in another dry test-tube. Add from the graduated cylinder 15 cc. of water to each test-tube and note on your watch the time of this addition of water (*1*). Cork the tubes and shake them continuously. Note the time when the powder has dissolved (*2*) and when the crystal has dissolved (*3*). Account for this difference (*4*).

b. Powder in your mortar about 12 g. of potassium lichromate and transfer this to a 100 cc. flask. Pour upon

(2)

(3)

(4)

(5)

(1)
(2)
(3)
(4)

[redacted]

this salt 45 to 50 cc. of water and shake the mixture vigorously. If, after 10 minutes or more, there remains no solid at the bottom of flask, too much water has been employed. It is only necessary here to add a little more of the dichromate and thus have an excess of the solid remaining undissolved in the presence of its saturated solution.

Support a burette [Storeroom] upon a ring-stand, take the temperature of this saturated solution of potassium dichromate (*5*) and pour solution into the burette. Run off a little of the solution at once in order to fill the burette nozzle and return this portion to the burette.

Weigh [Balance] a clean, dry evaporating dish (*6*) and place this dish close under the burette. Now read the height of solution in the burette (reading the lower side of meniscus) (*7*) and run into the evaporating dish about 20 to 25 cc. of this solution (*8*), reading the column in the burette again accurately (*9*). Weigh the dish and contents [Balance] (*10*) and then evaporate the water from this solution by placing the dish with its contents upon a water-bath, or sand-bath. When the solution is evaporated to dryness, cool the dish with its residue and reweigh [Balance] (*11*).

Determine, by difference, the weight of dry potassium dichromate obtained from the solution (*12*) and also the weight of the water driven off (*13*).

Calculate the weight of this salt dissolved by 100 cc. of water at the observed temperature (*14*).

From the volume of solution evaporated (*8*) calculate the weight of salt that would be dissolved in 1000 cc. of this solution (*15*).

Calculate number of gram-molecular weights in which this last value could be expressed (molal solubility [R. 8]) (*16*).

(*5*) Temp. sat. sol. of potass. dichromate =

(*10*) Wt. evap. dish + potass. dichromate sol. =
(*6*) Wt. evap. dish alone = ________
Wt. potass. dichromate sol. (*12* + *13*) =

(*9*) Final reading of sol. in burette =
(*7*) Initial reading of sol. in burette = ________
(*8*) Vol. of sol. taken =

(*11*) Wt. evap. dish + residue potass. dichromate =
(*6*) Wt. evap. dish alone = ________
(*12*) Wt. residue of potass. dichromate =

(*10*) Wt. evap. dish + potass. dichromate sol. =
(*11*) Wt. evap. dish + residue potass. dichromate = ________
(*13*) Wt. of water driven off =

(*14*) Wt. water driven off : wt. residue = 100 :

(*15*) Vol. potass. dichromate sol. : 1000 cc. = wt. dichromate : x

(*16*) G. M. W. potass. dichromate = 294.4
$294.4 : x = 1 :$

c. Place about 1 g. of pulverized calcium sulphate in test-tube, add 10 cc. of water, shake for a few minutes a filter the mixture, collecting 5 or 6 drops of the clear filtra upon a watch-glass and evaporating it to dryness (*17*).

Place about 1 g. of pulverized calcium carbonate in a test tube, shake with a little water. As the carbonate ofte contains a small quantity of a more soluble hydrogen carbonate, reject this water with which the salt is first shaken and pour upon the undissolved portion another 10 cc. of water, shake and filter, collecting 5 or 6 drops of this clear filtrate upon a watch-glass and evaporating it to dryness. Save the watch-glass with its residue for comparison in **31** *c.*

Now compare the deposits left upon evaporating approximately equal volumes of these two saturated solutions (*18*).

Which of the two substances is the more soluble (*19*)? (see Appendix IV).

31. The Effect of Temperature upon the Process of Solution

a. Place about 6 g. of sodium chloride in a test-tube and boil with 10 cc. of water. Decant the clear solution immediately into another test-tube and set aside to cool (*1*).

Is salt much less soluble in cold than in hot water (*2*)?

b. Place about 6 g. of potassium dichromate in a test-tube and boil with 10 cc. of water. Allow the clear solution to cool. Is potassium dichromate much more soluble in hot than in cold water (*3*)?

Compare the solubility curves for sodium chloride and potassium dichromate by reference to Appendix V.

c. Repeat a part of Experiment **30** *c*, boiling the final nixture of 1 to 2 g. of washed calcium carbonate and 10 cc. f water. Filter the solution, collect 5 or 6 drops of the

RECORD

(17)

(18)

(19)

(1) Some of The $NaCl$ came out of solu

(2) More soluble in hot water

(3) More Soluble in hot water

clear filtrate upon a watch-glass and note, upon evapora whether or not this salt is more soluble in hot than in water (see 30 *c*) (*4*).

32. Properties of Solutions

a. Pour about 50 cc. of water into a small beaker a place the beaker upon a ring-stand. Suspend a thermomet [Storeroom] by a thread from o of the rings on this stand an allow the bulb of the thermomete to hang immersed midway in the liquid as in Fig. 10. Boil the water by applying the flame directly beneath the beaker and record the temperature (*1*), or boiling point of pure water.

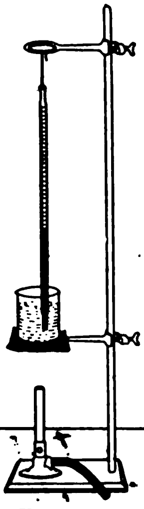


Fig. 10.

b. Into a small beaker pour about 50 cc. of water and adjust it in the same manner as described in *a*. Record the temperature of the water (which should be at room temperature) (*2*). Now add 8 to 10 g. of calcium chloride and observe the temperature of solution thus prepared (*3*).

Heat the solution to boiling and observe, as before (in *a*), the temperature of the boiling solution (*4*).

Add another 8 to 10 g. of calcium chloride to this hot solution and heat again, and determine the boiling point of this, the more concentrated, solution (*5*).

Save this solution for *d*.

(4)

(1) The water boiled at 98.9°

(2) The water was at 19°

(3) The water was lowered To 10°

(4) The solution boiled at 101°

(5) The solution boiled at 102.3°

c. Repeat *b*, substituting ammonium chloride f calcium chloride. Is there a change of temperature i process of solution (*6*)?

Compare this change with that in *b* (*7*).

Has the exothermal or endothermal effect in the fo tion of solutions anything to do with the solubility cu of these products [R. 9] (*8*)?

Save the solution for *d*.

d. Pour out a few cc. of the solutions from *b* and *c* in separate watch-glasses and set these aside for a day or tw to evaporate to dryness (*9*).

If a solution of a deliquescent salt does not evaporat to dryness spontaneously, how may the dry salt be obtained from the solution (*10*)?

e. If pulverized ice were added to water until the ice no longer melted, what would be the temperature of the solution (*11*)?

If ice were added to an aqueous solution of some substance until the ice no longer melted, how would the temperature registered differ from the temperature of the ice [R. 10] (*12*)?

Why does salt thrown upon ice cause the ice to melt (*13*)?

33. Distribution of Substances between Solvents; Extraction

a. Place a small crystal of iodine in a test-tube, add about 5 cc. of carbon disulphide and shake. If the iodine dissolves, note the color of the solution (*1*).

b. Place a small crystal of iodine in a test-tube, add 10 cc. of water and shake vigorously for several minutes. If iodine dissolves, note the color of solution (*2*) and pou into another clean test-tube this solution freed from any

[redacted]

(6)
(7)

(8)

(9)

(10)

(11)

(12)
(13)

(1) purple

(2) yellow brown

particles of iodine undissolved. Add a few drops of carbon disulphide to this test-tube and shake the mixture. Is iodine more soluble in carbon disulphide than in water (*3*)

In what proportion will the iodine distribute itself between these two immiscible solvents [R. 11] (*4*)?

Finally pour off the aqueous layer into a third test-tube, to which add again 1 or 2 cc. of carbon disulphide and shake. What can you state in regard to the comparative solubility of iodine in water and carbon disulphide (*5*)?

c. Shake a few cc. of potassium iodide solution with one small crystal of iodine in a test-tube. Note the color of the solution (*6*).

Ascertain if iodine is more soluble in this solution than in carbon disulphide (*7*).

d. Into a small test-tube containing 1 to 2 cc. of ether drop a crystal of iodine and shake till all is dissolved. Note the color of the solution (*8*). Pour off 1 cc. of this clear solution into another test-tube and add 15 to 20 cc. of water. Close the tube with a cork to prevent evaporation of the ether and shake well (*9*).

What component of the ether solution is extracted to a large degree by the water (see 29 *b*) (*10*)?

Filter this aqueous solution and add to the filtrate a few drops of carbon disulphide. Shake and compare the result with that obtained in *b* (*11*).

How do you account for this difference (*12*)?

RECORD

(3) more soluble in carbon Tetrachloride

(4) It will distribute itself in proportion to the solubilities in the two solvents.

(5) Iodine has a low solubility in water and a high one in carbon disulf

(6)

(7)

(8)

(9)

(10)

(11)

(12)

CHAPTER VIII

CHLORINE AND HYDROGEN CHLORIDE, AND CHEMICAL EQUILIBRIUM

CHLORINE

34. Detection of Chlorine

[*Instructions:* Pour a few cc. of starch emulsion [side-shelf] into a test-tube, add a drop or two of potassium iodide solution and then prepare a few strips of filter paper by dipping them into this solution. When one of these prepared strips is held in an atmosphere of chlorine, bromine, fluorine, ozone, and such gases, iodine will be liberated and this, in turn, will be recognized by the appearance of a blue color, — the product formed when iodine dissolves in starch.]

a. Place small quantities of manganese dioxide, lead dioxide, and potassium permanganate each in separate test-tubes, and add thereto a few cc. of concentrated hydrochloric acid. Note color and odor of gas evolved and test for the presence of chlorine as just instructed (*1*).

b. This production of chlorine from hydrochloric acid is one of oxidation; the hydrogen (here combined with the chlorine) is thus removed in the form of water. Try the effect of lead monoxide upon concentrated hydrochloric acid and account for the difference in action here from that in *a*, where lead dioxide was used (*2*).

35. Preparation of Chlorine. [Hood] [Two Students Working Together]

a. Fit up a 250 cc. flask with a dropping-funnel (see *Note* 18) and a short glass exit tube. Connect this exit tube by

(1) The gas is chlorine, green. with a pugnent odor.

(2) lead monoxide has not as gr
a solubility as lead dioxide and
Therefore will not oxidize H

[redacted]

a very small piece of rubber tubing to a longer glass tube bent at right angles, as shown in Fig. 11. Allow the end of the long bent glass exit tube to extend to the bottom of a small beaker containing 10 to 15 cc. of sodium hydroxide solution, which serves to absorb the first portions of chlorine that are to be discarded. Place in the flask about 20 g. of manganese dioxide. Prepare in your graduated cylinder a mixture of one part concentrated hydrochloric acid and one part water, amounting possibly to 100 cc. in all. When the flask is fixed in its position upon the ring-stand, pour into the dropping-funnel a portion of this diluted acid and admit just sufficient acid to moisten all of the manganese dioxide in the flask. Afterwards pour all the acid into the funnel and allow it to run directly into the flask. Apply a flame beneath the flask and regulate the heat so as to give a gentle evolution of gas, — a point easily determined by observing the escape of bubbles through the sodium hydroxide solution. When these bubbles are completely absorbed by this solution, the flask is to be considered free from air. Remove the beaker, force the end of the exit tube through a piece of filter paper and insert the protruding end to the bottom of a wide-mouthed jar, thereby making the filter paper serve as a temporary cover for the jar and a prevention against the intermingling of air with the chlorine collected.

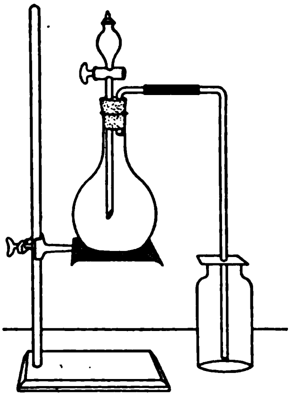


Fig. 11.

RECORD

The extension of the green-yellow color throughou jar is evidence that the jar is practically filled with chl Remove the exit tube and paper disk, cover the jar a glass plate and insert the exit tube into a second b in the same manner as before. Fill in this way two and one test-tube with the gas and reserve them for **36**.

Empty the contents of the flask at once into the sink the hood and wash out the sink with considerable water.

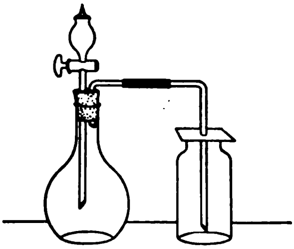


FIG. 12.

Construct equations for t reaction between manganese d oxide and hydrochloric acid (*1*).

b. The production of chlorin may be accomplished without the application of heat by substituting an equal weight of potassium permanganate for the manganese dioxide used in *a*. The flask and receiver are here arranged upon the same level, as shown in Fig. 12. The hydrochloric acid must be admitted to the flask very slowly, drop by drop, throughout the entire operation in order to obtain a steady evolution of the gas.

36. Properties of Chlorine

a. Into one bottle of the gas from **35** sprinkle a little powdered antimony [R. 12] (*1*).

Write an equation for the reaction (*2*).

b. Into the second bottle of chlorine insert a lighted splint. Is chlorine combustible or a supporter of this type of combustion (*3*)?

c. Fill a test-tube with hydrogen from a Kipp's apparatus, or laboratory supply, and bring this test-tube mouth to

[redacted]

(1) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(1) white fumes
(2) $Cl_2 + 2Sb \rightarrow SbCl$

(3) Non-supporter of combustion.

mouth with the test-tube from **35** filled with chl Mix the gases by repeated inversion (taking care n expose the mixture to direct sunlight). Hold the m of each tube to the Bunsen flame and construct the equa for the reaction (*4*).

Blow the breath into one of the tubes and insert als moist piece of litmus paper (see **37**) (*5*).

HYDROGEN CHLORIDE

37. Detection

[*Instructions:* When a gas dissolves in a liquid, such as water, an produces a marked lowering in the vapor pressure of the solutio from that of the pure solvent, we may expect that this difference i vapor pressure will be detected by precipitation of that portion o vapor which is in excess of the vapor in equilibrium with the newl formed solution. The breath is an atmosphere saturated with moisture and when gases such as the hydrogen halides come in contac with it they dissolve in this moisture, and the excess of vapor ove that required for equilibrium, by a solution of this particular gas, i precipitated; the gas is thus said to "fume" in moist air.

The presence of ammonia which combines with these sam hydrogen halides to produce "white fumes" (solid compounds) observable even with traces of these substances, is much more indicative of their presence.]

a. Select samples of several chlorides, such as sodiu chloride, ammonium chloride, and barium chloride, and plac them in separate test-tubes. Add a few drops of concentrated sulphuric acid to each tube and test for the presenc of gas, — here hydrogen chloride, by blowing the breat across the mouth of each test-tube and inserting a rod previously dipped in ammonium hydroxide solution (*1*).

Do any of these mixtures require heating before the reaction is apparent (*2*)?

b. Try the effect of phosphoric acid upon finely pulverized salt, applying heat to the tube if necessary (*3*).

RECORD

(4)

(5)

(1) white fumes

(2)- None of them required heatin

(3)

Account for the readiness with which these ch give up their chlorine in the form of hydrogen chlori the action of these acids [R. 13] (*4*).

38. Preparation of Hydrogen Chloride [Hood]

Fit up an apparatus as shown in Fig. 12. Place in a 25 flask about 30 g. of common salt and admit concentr sulphuric acid through the dropping-funnel, drop by d Place about 15 cc. of water in a test-tube and bring t test-tube directly under the glass delivery tube. The e of the delivery tube should come close to the surface of t water in the tube, but not actually dip beneath this surfac When the reacting materials indicate that the evolution gas is proceeding steadily, and a few minutes have elaps for the formation of a solution of this gas in the water the test-tube, remove the test-tube, cork it and set asi for **39**.

Now collect this gas by the upward displacement of a in three wide-mouthed bottles, temporarily covered with perforated filter paper as described in **35**. **Cover each bottl** when full, with a glass plate and set aside for **39**.

Pour out the liquid contents of the generating flask in a beaker and reserve for **40**.

Write two equations for the interaction of salt and sulphuric acid and designate which equation represents t reaction in this operation (*1*).

39. Properties of Hydrogen Chloride and Hydrochloric Ac

a. Insert a lighted splint into one of the jars of hydrog chloride collected in **38** and state whether this gas is co bustible or a supporter of this type of combustion (*1*).

(4)

(1)

(1)

b. Invert the second jar over a beaker of water a note the result (*2*).

Account for any gas that remains in this jar (*3*).

c. Devise a method for proving that this gas is heavie than air, and use the third bottle for this experiment (*4*).

d. Distribute the aqueous solution of this gas, 15 cc. o which were prepared in the test-tube in 38, between six test-tubes. Test the reaction of the solution to litmus paper (*5*).

e. Boil one portion of the hydrochloric acid solution in a test-tube till the volume is reduced by one half and again test with litmus (*6*).

Can the hydrogen chloride be driven off completely by boiling [R. 14] (*7*)?

f. Drop a small piece of magnesium ribbon into the second test-tube and write the equation for the action (*8*).

Compare here the action of this solution with that of an equal volume of the concentrated hydrochloric acid on your desk (*9*).

g. Drop a small piece of crystallized sodium carbonate into the third test-tube [R. 15] (*10*).

The presence of what constituent in hydrochloric acid is indicated by *f* and *g* (*11*)?

h. Add a drop or two of silver nitrate solution to the fourth test-tube (*12*).

Allow the precipitate to settle, pour off the supernatant liquid, add a little water to the residue in the test-tube and boil the mixture. Set the tube aside to cool and ascertain, by the appearance of crystals, if this precipitate is soluble in hot water (*13*).

Construct an equation for the reaction involved (*14*).

i. Repeat *h*, substituting a drop or two of mercurous

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)

(13)

(14)

nitrate solution for the silver nitrate and express the re tion by an equation (*15*).

Is the precipitate soluble in hot water (*16*)?

j. Repeat *h*, substituting a drop or two of lead nitra solution for the silver nitrate and express the reaction by a equation (*17*).

Is the precipitate soluble in hot water (*18*)?

k. Pour 1 cc. of a solution of some chloride, for example sodium chloride, into each of three test-tubes and apply the tests in *h* (equation) (*19*), *i* (equation) (*20*), and *j* (equation) (*21*). Compare the precipitates in each case with the corresponding precipitates obtained when the free acid was used.

The formation of these precipitates may, therefore, be looked upon as a test for the presence of that radical, — the chloride radical, common to all chlorides.

40. Chemical Equilibrium

a. Reversible Action in the Production of Hydrogen Chloride. Examine the product crystallizing out in the beaker which contains the liquid contents from the generating flask used in **38** for the preparation of hydrogen chloride (*1*).

Place a few cc. of a saturated solution of sodium hydrogen sulphate in a test-tube and slowly add to this a little concentrated hydrochloric acid, shaking the mixture during the addition of the acid. Examine with a lens the product formed (*2*).

Write the equation for the reaction (*3*). How do you harmonize this result with that obtained in **38** (*4*)?

What conditions determine the direction of a reversible action (*5*)?

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

(*20*)

(*21*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

b. Reversible Action in the Production of Ferric Thiocyanate. To a test-tube containing 10 cc. of water add one drop of ammonium thiocyanate solution. To another test-tube containing also 10 cc. of water add a drop of ferric chloride solution. Mix the two solutions and write an equation for this reaction by which the soluble red product, ferric thiocyanate ($Fe(SCN)_3$), is here produced (*6*).

Distribute the 20 cc. of solution between four test-tubes. To one add a drop of ferric chloride solution, to another add a drop of ammonium thiocyanate solution, and to the third add a drop of ammonium chloride solution. Compare each of the three solutions thus obtained with the sample of the original solution left in the fourth test-tube (*7*).

Is the reaction a reversible one (*8*)?

Does the formation of a volatile substance or a precipitate, as in *a*, tend to make a reaction more nearly complete (*9*)?

(6)

(*7*)

(*8*)

(*9*)

CHAPTER IX

BROMINE, IODINE, AND FLUORINE, AND THEIR HYDROGEN COMPOUNDS

Bromine

41. Preparation of Bromine. [Hood]

Pulverize in a mortar about 2 g. of manganese dioxide and transfer this to a test-tube. Pulverize next about 1 g. of potassium bromide and transfer this likewise to the same test-tube. Mix the two ingredients by shaking. Measure into a second test-tube 1 cc. of water and cautiously add, during constant shaking and cooling, an equal volume (1 cc.) of concentrated sulphuric acid. (Never, contrariwise, add water to concentrated sulphuric acid.) Now add to the first test-tube, containing the manganese dioxide and potassium bromide, just sufficient of this cooled diluted acid to moisten the entire mass. Does a reaction take place at once (*1*)?

Finally apply a gentle heat to the moistened mixture and note the color and behavior of the vapors (*2*).

Apply to mouth of tube a piece of filter paper moistened with starch-potassium iodide emulsion (see **34**) (*3*).

Carefully pour the heavy bromine vapors from this test-tube into another clean tube containing 5 to 10 cc. of water, and shake. Is bromine soluble in water (*4*)?

Collect in this way more of the bromine vapors as they issue from the tube and save the bromine-water for **42**.

(*1*)

(*2*)

(*3*)

(*4*)

42. Properties of Bromine

Distribute the solution of bromine in water, as prepared in **41**, between three test-tubes. If this solution is not at hand, prepare another by shaking up one drop of bromine with 10 cc. of water in a test-tube.

a. To one of the test-tubes containing bromine-water add a few cc. of ether and shake. By observing the depth of color in the two liquid layers estimate the relative solubility of bromine in each liquid (*1*).

b. Repeat *a*, using another of the test-tubes of bromine-water but substituting a few cc. of chloroform (or carbon disulphide) for the ether (*2*).

c. Pour a little bromine-water from the third test-tube into a tube containing starch emulsion (*3*).

43. Preparation of Hydrogen Bromide. [Hood]

[*Instructions:* Sulphuric acid was used in Experiment **37** for the liberation of free hydrogen chloride from a chloride. The use of this acid with a bromide is accompanied by secondary reactions which will be discussed later, **76** *e*.]

a. Pulverize about 1 g. of potassium bromide and transfer this to a test-tube. Pour into the test-tube a concentrated phosphoric acid solution sufficient to cover the bromide. Test for a hydrogen halide given off (see **37**) (*1*).

Warm, if necessary. Note the odor of the gas (*2*).

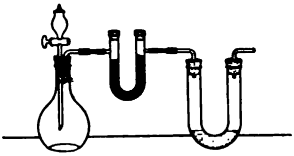


FIG. 13.

b. Arrange an apparatus as shown in Fig. 13. A 250 cc. flask, provided with dropping-funnel and exit tube, is connected to a U-tube containing bits of broken bisque plate

(*1*)

(*2*)

(*3*)

(*1*)

(*2*)

or glass mixed with a little red phosphorus. The other arm of the U tube is then joined to a second U-tube (preferably a larger one) [Storeroom] containing about 10 cc. of water. Place in the flask about 5 g. of red phosphorus, 10 g. of sand, and 10 cc. of water and mix these ingredients thoroughly by shaking. Carefully pour into the funnel 7 to 8 cc. of bromine (use extreme care not to allow any bromine to come in contact with the skin) and allow the bromine to fall upon the mixture in the flask drop by drop.

Phosphorus unites readily with bromine to give a phosphorus bromide which at once is decomposed by the water, giving an acid of phosphorus and hydrogen bromide. The latter, as a gas, is rid of any free bromine by the red phosphorus in the first U tube, and passes over into the second U tube for absorption by the water. After all of the bromine has entered the flask the reaction is practically complete. Disconnect the second U tube and reserve the solution for use in 44.

Apply the moist air and ammonia tests for the presence of a hydrogen halide issuing from the further end of the first U tube (R).

44 Properties of Hydrobromic Acid

a. Distribute the 10 cc. of hydrobromic acid, as collected in 43 between six test-tubes. Test the solution with litmus paper (R).

b. Drop a small piece of magnesium ribbon into one of the test tubes and construct the equation for the reaction (E).

c. To a second test-tube of this acid add a few drops of silver nitrate solution. Note the color of precipitate [illegible] construct the equation for its formation (E).

(3)

(1)

(2)

(3)

or glass mixed with a little red phosphorus. The other arm of the U-tube is then joined to a second U-tube (preferably a larger one) [Storeroom] containing about 10 cc. of water. Place in the flask about 5 g. of red phosphorus, 10 g. of sand, and 10 cc. of water and mix these ingredients thoroughly by shaking. Carefully pour into the funnel 7 to 8 cc. of bromine (use extreme care not to allow any bromine to come in contact with the skin) and allow the bromine to fall upon the mixture in the flask drop by drop.

Phosphorus unites readily with bromine to give a phosphorus bromide which at once is decomposed by the water, giving an acid of phosphorus and hydrogen bromide. The latter, as a gas, is rid of any free bromine by the red phosphorus in the first U-tube, and passes over into the second U-tube for absorption by the water. After all of the bromine has entered the flask the reaction is practically complete. Disconnect the second U-tube and reserve the solution for use in **44**.

Apply the moist air and ammonia tests for the presence of a hydrogen halide issuing from the further end of the first U-tube (*3*).

44. Properties of Hydrobromic Acid

a. Distribute the 10 cc. of hydrobromic acid, as collected in **43**, between six test-tubes. Test the solution with litmus paper (*1*).

b. Drop a small piece of magnesium ribbon into one of the test-tubes and construct the equation for the reaction (*2*).

c. To a second test-tube of this acid add a few drops of a silver nitrate solution. Note the color of precipitate and construct the equation for its formation (*3*).

(3)

(1)

(2)

(3)

Pour off the supernatant liquid, add 4 to 5 cc. of water to the precipitate and boil the mixture in order to ascertain the solubility of the precipitate in hot water (*4*).

Compare this result with that obtained in **39** *h* (*5*).

d. Repeat *c*, substituting a mercurous nitrate solution for the silver nitrate. Construct the equation (*6*).

Try the action of boiling water, and compare result with that in **39** *i* (*7*).

e. Repeat *c*, substituting a lead nitrate solution for the silver nitrate. Construct equation (*8*).

Try the action of boiling water and compare result with that in **39** *j* (*9*).

f. Dissolve a small crystal of potassium bromide in 5 cc. of water. Distribute the solution between three test-tubes and try again the action of solutions of silver nitrate, mercurous nitrate, and lead nitrate upon this salt. Do the results accord with those obtained in *c*, *d*, and *e* for the free acid (*10*)?

If these results accord, we may construe these reactions as tests for what radical (*11*)?

g. Drop a little powdered manganese dioxide, or red lead, into another one of the test-tubes of hydrobromic acid and warm the mixture. What gas is evolved (*12*)?

Is this a test for the bromide radical? Determine by dissolving a small crystal of potassium bromide in 2 to 3 cc. of water, adding manganese dioxide and heating (*13*).

Why was sulphuric acid used in **41** (*14*)?

h. Into the last test-tube of the hydrobromic acid, pour a few drops of carbon disulphide and shake. Is the hydrobromic acid contaminated with bromine (*15*)?

Add, now, a few drops of chlorine-water and note whether bromine is liberated by this reagent (*16*).

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

[redacted]

Write the equation for the action (*17*).

What can you say of the relative affinities of chlorine and bromine for hydrogen (*18*)?

i. Dissolve a small crystal of potassium bromide in 2 to 3 cc. of water, add carbon disulphide and then a few drops of chlorine-water. Does the same relative affinity of chlorine and bromine for hydrogen hold for potassium (and other metallic elements) (*19*)?

IODINE

45. Preparation of Iodine

Prepare a mixture of pulverized potassium iodide (about 1 g.) and pulverized manganese dioxide (about 2 g.) as described in **41**, and place this in an evaporating dish. Pour upon the mixture 2 cc. of the diluted sulphuric acid (1 cc. water and 1 cc. acid) as prepared in **41** and cover the dish with a watch-glass. Pour a little cold water in this watch-glass (or cover) so that the lower surface may be cooled sufficiently for the condensation of iodine vapors. Now heat the evaporating dish very gently and examine the sublimate (*1*).

Test the vapors with a strip of filter paper moistened with starch emulsion alone (*2*).

46. Properties of Iodine

a. Scrape off a portion of the iodine sublimate collected in **45**, or, if this is not at hand, procure from the side-shelf a small crystal of iodine, and shake this iodine vigorously with 10 cc. of water in a test-tube. Pour off 5 cc. of the clear solution into a separate test-tube. Is iodine very soluble in water (*1*)?

b. To the test-tube containing about 5 cc. of iodine-water add 5 cc. of a starch emulsion (*2*).

(*17*)

(*18*)

(*19*)

(*1*)

(*2*)

(*1*)

(*2*)

Pour the mixture into a graduated cylinder and add water until the color no longer persists. Is this blue color a delicate test for the presence of iodine (*3*)?

When the solution in the graduated cylinder is practically colorless remove a small portion in a test-tube and cool with ice or cold water (*4*).

Is the test more or less delicate at a lower temperature (*5*)?

Is this test applicable for iodine in combination? Ascertain by adding a little starch emulsion to a few drops of a solution of any iodide (*6*)?

47. Preparation of Hydrogen Iodide and Hydriodic Acid. [Hood]

a. Repeat **43** *a*, substituting potassium iodide for the potassium bromide (*1*).

b. Repeat **43** *b*, using the same apparatus and arranging it exactly as in Fig. 13. In the flask, however, place a mixture of about 15 to 20 g. of iodine and 1 g. of red phosphorus intimately mixed by grinding them together in a mortar. Place a little water in the dropping-funnel and cautiously allow this water to drop very slowly upon the mixture in the flask. The hydrogen iodide liberated will be rid of free iodine by the red phosphorus in the first U-tube and then, in turn, will be dissolved by the water (10 cc.) in the second U-tube to produce hydriodic acid. After no further action is apparent, upon the continued addition of water to the flask, remove the second U-tube and reserve for **49**.

Test the gas issuing from the further end of the first U-tube with moist air, and ammonia (*2*).

(3)

(4)

(5)

(6)

(1)

(2)

48. Preparation of Hydriodic Acid; Involving the Collection of Fractional Distillates. [Hood]

Fit a small flask with a one-hole cork carrying a piece of glass tubing which will reach to the bottom of the flask. In this flask place 3–4 g. of iodine (previously pulverized) and 50 cc. of water and insert the cork and glass tubing. Now conduct a current of hydrogen sulphide from a Kipp's apparatus, or laboratory supply, through this mixture of iodine and water, agitating the mixture constantly. The cork should be loosened several times at the beginning of the operation to allow for the escape of inclosed air. When all of the iodine has disappeared, warm the solution and filter it from the sulphur which has been precipitated by the action of the iodine upon the hydrogen sulphide.

Procure a 125 cc. distilling flask, a thermometer, and a Liebig condenser [Storeroom] and set up exactly as shown in Fig. 6.

Place the dilute hydriodic acid solution in the flask and distill, using only a small flame, not closer than a few inches from the bottom of the flask itself, and checking the heat supply just short of the disappearance of the last traces of liquid in the flask. Collect the distillates in a series of test-tubes: the first fraction, that portion coming over at 100°; the second fraction, that portion coming over between 100° and 105°; the third portion at 105–110°, and so on. Note the highest temperature reached (*1*). Pour the residue remaining in the flask into a separate test-tube and reserve all of these test-tubes for **49**.

What is the cause of color in the higher fractions? Apply a test to 1 or 2 cc. of one of these portions and confirm your decision (*2*).

(*1*)

(*2*)

Add one drop of each of these various fractions to a drop or two of silver nitrate solution contained in as many watch-glasses, and estimate the various degrees of concentration of hydriodic acid in each fraction and in the residue (*3*).

At what temperature did the most concentrated acid distill over (*4*)?

What other solutions show this peculiarity [R. 16] (*5*)?

49. Properties of Hydriodic Acid

If **47** *b* was done, use a solution from the second U-tube.

If **48** was done, select any one of the fractions collected above 120°.

If neither of these solutions are at hand, procure a special solution [Side-shelf].

a. Distribute the solution of hydriodic acid (which should measure about 10 cc.) between six test-tubes. Test the solution with litmus paper (*1*).

b. Try the action of magnesium upon the hydriodic acid solution in one of the test-tubes. Contact with a platinum wire will assist this reaction (*2*).

c. To the second test-tube add a drop or two of silver nitrate solution. Note the color of precipitate and construct an equation for its formation (*3*).

Pour off the supernatant liquid, add 4 to 5 cc. of water to the precipitate, and boil the mixture. Is this precipitate soluble in hot water (*4*)?

Compare the result with those in **39** *h* and **44** *c* (*5*).

d. Repeat *c*, substituting a mercurous nitrate solution for the silver nitrate. Construct equation (*6*).

Try the action of boiling water upon the precipitate (*7*).

Compare the result with those in **39** *i* and **44** *d* (*8*).

(*3*)

(*4*)
(*5*)

(*1*)

(*2*)

(*3*)

(*4*)
(*5*)

(*6*)
(*7*)
(*8*)

e. Repeat *c*, substituting a lead nitrate solution for the silver nitrate. Construct equation (*9*).

Try the action of boiling water upon the precipitate (*10*). Compare the result with those in **39** *j* and **44** *e* (*11*).

f. Dissolve a small crystal of potassium iodide in 5 cc. of water. Distribute the solution between three test-tubes and apply severally a few drops of the solutions of the three substances, silver nitrate, mercurous nitrate, and lead nitrate. Do the results accord with those obtained in *c*, *d*, and *e* for the free acid (*12*)?

May we interpret these reactions as tests for the iodide-radical (*13*)?

g. Drop a little powdered manganese dioxide, or red lead, into the fifth test-tube of hydriodic acid and warm the mixture. What gas is evolved (*14*)?

Is this a test for the iodide radical? Determine by dissolving a small crystal of potassium iodide in 2 to 3 cc. of water, adding manganese dioxide, or red lead, and heating (*15*).

h. Into the last test-tube of the hydriodic acid solution pour a few drops of carbon disulphide and shake (*16*).

Is the hydriodic acid contaminated with iodine? If so, pour off the supernatant aqueous layer and again add to this a few drops of carbon disulphide (*17*).

When the layer of carbon disulphide appears colorless, pour off about half of the aqueous layer into another test-tube and there again add a few drops of carbon disulphide. Now to one of these tubes add a few drops of chlorine-water and to the other tube a few drops of bromine-water. Note whether iodine is liberated in each case and construct equations for the reactions (*18*).

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

K

What can you say of the relative affinities of chlorine, bromine, and iodine for hydrogen (*19*)?

From **48** what can you now say of the relative affinities of iodine (as well as chlorine and bromine) on the one hand, and sulphur on the other, for the element hydrogen (*20*)?

i. Dissolve a small crystal of potassium iodide in 5 cc. of water, divide into 2 portions, and add a few drops of carbon disulphide to each. Now add to one test-tube a few drops of bromine-water and to the other a few drops of chlorine-water (*21*).

Does this same relative affinity of chlorine and bromine for hydrogen (as in *h*) hold also for potassium (and other metallic elements) (*22*)?

HYDROGEN FLUORIDE

50. Preparation of Hydrogen Fluoride

Melt upon a glass plate a little paraffin, holding the plate far above a Bunsen flame. When the paraffin has been rubbed all over the upper side of this plate, remove the plate and cool it. By means of the end of a file draw some design in this thin paraffin layer so that the glass will be exposed where the design is to be copied. Partially moisten about 3 g. of calcium fluoride (fluorspar) in a leaden dish [Storeroom] with a few drops of concentrated sulphuric acid. Now place the glass plate, paraffin side down, upon the leaden dish, and set the dish and its cover aside in a warm place for a short time. The temperature of the dish must not be raised above the melting-point of the paraffin. In the course of one-half hour remove the glass plate, warm it, and wipe off the melted paraffin (*1*).

(*19*)

(*20*)

(*21*)

(*22*)

(*1*)

[redacted]

Express the reaction between calcium fluoride and sulphuric acid by an equation (*2*).

Construct an equation for the action of hydrogen fluoride upon the silicon dioxide in the glass [R. 17] (*3*).

Apply the moist air and ammonia tests for the presence of a hydrogen halide when first the glass plate is removed (*4*).

How may fluorine be liberated from a fluoride (*5*)?

Why cannot fluorine, just as the other halogens, be prepared by the action of oxidizing agents upon its hydride [R. 18] (*6*)?

51. Identification of Halides

How would you identify the presence of chlorine, bromine, iodine, and fluorine in the form of their simple radicals? A brief statement concerning a distinctive test for the presence of each one of these radicals will here suffice (*1*).

(2)

(3)

(4)

(5)

(6)

(1)

[redacted]

CHAPTER X

THE OXYGEN COMPOUNDS OF THE HALOGENS. HYDROGEN PEROXIDE

[*Instructions:* Fit up a chlorine apparatus as described in 35 and use this source of chlorine, if no other is at hand, for 52, 53, and 54.]

52. Hypochlorous Acid

Prepare a few cc. of chlorine-water by passing chlorine through 5 to 6 cc. of water in a test-tube. Divide this solution into two portions.

To one portion add a few drops of indigo solution and note the effect of hypochlorous acid upon this coloring matter [R. 19] (*1*).

To the second portion of the solution add small pieces of paper bearing marks made by pencil, by ink, and also by newspaper print. Explain the effect upon each (*2*).

53. Hypochlorites. [Hood]

Place about 5 g. of calcium oxide (quick lime) in a small beaker and moisten it with a little water till all is slaked. Add a few more cc. of water till a paste is produced, and then place this beaker within another beaker containing a little ice cold water. While the paste is thus kept cooled and constantly stirred pass through it a current of chlorine for 10 to 15 minutes. Construct an equation to indicate the formation of a hypochlorite-chloride of calcium (*1*).

(1)

(2)

(1)

Filter the paste with the addition of a little water and soak a piece of colored calico in the filtrate. Is the calico affected (*2*)?

Remove the calico and insert it in a second beaker containing a few cc. of dilute sulphuric acid, and note the change observed (*3*). What rôle does the sulphuric acid play? Construct the equation for its action here upon calcium hypochlorite-chloride (*4*).

Soak a second piece of calico in the filtrate from the paste above and hang this strip in the air of the open laboratory. Explain the effect and state what acid is here concerned in the liberation of hypochlorous acid (*5*).

54. Chlorates. [Hood]

a. Dissolve about 3 g. of solid potassium hydroxide in about 7 cc. of water in a test-tube and saturate this solution with chlorine from the chlorine apparatus (as described in **35**). It is well to calculate roughly the volume of chlorine required for the saturation of this potassium hydroxide (a point reached when the solution is no longer soapy to the touch). Construct the equation for this action (*1*), and, calculating from six G. M. W. of potassium hydroxide here associated with three G. M. V. of chlorine, determine the volume of chlorine (at 0° and 760 mm.) required for the saturation of 3 g. of potassium hydroxide (*2*). Consider 5 bubbles of chlorine as about equal to 1 cc. of this gas and thus determine the number of such bubbles of chlorine that must pass into the solution. The crystals of potassium chlorate which begin to appear after a time will be much increased toward the end of the operation, and especially upon cooling the final mixture. At this latter stage filter

(*2*)

(*3*)

(*4*)

(*5*)

(*1*)

(*2*)

off the crystals and dry them immediately by pressing them between several layers of filter paper. The heat developed in this operation is sufficient to decompose the potassium hypochlorite, the first product of the reaction and stable only at lower temperatures (see **53**).

Construct an equation to show the transformation of potassium hypochlorite into potassium chlorate and potassium chloride (*3*).

Select a small sample of the filtrate and test its action to litmus. If not acid, add a few drops of dilute nitric acid until the acid reaction is apparent. Then add a few drops of silver nitrate solution and state what radical is present (*4*).

b. Examine the crystalline product from *a* with lens (*5*).

Dissolve a crystal in a few drops of water, add a drop or two of silver nitrate solution and note if any appreciable amount of the chloride radical is present (*6*).

Test, likewise, a crystal of the potassium chlorate upon the side-shelf and note if any chloride radical is present (*7*).

c. Heat this dried crystalline mass from *a* in a test-tube and apply the glowing splint test (*8*).

Construct an equation to show the formation of potassium perchlorate and potassium chloride at the point of melting of potassium chlorate (*9*).

Construct, next, an equation to show the complete decomposition of potassium chlorate (*10*).

Dissolve the residue, left after the decomposition of the chlorate by heating, in a few cc. of water, and add a drop or two of silver nitrate solution (*11*).

Compare the amount of chloride radical now present with that found to be present in the crystalline product before heating and explain (*12*).

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)

[redacted]

What can you say of the relative solubility of potassium chloride as compared with that of potassium chlorate (*13*)?

How may the potassium chlorate be purified from the former (see Appendix V) (*14*)?

55. Bromic and Iodic Acids. The Oxidizing Action of Chlorine-Water

a. To a test-tube containing a minute fragment of iodine (the size of a match-head) and 6 to 8 cc. of water add a few drops of carbon disulphide and shake. The large part of the iodine is taken up by the carbon disulphide. Now add a little chlorine-water, drop by drop, and shake vigorously. What indication have you of the withdrawal of free iodine from the aqueous solution (*1*)?

Construct an equation to indicate the formation of iodic acid from iodine by the action of chlorine-water (*2*).

b. Repeat *a*, substituting for the iodine 2 or 3 drops of bromine-water. The carbon disulphide layer now will contain a part of the bromine. Upon adding the chlorine-water do you note that its oxidizing action upon bromine is more or less rapid than its oxidizing action upon iodine in *a* (*3*)?

Construct an equation to indicate the formation of bromic acid from bromine by the action of chlorine-water (*4*).

c. To a test-tube containing about 10 cc. of water add 1 drop of sodium iodide solution and one drop of sodium bromide solution and then a few drops of carbon disulphide and shake. Now add a drop or two of chlorine-water to the test-tube and shake again (*5*).

Add a little more chlorine-water, a drop at a time, and

(*13*)

(*14*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

shake after each addition. Explain all the changes here observed (*6*).

May this method be effective as a means of detecting the bromide radical and iodide radical in the presence of each other (*7*)?

d. Add about an equal volume of dilute sulphuric acid to 3–4 cc. of potassium bromate solution in a test-tube and thus liberate the free bromic acid (equation) (*8*).

Now add to this tube one minute piece of iodine (size of a match-head) and shake well. If any iodine remains undissolved, pour off the clear supernatant liquid into another test-tube and to this latter tube add a few drops of carbon disulphide, and shake. What halogen is thus seen to have been liberated (*9*)?

Repeat the experiment, using a few cc. of potassium bromate solution alone, *i.e.* without the addition of sulphuric acid as above [illegible]

What is th[illegible]t, therefore, which reacts directly with the iodine (*11*)?

Construct an equation for the reaction involved (*12*).

What would result upon shaking a little iodine with free chloric acid (*13*)?

Construct the equation for this latter action (*14*).

What can you say of the relative affinities of chlorine, bromine, and iodine for oxygen (*15*)?

56. Peroxides

a. Prepare a solution of sodium peroxide by adding 2 g. of this substance, a very little at a time, to about 100 cc. of cold water contained in a flask. Shake and cool the mixture in a current of water during the process of solution. To

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

this solution, still kept cool, add dilute sulphuric acid, a drop at a time, until the mixture shows an acid reaction. Construct an equation for the formation of the product now in solution (*1*).

Divide the mixture into four parts and use at once in *b*, *c*, *d*, and *e*.

b. To one portion of this solution in a test-tube add finely powdered manganese dioxide. Test the escaping gas with a glowing splint and construct the equation for the reaction, bearing in mind the function of manganese dioxide in this case (*2*).

c. Prepare in a test-tube a mixture of 5 cc. of potassium permanganate solution and an equal volume of dilute sulphuric acid; a little free permanganic acid is now to be considered as present in this mixture. To the second portion of the hydrogen peroxide solution from *a* add a few drops of this free permanganic acid solution and apply the glowing splint test at the mouth of the tube (*3*).

The change in color is due to the formation of a manganous salt. Construct an equation for this reaction [R. 20] (*4*).

State what type of chemical action is shown here by hydrogen peroxide (*5*).

d. To the third portion of the hydrogen peroxide mixture add a drop of starch-potassium iodide emulsion. The excess of sulphuric acid still present in the mixture will, of course, liberate hydriodic acid from the iodide. Construct, therefore, the equation for this reaction as between hydriodic acid and hydrogen peroxide (*6*).

What type of chemical action is here shown by hydrogen peroxide (*7*)?

e. To the fourth portion add 5 cc. of ether and then

(1)

(2)

(3)

(4)

(5)

(6)

(7)

L

[redacted]

one or two drops of potassium dichromate solution, and shake (*8*).

The excess of sulphuric acid still present in the mixture will liberate here free dichromic acid, and this, in turn, will be acted upon by the hydrogen peroxide. Construct the equation [R. 21] (*9*).

f. Suspend the following named oxides in water in as many test-tubes and add dilute sulphuric acid. Shake during cooling and filter. Test the filtrates for the presence of hydrogen peroxide as above indicated in *e* (*10*).

What differences in constitution do we assign to a dioxide and to a peroxide (*11*)?

(*8*)

(*9*)

(*10*)

(*11*)

CHAPTER XI

IONIZATION

57. Simple Radicals

[*Instructions:* The precipitation of silver halides from solutions containing silver radicals and halide radicals is already known. The presence alone in these precipitates of silver and the halogen in question may be proved by liberating the particular halogen by the action of a strong acid and some oxidizing agent (see **34**) and by separating the silver through the action of some reducing agent, such as zinc. Analysis of these halides reveals the presence of no oxygen, or other elements, hence the radicals may be called simple radicals.]

Confirm the statement above for any solution containing the silver radical by trying the action of a few drops of sodium chloride solution upon a few drops of a silver sulphate solution in a test-tube (*1*).

58. Complex Radicals

a. Dissolve a small crystal of potassium perchlorate in a few cc. of water and divide the solution into two portions. Test one portion for the presence of the chloride radical (*1*).

Boil the second portion for a few minutes and test again for the chloride radical (*2*).

What can you say concerning the stability of this oxyhalogen radical in aqueous solution (*3*)?

b. In **54** *c* the decomposition of the dry potassium chlorate was found to proceed readily by the action of heat and the simple halide radical thus easily formed. Try now the

(1) $2NaCl + Ag_2SO_4 \rightarrow Na_2SO_4 + 2AgCl\downarrow$

white precipitate resulted

(1)

(2)

(3)

effect of heating a crystal of potassium perchlorate in a small test-tube for a few minutes. Apply the glowing splint test to the mouth of the tube containing the molten mass (*4*).

Dissolve the residue, when cool, in a few drops of water and add thereto a few drops of silver nitrate solution (*5*).

If the halide radical is now present, what can you say of the stability of the perchlorate radical in a dry salt when heated to a high temperature (*6*)?

The halogens, therefore, as present in the chlorate and perchlorate radicals, are firmly associated in aqueous solution with what other element (*7*)?

Give the formulæ for these complex chlorate and perchlorate radicals (*8*).

c. Take a few drops of silver nitrate solution in a test-tube and add to it a few drops of ammonium hydroxide solution, thus giving a soluble ammonio-argentic nitrate ($Ag(NH_3)_2NO_3$). To this solution now add a little sodium chloride solution (*9*).

Is the silver radical found to be present? If [illegible]ot, state formula of the complex radical containing [illegible] silver (*10*)?

Boil the solution in the test-tube for a few minutes, or until the odor of ammonia has disappeared (*11*).

Is the ammonio-argentic radical stable at the temperature of boiling water (*12*)?

d. Take again a few drops of silver nitrate solution in a test-tube and add to it a few drops of potassium cyanide solution till the liquid becomes clear and the soluble potassium argentic cyanide ($KAg(CN)_2$) is produced. To this solution now add a little sodium chloride solution (*13*).

Is the silver radical present? If not, what is the formula of the complex radical containing the silver (*14*)?

(4)

(5)

(6)

(7)

(8)

(9) $AgNO_3 + 2NH_4OH \rightarrow Ag(NH_3)_2NO_3 + 2H_2O$

[illegible]$Cl + Ag(NH_3)_2NO_3 \rightarrow$ no reaction with out heat

(10) $Ag(NH_3)_2NO_3$

(11) The precipitate of AgCl appears

(12) The $Ag(NH_3)_2NO_3$ is not stable at temperatures of boiling water

$2H_2O + Ag(NH_3)_2NO_3 \rightarrow AgNO_3 + 2NH_4OH$

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

(13) No precipitate

(14) Therefore Ag is not present.

[redacted]

Boil the solution in a test-tube for a few minutes only and state whether the argentic-cyanide radical is stable in boiling water (*15*).

59. Determination of Ionogens

The chemical reactions of the various radicals studied must now be referred to their ability to conduct an electric current. Those radicals made up largely of the metallic elements constitute the ions which take the positive charge and travel to the negative pole, or cathode, — they are called cations. Those radicals made up largely of the non-metallic elements take the negative charge and travel to the positive pole, or anode, — they are called anions. Those substances, therefore, which dissociate into ions are called ionogens.

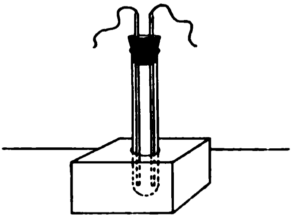


FIG. 14.

Examine a number of common substances and determine, if possible, the conditions under which they will conduct a current of electricity.

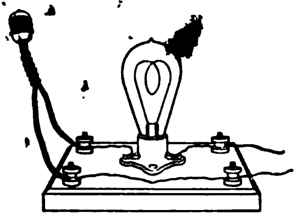


FIG. 15.

Procure for this purpose an electrolytic cell (Fig. 14) from the storeroom. Place in the cell the substance to be examined in just sufficient amount to cover the lower ends of the nickel (or tin) electrodes. Use great precaution that the electrodes do not come in contact with each other and, further, that the cell and these electrodes are thoroughly cleaned and dried before each experi-

(*15*)

ment. Connect the electrodes of the cell to the terminals on the lamp-board (Fig. 15) and note in the study of each particular substance whether or not the lamp glows. If it does not glow, the substance does not conduct the current in its present condition. If the lamp glows, the substance is a conductor and the ions present should be formulated in the notes with their proper "charges." The evolution of gas by electrolysis of some solution may also be used to determine conductivity of an ionogen.[1]

Examine in this way the following named substances:

a. Dry crystallized sodium chloride (*1*).
b. Distilled water (*2*).
c. Aqueous solution of sodium chloride (*3*).
d. Dry sugar (*4*).
e. Aqueous solution of sugar (*5*).
f. Glacial acetic acid (*6*).
g. Glacial acetic acid with the addition of water a little at a time (*7*).
h. Dilute sodium hydroxide solution (*8*).
i. Dilute hydrochloric acid solution (*9*).
j. Dry toluene (*10*).
k. Dry toluene containing hydrogen chloride (*11*).

What substance is here found to be the ionizing medium or agent (*12*)?

---

[1] A storage battery of three cells is admirably adapted as a source of electric current in this experiment. If the lighting system is to be employed resistances must be introduced such as will give a potential drop of about 10 volts between the electrodes. If a lamp-board is not available, introduce in its place a second electrolytic cell which, as was the lamp, must be connected in series with the first cell. Place in this second cell sufficient dilute sulphuric acid to cover the lower part of the electrodes, and note the passage of an electric current by observing the formation of bubbles of gas around the electrodes.

(*1*)
(*2*)
(*3*)
(*4*)
(*5*)
(*6*)

(*7*)
(*8*)
(*9*)
(*10*)
(*11*)

(*12*)

60. Relation of the Non-ionized to the Ionized Portion of Ionogens

The equilibrium between the ions of an ionogen and the remaining non-ionized portion follows directly the principles underlying the law of mass action [R. 22]. An increase in volume of solvent reduces the concentration of the ionic substances: the equilibrium, therefore, in any particular case will shift further and further toward the side of the ions as dilution proceeds. This was just observed in the addition of water to the slightly dissociated glacial acetic acid (see **59** *g*). A few experiments may be made to indicate the extent of these dissociations through observations upon the colors of ions.

a. From the appearance of a solution of potassium bromide what may we assume to be the colors of the potassium and bromide ions (*1*)?

Place about 0.5 g. of cupric bromide in a dry test-tube. Add one drop of water and state the color of the practically non-ionized cupric bromide (*2*).

Add, now, during constant stirring, a little more water, a drop at a time, and note the change in color (*3*).

Continue this addition of water till the change in color is complete. What is the color of cupric ion here and in other solutions of cupric salts known to you (*4*)?

How do you explain the color of the solution of cupric bromide before the dissociation is far advanced (*5*)?

b. Repeat *a*, stopping the addition of water when the green stage is just reached. Distribute this green solution between three test-tubes. Set one aside for comparison and to the second add about 2 g. of solid cupric chloride (*6*).

To the third add about 2 g. of solid potassium bromide (*7*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)
(*7*)

Is the dissociation of an ionogen promoted or repressed by the addition of substances yielding a common ion (*8*)?

c. Dissolve about 1 g. of cupric chloride in a few cc. of water and add a few drops of concentrated hydrochloric acid. Explain the result (*9*).

The displacement of each equilibrium just studied (in *b* and *c*) was due to the increase in concentration of an ion; a reverse displacement will follow immediately upon the withdrawal of an ion.

In general the chemical reactions involving ions may be classified under three types:

I. That of simple interaction between the ions of several ionogens, — usually described by the term "double decomposition" or "metathesis" (see **61**, **62**, **63**).

II. The charge and discharge of ions, — by other elements, by electrical energy, or a simple change in charge by reason of the variable valence of the particular element (see **64**).

III. The formation and decomposition of complex ions (see **65**).

61. Interactions between the Ions of Different Ionogens. [1]

When one ionogen in solution is brought together with a second ionogen the ions of the first will have a certain tendency to associate with the oppositely charged ions of the second ionogen to form two new ionogens, and these, together with the first ionogens, must be maintained in equilibria with all of the ions present. If in such a mixture the ionogens, possible of formation, do not differ greatly from each other in their degrees of dissociation, little, if any, chemical change may be expected. Upon mixing solutions of such ionogens neither thermal effect nor change in con-

(*8*)

(*9*)

ductivity (when considered at the final dilution) is observed, and the relative number of ions present may be considered constant.

If, in such a solution, one of the ionogens possible of formation is practically insoluble (*a*) or if it is less dissociated (*b*) than the others, then the equilibrium between this ionogen and its ions will be shifted far toward the side of the ionogen, — and the number of ions, therefore, will be greatly reduced.

a. The Insoluble Ionogen. The formation of insoluble products is well illustrated by the action of potassium chloride upon silver nitrate, as shown in the following diagram. The silver chloride, though dissociated in solution, is almost insoluble and, therefore, its ions when brought together in solution associate readily to form the molecular silver chloride, the excess of which over that small quantity maintained in equilibrium with the undissolved portion is immediately precipitated.

$$\begin{array}{lcll}
\mathrm{KCl} & \rightleftarrows & \mathrm{K^+} & + \mathrm{Cl^-} \\
\mathrm{AgNO_3} & \rightleftarrows & \mathrm{NO_3^-} & + \mathrm{Ag^+} \\
 & & \uparrow\downarrow & \;\;\downarrow\uparrow \\
 & & \mathrm{KNO_3} & \;\;\mathrm{AgCl}\ \text{(dissolved)} \\
 & & & \;\;\uparrow\downarrow \\
 & & & \;\;\mathrm{AgCl}\ \text{(solid)}
\end{array}$$

Verify this experiment by adding to a few cc. of silver nitrate solution a little potassium chloride solution, drop by drop, till no further precipitation of silver chloride is apparent. Filter off the silver chloride and evaporate the filtrate to crystallization, and finally to dryness, upon the sand-bath. Examine the crystals and compare them with the potassium nitrate upon the side-shelf (*1*).

(*1*)

M

Dissolve the final mass in a few cc. of water in a test-tube. Do you note the presence of traces of undissolved silver chloride (*2*)?

Explain the effect of evaporation of a solution (such as potassium nitrate) upon the equilibrium which obtains between the ionogen and its ions (*3*).

b. The Slightly Dissociated Ionogen. This product may be very soluble and thus no sign of its production apparent to the eye. As an illustration, the action of nitric acid upon potassium hypochlorite in giving the soluble, slightly dissociated hypochlorous acid is shown in the following diagram. By distillation this hypochlorous acid is easily removed and thus the association of those ions leading to its production will proceed to completion. The formation of any volatile product in this manner removes indirectly from the solution those ions that produce it.

$$\begin{array}{lllll} \mathrm{KClO} & \rightleftarrows & \mathrm{K^+} & + & \mathrm{ClO^-} \\ \mathrm{HNO_3} & \rightleftarrows & \mathrm{NO_3^-} & + & \mathrm{H^+} \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ & & \mathrm{KNO_3} & & \mathrm{HClO}\text{ (dissolved)} \\ & & & & \uparrow\downarrow \\ & & & & \mathrm{HClO}\text{ (vapor)} \end{array}$$

The action of sulphuric acid upon sodium chloride may be cited as another example of the production of a volatile product. Hydrogen chloride is, in fact, soluble in water with marked dissociation; these conditions, however, are reversed in this mixture of concentrated sulphuric acid and salt.

(2)

(3)

62. The Hydrogen and the Hydroxide Ions

a. In **59** *b* the conductivity of pure water was found to be negligible. In water, therefore, the hydrogen and hydroxide ions are present only in the slightest concentration. The effect of water upon litmus and upon phenolphthalein is nil.

b. Test a solution of dry hydrogen chloride in toluene with litmus paper and with phenolphthalein (*1*).

Try, also, its action upon a piece of dry marble (*2*).

Try, also, its action upon a piece of magnesium (*3*).

Compare these results with those found for the hydrogen chloride in aqueous solution, as in **39** (*4*).

What ion present in the aqueous solution is characteristic of hydrochloric acid and all acids (*5*)?

c. Dissolve a very small piece of sodium hydroxide in a few cc. of water. Examine the solution in its action to litmus, and also to phenolphthalein (*6*).

What ion is characteristic of sodium hydroxide solution and all bases (*7*)?

d. Solutions which contain per liter that amount of an acid just sufficient to give 1.01 g. of ionizable hydrogen, or that amount of a base just sufficient to give 17.01 g. of ionizable hydroxyl are called normal [R. 23].

63. Union of the Hydrogen and Hydroxide Ions; Neutralization. [Two Students Working Together]

a. Clean a burette and pour into it about 50 cc. of normal sodium hydroxide solution [Special]. One liter of this solution should contain 40 g. of sodium hydroxide. If the solution provided is not strictly normal, a "normality factor" for its concentration will be given.

(*1*)
(*2*)
(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

Clean the graduated cylinder, pour into it 10 cc. of concentrated hydrochloric acid and then sufficient water to make up a volume of 50 cc. of this diluted acid. Transfer this solution to a second burette.

Read the volumes in both burettes (*1*) and run into a small beaker about 15 cc. of the solution from the burette containing the acid (*2*). Add one or two drops of phenolphthalein and then, bringing the beaker under the burette which contains the alkali, allow this alkaline solution to run into the acid solution, drop by drop, during constant stirring, until the faintest perceptible pink tinge is acquired by the whole solution. Record the reading of the burette containing the alkali (*3*). If unsuccessful in the first attempt, it is well to start with another portion of acid from the second burette and titrate again against the alkaline solution.

When the end-point, as shown by the color of the phenolphthalein, is reached, concentrate the solution upon a sand-bath until crystallization begins. Test the solution with litmus paper (*4*).

Remove a sample of the crystals and examine them with a lens (*5*).

By reference to the diagram below (for a decinormal solution) state what ions are removed when an acid and a base neutralize each other (*6*).

$$\begin{array}{lcccl}
 & (84\%) & & (0.0_6 1\%) & \\
(10\%)\ \mathrm{NaOH} \rightleftarrows & \mathrm{Na}^+ & + & \mathrm{OH}^- & (90\%) \\
(9\%)\ \mathrm{HCl} \rightleftarrows & \mathrm{Cl}^- & + & \mathrm{H}^+ & (91\%) \\
 & \updownarrows & & \updownarrows & \\
 & \mathrm{NaCl} & & \mathrm{H_2O} & \\
 & (16\%) & & (100-\%) &
\end{array}$$

Burette containing acid

Final reading = 21.8

(*1*) Initial reading = 6.8

(*2*) Acid taken = 15

Burette containing alkali

(*3*) Final reading = 32.2

(*1*) Initial reading = 3.5

Alkali taken = 28.7

(*4*) basic; turned red litmus blue

(*5*) They are NaCl or salt

(*6*) When an acid and a base neutralize each other the OH^- and H^+ are removed.

Eliminating the ionogens and ions not concerned in the direct process of neutralization construct an equation to apply for neutralization of acids and bases in general (*7*).

Define neutralization in terms of the ionic hypothesis (*8*).

b. Assuming the alkaline solution, as made up in *a*, to be approximately normal and knowing the volume of this alkaline solution required for the neutralization of a given volume of acid solution, calculate the number of cc. of the normal alkaline solution required for neutralization of 1 cc. of the acid solution. The value thus obtained is based upon the acid solution as unity and gives directly the normality of this acid solution (*9*).

c. From the volume of acid solution prepared and the volume of concentrated acid used in its preparation estimate the normality of concentrated hydrochloric acid (*10*).

d. Calculate the number of grams of hydrogen chloride per liter in the diluted acid (*11*).

Calculate, also, the weight of this substance in one liter of the concentrated hydrochloric acid (*12*).

e. Consider, for example, the slightly ionized acetic acid (see **59** *f*). Will its neutralization with an alkali proceed as rapidly as the neutralization of the highly dissociated hydrochloric acid (usually known, therefore, as a strong acid) [R. 23] (*13*)?

Will one liter of normal solution of any acid require the same amount of an alkali for complete neutralization (*14*)?

f. Consider, also, the slightly ionized ammonium hydroxide. In what way only will its neutralization by an acid differ from that of any more active base (known as a strong base) (*15*)?

g. A table in the Appendix (VI) contains a list of iono-

(7) $(\text{melul})_n\, OH_x + H_z(-\text{radica})_w \rightarrow$ base + water

(8)

(9)

(10)

(11)

(12)

(13)

(14)

(15)

[redacted]

gens, and the degree of dissociation for them in decinormal concentration. From this table one may predict what changes are likely to occur upon mixing various ionogens. The figures in parentheses in the diagram just given (in *a*) clearly indicate the great tendency for the formation of a slightly ionized product, water.

64. Discharge of Ions. [11]

a. Into a test-tube containing a few cc. of diluted cupric sulphate solution drop a granule or two of zinc and allow the action to proceed till the blue color has disappeared. What is the dark precipitate here formed [R. 25] (*1*)?

Filter off the precipitate and evaporate the clear solution to dryness upon a sand-bath. Compare the product here with that obtained in **11** *e* (*2*).

Express by an equation the reaction between cupric ion and metallic zinc (*3*).

What other metals will act in this way upon cupric ion (see Appendix III) (*4*)?

b. Into a test-tube containing 1 or 2 cc. of silver nitrate solution drop a few disks of copper. What is the precipitate here formed [R. 26] (*5*)?

Allow the reaction to proceed till a blue color appears (a slight warming will hasten this reaction), and then filter off the precipitate and test the clear solution for argentic ion (*6*).

What ions are present in this filtrate (*7*)?

Construct an equation to explain this action of copper upon the ionized silver nitrate (*8*).

What becomes of the molecular or non-ionized silver nitrate (*9*)?

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

c. By reference to **12** state the action of zinc and other metals upon hydrogen ion (*10*).

Explain in terms of the ionic hypothesis the differences in activity of the various metals examined (*11*).

Construct a list of the more common metals in the order of their decreasing ability to discharge hydrogen ion (*12*).

Where do copper and silver come in this series (of displacements) in which hydrogen also is to be given a position [R. 27] (*13*)?

d. By reference to **13** *b* relate the action of zinc upon acetic acid (a weak acid) with the action of this metal upon a strong acid (as in **11**), and account for this difference (*14*).

Compare the action of acetic acid here with its action in the presence of bases as in **63** *e* (*15*).

e. Recall the action of chlorine upon the bromide radical, — that is, the bromide ion, and also the action of bromine upon the iodide ion (**49** *h*), and again the action of iodine upon the sulphide ion (**48**). Arrange these four elements (chlorine, bromine, iodine, and sulphur) in a series which shows their decreasing ability to take an electric charge (*16*).

In such an electromotive series of the nonmetals where would fluorine be placed [R. 28] (*17*)?

From observation in **48** what would you judge to be the approximate position of oxygen in this series [R. 29] (*18*)?

f. In addition to the discharge of an ion by another element higher up in the electromotive series, we may consider the discharge of an ion by the action of an electric current alone. Thus, in the electrolysis of cupric chloride the cupric ions will be discharged at the negative pole and metallic copper deposited. The chloride ions will be discharged and liberated as chlorine at the positive pole.

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

In the case of the discharge of many ions, especially the complex ions, the free substances thus liberated will undergo secondary reactions with the solvent. Explain in this way, by a series of equations, the production of hydrogen at the negative pole and oxygen at the positive pole when a solution of sodium sulphate is electrolyzed (*19*).

If the lamp-board in **59** were to be replaced by another electrolytic cell the electrolysis of sulphuric acid should here be explained by a series of equations (*20*).

g. The discharge of an ion often proceeds spontaneously. Recall the action of manganese dioxide upon hydrochloric acid (**35** *a*) and note the decomposition of Mn^{++++} into Mn^{++} [R. 30]. Construct an equation from the ionic standpoint to show this decomposition of manganese tetrachloride (*21*).

65. Formation and Decomposition of Complex Ions. [III]

a. Recall the action of ammonia upon the silver ion, as shown in **58** *c*, to produce the complex ammonioargentic ion, $Ag(NH_3)_2^+$. What was the action of heat upon this complex ion (*1*)?

Express the decomposition of this complex ion by an equation (*2*).

b. Recall the action of heat upon hypochlorite ions (**54** *a*) and express by an equation the consequent production of chlorate and chloride ions from hypochlorite ions (*3*).

c. Express by a simple equation, involving the loss of oxygen, the decomposition of the dichromate ion $(Cr_2O_7)^{--}$ into chromic ion Cr^{+++} as illustrated in **69** *f* [R. 31] (*4*).

d. Express by a simple equation, involving the loss of oxygen, the decomposition of the permanganate ion $(MnO_4)^-$ into manganous ion Mn^{++} (see **56** *c*) [R. 32] (*5*).

(*19*)

(*20*)

(*21*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

66. Ionic and Non-ionic Actions

Recall the action of zinc upon concentrated sulphuric acid (see **13**). The production of sulphur products by the action of this metal upon molecular sulphuric acid may be accompanied also by the ionic reaction between the metal and hydrogen ion (in slight concentration), resulting in the discharge of the latter.

Repeat **13** *a* and try, also, the action of magnesium ribbon upon concentrated sulphuric acid; note if the ionic action in this case is more apparent (*1*).

How would you classify that action illustrated in **59** *b* where a solution of potassium bromate, sulphuric acid, and iodine were brought together (*2*)?

(*1*)

(*2*)

N

CHAPTER XII

SULPHUR

67. Sulphur

a. Place a very small piece of roll sulphur in a test-tube, add a few cc. of carbon disulphide and shake. Pour off the clear solution into a watch-glass and allow evaporation to take place spontaneously [Hood].

Examine the product with a lens and make a drawing of a single crystal (*1*).

Are the crystals transparent (*2*)?

Do they remain transparent after one or two days (*3*)?

b. Half fill a porcelain crucible with roll sulphur, set it upon a ring-stand and apply a gentle heat until all the sulphur has just melted. Remove the flame and allow the molten sulphur to cool just to that point where a crystalline crust has formed upon the surface. Puncture this crust and pour out the molten sulphur into a beaker of water, setting the beaker and this product aside for *c.*

Examine now the crystals adhering to the sides of the crucible and compare them with the crystals obtained in *a*, making a drawing of one of them (*4*):

Are the crystals transparent (*5*)?

Do they remain transparent after a day or two (*6*)?

Account for any change that may be observed (*7*).

c. Remove the yellow solidified sulphur from the beaker of water set aside in *b.* Dry the product between filter

(*1*)
(*2*)
(*3*)

(*4*)
(*5*)
(*6*)
(*7*)

papers and test its solubility in carbon disulphide exactly as described in *a* (*8*).

d. Place about 10 g. of roll sulphur in a test-tube and heat the tube strongly. Observe that the liquid becomes dark and viscous (about 200–250°); but as the temperature rises it again becomes limpid and finally boils (about 445°). Pour out the boiling liquid (burning vapors here do not interfere with the results) into a beaker of water. Dry the product between filter papers and divide into two portions. Test the solubility of one portion in carbon disulphide (collecting on a watch-glass a portion of the clear solution for spontaneous evaporation) (*9*).

Allow the second portion to stand for a day or two and again test its solubility in carbon disulphide (*10*).

Remove a portion of the sulphur adhering to the walls of the test-tube, from which the molten sulphur was poured, and test the solubility of this slowly cooled sulphur in carbon disulphide, comparing the solubility here with that of roll sulphur in *a*, (*11*).

Enumerate these various modifications obtained during the heating of sulphur and explain the differing results of rapid and slow cooling [R. 33] (*12*).

68. Hydrogen Sulphide. [Hood]

a. The combination of metals with sulphur to form sulphides has been studied in **5** and **6**. Take now a very small sample of ferrous sulphide from the side-shelf and drop it into about 1 cc. of dilute hydrochloric acid in a test-tube. Note the odor of the gas evolved (*1*).

Dip a strip of filter paper in a solution of lead nitrate and apply this prepared strip to the mouth of the tube (the

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)

[redacted]

formation of a black lead sulphide serves as a test for the presence of hydrogen sulphide) (*2*).

Hold a silver coin in the vapors at the mouth of the test-tube (silver sulphide also is black) [R. 34] (*3*).

Construct an equation for the reaction between silver and hydrogen sulphide in the presence of oxygen (*4*).

b. Attach a glass nozzle to a Kipp's apparatus furnishing hydrogen sulphide, or to the laboratory supply. When all air has been displaced from the apparatus (or tubing) ignite the gas at the tip of nozzle and note color of flame (*5*).

Hold a cool porcelain dish in the middle of the flame for a few moments. Withdraw dish and examine deposit (*6*).

If this deposit is made in the interior region of the flame, what may we assume to be the stability of hydrogen sulphide at the temperature of the burning gas (*7*)?

Construct an equation for the simple decomposition of hydrogen sulphide (*8*).

Construct an equation for the complete combustion of this gas (*9*).

Construct an equation for its partial combustion with the deposition of sulphur, as just observed (*10*).

c. The combination of certain sulphides with sulphur may lead to polysulphides. Place a small crystal of sodium sulphide in a test-tube, add a few cc. of water and then a pinch of powdered sulphur. Shake well and filter. To the clear filtrate add dilute hydrochloric acid and note odor of gas evolved (*11*).

What product is observed in suspension in the acidified mixture (*12*)?

In general, polysulphides, when decomposed by acids, react in this manner.

(2) $Pb(NO_3)_2 + H_2S \rightarrow \underset{\text{black}}{PbS\downarrow} + 2HNO_3$

(3) $2Ag + H_2S + O \rightarrow Ag_2S + H_2O$

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)

69. Properties of Aqueous Hydrogen Sulphide. [Hydrosulphuric Acid]

a. Saturate about 15 cc. of water in a test-tube with hydrogen sulphide. (Clean carefully the test-tube and also the glass tubing through which the gas is delivered from the Kipp's apparatus or laboratory supply.) Test the solution thus prepared with litmus paper (*1*).

Distribute the solution between three test-tubes for use in *b*, *c*, and *d*.

b. Boil vigorously one portion of the hydrosulphuric acid for a few minutes. From time to time note the odor of the solution and its reaction to litmus (*2*).

Compare this result with that found for hydrochloric acid in **39** *e* (*3*).

c. Into the second portion of hydrosulphuric acid drop 2–3 g. of powdered iron and shake well. Does the odor disappear rapidly (*4*)?

After a few minutes filter the mixture and wash the insoluble product upon the filter (pouring water upon the filter and allowing this water to run through) until there is no longer any odor of hydrogen sulphide. Then puncture the filter paper at its apex and wash this insoluble product into a test-tube by means of a little water. Add to the test-tube a little dilute hydrochloric acid and note odor (*5*).

Construct an equation for the action of hydrogen sulphide upon iron from the ionic standpoint (*6*).

Account for the slowness of this action of iron upon the hydrosulphuric acid [R. 35] (*7*).

Construct an equation for the action of hydrochloric acid upon the final insoluble product, illustrating by a diagram from the ionic standpoint (*8*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

d. Allow the third portion of the solution of hydrosulphuric acid to stand exposed to the air for several days and construct an equation to explain this result from the standpoint of the ionic hypothesis (*9*).

What relative positions are taken by oxygen and sulphur in the electromotive series of the nonmetals (see **64** *e*) (*10*)?

e. If **48** was performed, construct an equation from the standpoint of the ionic hypothesis to explain the results there obtained (*11*).

If **48** was not performed, place one small crystal of iodine in a test-tube, add a few cc. of water and saturate the mixture with hydrogen sulphide. Explain the result from the ionic standpoint (*11*).

Confirmation is here afforded for the relative positions already assigned to iodine and sulphur in the electromotive series of the nonmetals (see **64** *e*). What may we consider to be the action of bromine or chlorine upon hydrosulphuric acid (*12*)?

f. Place 2–3 cc. of potassium dichromate solution in a test-tube, add an equal volume of dilute sulphuric acid and saturate the solution with hydrogen sulphide. What product may be considered as present in the solution before the hydrogen sulphide was admitted (*13*)?

Account for the change in color and formation of precipitate [R. 36] (*14*).

By reference to *d*, *e*, **64** and also **65** *c*, state what ionic changes are brought into consideration (*15*).

g. Place 2–3 cc. of potassium permanganate solution in a test-tube, add an equal volume of dilute sulphuric acid and saturate this solution with hydrogen sulphide. What

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

product may be considered as present in the solution before the hydrogen sulphide was admitted (*16*)?

Account for the change in color and formation of precipitate [R. 37] (*17*).

By reference to *d*, *e*, **64** and also **65** *c*, state what ionic changes are brought into consideration (*18*).

70. Properties of the Sulphides of the Alkali Metals

a. Place 6–7 cc. of sodium hydroxide solution in a test-tube and saturate this solution with hydrogen sulphide. Distribute the final solution between four test-tubes for use in *b*, *c*, *d*, and *e*.

Construct an equation for the formation here of sodium hydrosulphide (*1*).

Test reaction of the solution to litmus (see *b* and *f*) (*2*).

How may the normal sodium sulphide be prepared from this solution of hydrosulphide (*3*)?

b. Warm one portion of the solution from *a* for a few minutes. Test for the escape of gas (*4*).

Construct an equation to explain this reaction (*5*).

Is the remaining solution more marked in its action upon litmus than the solution as first prepared in *a* (*6*)?

c. To the second portion of this solution add a little dilute hydrochloric acid (*7*).

Formulate this action from the ionic standpoint (*8*).

In what way does the escape of hydrogen sulphide affect the progress of the reaction (*9*)?

d. To a third portion of the sodium hydrogen sulphide solution add a pinch of powdered roll sulphur and shake well. Does any of the sulphur dissolve (solution here is indicated by the development of a yellow color) (*10*)?

(*16*)

(*17*)

(*18*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

Filter the solution thus obtained and acidify the filtrate with dilute hydrochloric acid (using an excess of acid) (*11*).

Compare this result with that in *b* (*12*).

Construct equations to explain the formation of gas and precipitate (*13*).

e. Allow the fourth portion of the solution from *a* to stand exposed to the air for several days. Account for any change in color that may be produced (*14*).

Construct equations to explain steps involved [R. 38] (*15*).

f. If heat, as in *b*, and dissolved oxygen, as in *e*, both tend to decompose sodium hydrogen sulphide, what conditions should be present to insure the purity of a solution of sodium hydrogen sulphide and its consequent neutral reaction to litmus (*16*)?

71. Hydrolysis

a. From **70** we learned that an aqueous solution containing only sodium hydrogen sulphide is neutral to litmus and, therefore, gives no perceptible amount of hydrogen ion. Dissolve a small piece of sodium sulphide in a few cc. of water and test the reaction of this solution to litmus (*1*).

What ionic substance is here shown to be present (*2*)?

Formulate the action between sodium sulphide and water from the standpoint of the ionic hypothesis (*3*).

What ionic substance is shown to be the less dissociated product (*4*)?

b. Formulate by a similar diagram the action of sodium hydrogen sulphide with hydrochloric acid, showing the hydrogen sulphide as the less dissociated product (*5*).

Formulate in the same way the action of hydrochloric acid upon sodium sulphide (*6*).

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

Does the escape of hydrogen sulphide materially aid in carrying these actions to completion (*7*)?

c. Dissolve a small crystal of ferric sulphate in a little water and test the reaction of this solution to litmus (*8*).

Assuming ferric hydroxide to be the least dissociated substance possible of formation, illustrate by a diagram from the ionic standpoint this metathesis between ferric sulphate and water (hydrolysis) (*9*).

d. Test the action of a solution of sodium chloride to litmus and account for the result (*10*).

72. Properties of the Sulphides of Heavy Metals

a. Place about 2 cc. of a cupric sulphate solution in a test-tube, dilute with 15–20 cc. of water, and saturate the solution with hydrogen sulphide (*1*).

Construct the equation for the reaction (*2*).

Pour a few cc. of this mixture into another test-tube and add thereto an excess of dilute sulphuric acid and shake (*3*).

Account for these two results from the standpoint of the ionic hypothesis (*4*).

b. Repeat *a*, substituting about 2 cc. of cadmium sulphate solution for the cupric sulphate solution. Construct the equation and account for the results (*5*).

c. Place about 2 cc. of zinc sulphate solution in a test-tube, dilute with 15–20 cc. of water, and saturate this solution with hydrogen sulphide (*6*).

Filter off the white precipitate of zinc sulphide and add to filtrate a few drops of ammonium hydroxide solution (*7*).

Construct the equation and account for this additional precipitation of zinc sulphide (*8*).

d. Dissolve a small crystal of ferrous ammonium sul-

(7)

(8)

(9)

(10)

(1)
(2)

(3)

(4)

(5)

(6)

(7)

(8)

o

phate in 10–15 cc. of water and saturate this solution with hydrogen sulphide. Construct an equation for the reaction possible, employing the simple formula of ferrous sulphate in place of that for the double salt (*9*).

How may this action be explained from the standpoint of the ionic hypothesis (*10*)?

Add a few drops of ammonium hydroxide solution to the reaction mixture at hand and account for the reaction (*11*).

e. Recall the action of sodium sulphide in aqueous solution and consider this sulphide as an example of that class of sulphides easily hydrolyzed. What two additional classes of sulphides may now be mentioned when reference is made directly to their degree of ionization as compared with that of hydrogen sulphide (*12*)?

73. Sulphur Dioxide

a. Heat your platinum wire, touch a bit of sulphur with the glowing end, and then introduce the adhering sulphur into the flame. Withdraw the wire and note the odor and flame of burning sulphur (*1*).

Write the equation for this combustion (*2*).

b. Heat a few particles of iron pyrites in a hard glass test-tube and determine the nature of the sublimate by examining it according to directions in *a* (*3*).

Determine, also, what gas is evolved (*4*).

74. The Preparation of Sulphuric Acid

Arrange an apparatus as in Fig. 16. *A* represents the 1-liter bottle, or a wide-mouthed bottle of about one liter capacity. This bottle should be carefully cleaned and rinsed with water but not thoroughly dried; a thin film of water,

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)
(*2*)

(*3*)
(*4*)

therefore, will still remain on the inside walls. Place about 5 g. of copper disks in each of the flasks *B* and *C*, and connect these flasks to the liter bottle, as shown in the figure. Pour into flask *B* about 10 cc. of concentrated nitric acid; the red fumes of nitrogen tetroxide will at once pass over into bottle *A*. Pour into flask *C* about 10 cc. of concentrated sulphuric acid and apply a flame beneath the flask.

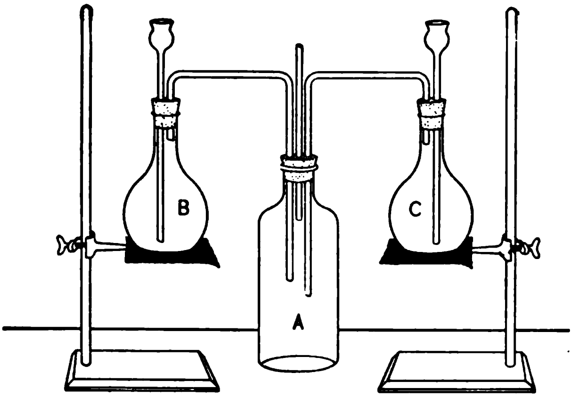


FIG. 16.

The sulphur dioxide thus generated should be driven over into bottle *A* until the red fumes therein are completely decolorized. Write an equation for the action at this stage (*1*).

[*Instructions:* If there are at hand laboratory supplies of nitric oxide and sulphur dioxide the generating of these gases may be dispensed with and flask *A* directly connected to the Kipp apparatus furnishing nitric oxide and to the metal cylinder furnishing sulphur dioxide. The oxygen of the air, which of course is present in flask *A*, serves for the oxidation of nitric oxide to nitrogen tetroxide.]

Disconnect flask *B* and replace it with a clean flask containing water only. Heat the water to boiling and allow

(1)

the steam to enter bottle *A*. If the fumes in bottle *A* are thoroughly decolorized by the presence of an excess of sulphur dioxide note again the appearance of red fumes upon the admission of this steam. Construct an equation for the reaction at this stage (*2*).

Finally pour out from the liter bottle this dilute sulphuric acid and evaporate it to a small volume in an evaporating dish set upon a sand-bath. Reserve for **75**.

75. Properties of Sulphuric Acid

a. Pour into a watch-glass a few drops of concentrated sulphuric acid, as prepared in **74**, or of the acid on your desk, and dip a match stick into it. Write with this acid upon a piece of paper and set both match stick and paper aside in a warm place. Describe the property of the acid here observed (*1*).

b. Test the action of the acid, as prepared in **74**, or obtained from the desk, to litmus paper (*2*).

c. Dilute a little of the acid, either from **74** or from the desk, with water, add to it a few drops of a barium chloride solution and construct the equation for the reaction (*3*).

Ascertain if this action is reversible by adding considerable dilute hydrochloric acid to the mixture (*4*).

The formation of a white precipitate in the presence of hydrochloric acid constitutes an admirable test for the presence of the sulphate radical. Test a few drops of a solution of any sulphate with barium chloride (*5*).

76. Reduction of Sulphuric Acid

a. Place a small piece of sulphur in a test-tube containing 2–3 cc. of concentrated sulphuric acid and heat the mixture. Note the odor (*1*).

(2)

(1)

(2)

(3)

(4)

(5)

(1)

Construct an equation for the oxidation of sulphur to sulphur dioxide by means of sulphuric acid (*2*).

b. Place a little charcoal in a test-tube containing 2–3 cc. of concentrated sulphuric acid and heat in a similar manner as in *a.* Note the odor and state whether carbon acts in the same way as the sulphur employed in *a* (*3*).

Construct an equation for the oxidation of carbon to carbon dioxide by means of sulphuric acid (*4*).

c. Place a few disks of copper in a test-tube, add about 1 cc. of concentrated sulphuric acid, and heat the mixture. Note the odor (*5*).

Construct an equation for the oxidation of copper to cupric oxide by means of sulphuric acid (*6*).

Construct an equation for the action of sulphuric acid upon this oxide (*7*).

Combine these equations for the complete reaction between copper and sulphuric acid (*8*).

d. Pass a current of hydrogen sulphide through 2–3 cc. of concentrated sulphuric acid in a test-tube. The formation of sulphur dioxide is apparent and is here accompanied by the precipitation of sulphur. Construct, therefore, an equation for this simple reduction of sulphuric acid by the action of hydrogen sulphide above (*9*).

e. Pulverize a small crystal of potassium bromide, place it in a test-tube and add thereto a few drops of concentrated sulphuric acid. Warm the mixture and breathe across the mouth of the tube in order to detect the possible presence of a halide acid (*10*).

Note, also, the marked odor evolved and the color of the heavy vapors (*11*).

Assuming that hydrogen bromide is here first liberated,

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

construct an equation for the reduction of sulphuric acid by the action of this gas (*12*).

Is the decomposition of hydrogen bromide sufficient to furnish a concentration of active hydrogen that will reduce sulphuric acid beyond the stage of sulphurous acid (sulphur dioxide)? Ascertain by examining the walls of the tube for the presence of free sulphur, and the issuing vapors for the presence of hydrogen sulphide (use here as a test a strip of filter paper moistened with lead nitrate solution) (*13*).

f. Pulverize a small crystal of potassium iodide, place it in a test-tube and add a few drops of concentrated sulphuric acid. Warm the mixture and breathe across the mouth of the tube to detect the presence of a halide acid (*14*).

Note odor of gases evolved and color of heavy vapors (*15*).

Apply to the mouth of the tube a strip of filter paper moistened with lead nitrate solution and examine this for colored precipitates which may indicate the presence of hydrogen sulphide and hydrogen iodide (*16*).

Construct an equation for the complete reduction of sulphuric acid by the action of hydrogen iodide (*17*).

The reduction products of sulphuric acid may react with concentrated sulphuric acid still present in the manner as determined in *a* and *d*. Construct, therefore, the equation for the reduction of sulphuric acid by means of hydrogen sulphide and ascertain, by studying the odors and the condensations upon the walls of the test-tube, if the expected products are present (*18*).

Enumerate all of the products which can be identified in the reaction of hydrogen iodide upon concentrated sulphuric acid (*19*).

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

77. Primary and Secondary Sodium Sulphates. [Two Students Working Together]

a. Pour very slowly and with constant stirring about 5 cc. of concentrated sulphuric acid into 40–45 cc. of water in a beaker. When the warm solution has reached the temperature of the laboratory transfer it to a burette. Into a second burette pour 25–30 cc. of the standard sodium hydroxide solution supplied in the laboratory [Special].

Ascertain what volume of the alkaline solution will just neutralize 5 cc. of the acid solution (*1*).

Concentrate this neutralized portion to a small volume in an evaporating dish and set aside to crystallize. Dry the crystals on a filter paper.

b. Run out a volume of the same acid solution twice as large as that used in *a* (that is, 10 cc.), and then run into this acid solution the same volume of the standard alkaline solution as used in *a* (*1*).

Set the beaker or evaporating dish containing the mixture upon a water-bath and concentrate to small volume and then set aside to crystallize. Filter off the crystals and dry them upon filter paper, as before.

c. Compare the crystals from *a* and *b* as to form (*2*), taste (*3*), and reaction of their aqueous solutions to litmus (*4*). Confirm these results by studying the same properties of the pure substances or solutions of these.

Account for the difference in action to litmus displayed between the aqueous solutions of these two substances (*5*).

d. Calculate the weight of either salt required per liter of solution in order to give a normal aqueous solution of each salt in respect to: Sodium ion, hydrogen ion (if any), and sulphate ion (*6*).

(1)

(1)

(2)

(3)

(4)

(5)

(6)

e. What is the effect of heat upon perfectly dry specimens of sodium hydrogen sulphate [R. 39] (*7*), and also upon sodium sulphate (*8*)?

f. What is the effect of heat upon sulphates of weak bases? Determine by heating strongly [Hood] with a blast lamp a small quantity of ferric sulphate contained in a porcelain crucible. Disregard the water first driven off (*9*).

78. Properties of Sulphurous Acid

a. From the laboratory supply of liquid sulphur dioxide pass a stream of this gas into 20–25 cc. of water in a test-tube. Note the odor of the solution (*1*).

Distribute the solution between six test-tubes for use in *b*, *c*, *d*, *e*, *f*, and *g*.

b. Test the reaction of one portion of the sulphurous acid solution to litmus (*2*).

Boil the solution for a few minutes and note the odor and the action to litmus as this boiling proceeds (*3*).

In this respect does the aqueous solution of sulphur dioxide resemble that of hydrogen chloride or hydrogen sulphide (*4*)?

c. To a second portion add barium hydroxide solution and construct an equation for the reaction (*5*).

Add a few drops of dilute hydrochloric acid to this mixture and note, by the odor, what gas is evolved (equation) (*6*).

d. To another portion add barium chloride solution and account for the slight precipitation in this case (*7*).

e. To the fourth portion add a little hydrogen peroxide solution and test for the presence of sulphate ion (*8*).

Construct equation for the oxidation of sulphite ion (*9*).

(7)

(8)

(9)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

f. To the fifth portion add a little bromine-water until the color is permanent; then test for sulphate ion (*10*).

Construct an equation for the oxidation of sulphite ion by bromine-water (*11*).

g. Allow the sixth portion of the sulphurous acid solution to stand exposed to air for a day or two. After this time ascertain by warming if any perceptible odor of sulphur dioxide indicates still the presence of sulphurous acid in the solution (*12*).

Test, also, for the possible presence of the sulphate ion and account for its formation in this case (*13*).

h. Acidify 2–3 cc. of potassium dichromate solution with an equal volume of dilute sulphuric acid. What substance is now to be considered present in the solution (*14*)?

Pass a stream of sulphur dioxide through this acidified mixture until no further change is observed. Construct an equation for this reduction of the acidified potassium dichromate by means of sulphurous acid (*15*).

i. Repeat *h*, substituting 2–3 cc. of potassium permanganate solution for the potassium dichromate solution. Treat the acidified solution with sulphur dioxide and construct the equation for the reaction (*16*).

j. Fill a wide-mouthed bottle with sulphur dioxide by upward displacement of air, and then introduce into this jar small pieces of moistened calico, litmus paper, or grass. State the effect of sulphurous acid upon these objects (*17*).

79. Sulphites

a. Dissolve about 2 g. of sodium sulphite in 8–10 cc. of water in a test-tube. Test the reaction of this solution to litmus and explain by reference to the ionic hypothesis (*1*).

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*1*)

P

Divide solution into three portions for use in *b*, *c*, and *d*.

b. To one portion of the sodium sulphite solution add a few drops of dilute hydrochloric acid and note odor (*2*).

Construct the equation for this action (*3*).

c. To the second portion add a few cc. of hydrogen peroxide solution and shake well. Add now a little barium chloride solution and an excess of dilute hydrochloric acid (*4*).

What is the effect of hydrogen peroxide upon the sulphite ion (see **78** *e*) (*5*)?

d. To the third portion of the solution add a little bromine-water till the red color is permanent, then heat the solution to remove this excess of bromine and add barium chloride solution with an excess of hydrochloric acid (*6*).

Construct an equation to show the oxidizing action of bromine-water upon the sulphite ion and compare the result with that in **78** *f* (*7*).

e. Strongly heat about 1 g. of sodium sulphite in a porcelain crucible over a blast lamp. When cool acidify residue with dilute hydrochloric acid and note odor (*8*).

What salt, therefore, was formed in this fusion (*9*)?

Pour out the acidified mixture into a test-tube and test for the presence of the sulphate ion (*10*).

The oxidation of a portion of the sodium sulphite is accomplished at the expense of another (the reduced) portion. Construct an equation to indicate this decomposition (*11*).

If any free sulphur is observed in the acidified mixture how may its presence be accounted for (*12*)?

What reaction may first be expected upon heating a hydrogen sulphite salt (*13*)?

What can you say of the relative stability of sulphates and sulphites (*14*)?

(*2*)
(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)
(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

80. Thiosulphates

a. Dissolve about 5 g. of sodium sulphite in 15–20 cc. of water in a small flask. Add 3–4 g. of powdered sulphur to the solution and boil the mixture over a small flame for 10 to 15 minutes. Filter and acidify one portion of the filtrate with dilute hydrochloric acid. Note the odor (*1*).

Construct, first, an equation for the liberation of thiosulphuric acid by the action of the hydrochloric acid (*2*).

Construct, also, an equation for the decomposition of this thiosulphuric acid into sulphurous acid and sulphur (*3*).

b. Into the second portion of the sodium thiosulphate solution drop a small crystal of iodine and shake well. Construct an equation for the reaction (*4*).

How may we identify the presence of an iodide in this final solution (*5*)?

81. Reduction of Sulphur Compounds

Select about 1 g. of any salt of a sulphur oxy-acid; mix it with an equal quantity of anhydrous sodium carbonate and moisten the mixture with water. Slightly char the end of a match stick, or preferably select one of the charred splints specially provided, and insert the charred end of the stick into the moistened mixture. Introduce the mixture, now adhering to the charred end, into the reducing portion of a small Bunsen flame and heat it gently. Remove the heated mass to a clean silver coin lying in a watch-glass and with one drop of water moisten the hot mass while in contact with the coin. Examine the coin for the appearance of any black silver sulphide (*1*).

Add a drop of dilute hydrochloric acid; note odor (*2*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*1*)
(*2*)

Construct an equation for the reduction of a sulphate by means of carbon (*3*).

Construct also an equation for this "hepar" test reaction between silver and the hydrogen sulphide in the presence of oxygen (*4*).

82. Preliminary Identification of Negative Radicals

Obtain [Instructor] an unknown salt and examine it. The positive radicals need not be considered, as only the more or less soluble salts of sodium, potassium, or calcium will be used. Of the negative radicals, — anions, so far discussed, the following will be presented:

Hydroxide
Chloride
Bromide
Iodide
Chlorate
Bromate
Iodate
Peroxide
Sulphide
Polysulphide
Sulphite
Sulphate
Thiosulphate

Examine the salt and record your observations as indicated.

a. Appearance: Form, color, and odor of compounds to be noted (*1*).

b. Solubility: Dissolve a few particles of the salt in water, heating if necessary (*2*).

Test the aqueous solutions with litmus (*3*).

c. Stability: Heat a few particles of the compound in a dry test-tube. Note changes in the substance (*4*).

Note the evolution of gas or vapors (*5*).

If water vapor alone is evolved the vapor will give a neutral reaction to litmus (*6*).

(3)

(4)

(1)

(2)

(3)

(4)

(5)

(6)

A colorless, odorless gas may be oxygen from a peroxide, a chlorate, bromate, or iodate (*7*).

d. Reaction to Moderately Dilute Sulphuric Acid: Place a few particles of the substance in a test-tube, add 1–2 cc. of water, and then an equal volume of a diluted sulphuric acid (1 part concentrated acid : 1 part water), and warm (*8*).

A colorless gas fuming in moist air may be a halide acid from a chloride, bromide, or iodide (*9*).

A colorless gas which does not fume, but possesses marked odor, may be hydrogen sulphide or sulphur dioxide from a sulphide, polysulphide, sulphite, or thiosulphate (*10*).

A colorless, odorless gas:—oxygen from a peroxide (*11*).

A colored gas may be the vapor of bromine or iodine from the corresponding halides (*12*).

A precipitation of sulphur indicates polysulphides or thiosulphate (*13*).

Absence of reaction would indicate a sulphate or a hydroxide, — the base itself (*14*).

e. Reactions to Silver Nitrate (in presence of dilute nitric acid): Dissolve a few particles of the substance in water, and add to the solution a few drops of dilute nitric acid and then a few drops of silver nitrate solution (*15*).

A white to yellow precipitate indicates chloride, bromide, iodide, bromate, or iodate (*16*).

A black precipitate indicates sulphide, polysulphide, or thiosulphate (soluble in concentrated nitric acid) (*17*).

f. Reaction to Barium Chloride (in presence of dilute hydrochloric acid): Dissolve a few particles of the substance in water and add to the solution a few drops of dilute hydrochloric acid and then barium chloride solution (*18*).

A white precipitate indicates a sulphate (*19*).

(7)

(8)

(9)

(10)
(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)
(19)

CHAPTER XIII

NITROGEN AND AMMONIA

83. Determination of the Proportion by Volume of Oxygen in Air

The withdrawal of oxygen from a definite volume of air is accomplished by the use of a freshly prepared alkaline solution of potassium pyrogallate.

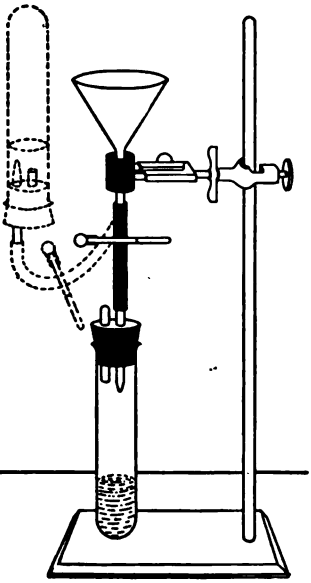


Fig. 17.

Provide your large test-tube with a closely-fitting two-hole cork. Attach a short piece of rubber tubing, bearing a pinch clamp, to the stem of a glass funnel, and then attach the other end of this rubber tubing to a short piece of glass tubing (preferably a glass nozzle) which, in turn, is to be fitted into one hole of the cork. Close the other hole in the cork with a glass rod. Neither glass rod nor glass tubing should extend appreciably beneath the under surface of

the cork. Support the funnel in a clamp on a ring-stand and, when all is arranged as in Fig. 17, pour a little water into the funnel, open the clamp, and test for air-tightness. If the apparatus is air-tight remove the water, return the funnel and stopper attachment to the position indicated, and withdraw the glass rod from the stopper.

Prepare at once the potassium pyrogallate solution by mixing 3 cc. of the pyrogallol solution [Special] with 20 cc. of the concentrated potassium hydroxide solution [Special]. Pour this mixture at once into the funnel, open the clamp just enough to allow the glass tubing and rubber connection to be filled with the brown solution, then firmly attach the test-tube to the cork and reinsert the glass rod, thus inclosing a volume of air equal to the content of the test-tube up to the bottom of the cork.

[*Instructions:* Hold the test-tube during these operations by the rim or by means of a test-tube holder; warming the test-tube by contact with the hands will interfere with correct readings.]

Now open the clamp and allow a few drops of the pyrogallate solution to enter the test-tube. As oxygen is absorbed a partial vacuum is produced and more of the solution may be admitted. When the liquid ceases to enter the tube close the clamp and invert the tube once or twice to the position indicated by the dotted lines in the figure. The liquid is thus brought thoroughly in contact with the inclosed air. Return the test-tube to its original position and allow more of the liquid to enter if possible. Finally invert the test-tube, reopen the clamp, and equalize the levels of liquid in test-tube and funnel by raising or lowering the former. Then close the clamp and return the test-tube to its original position. By means of paper labels or rubber bands mark

[redacted]

the height of the liquid in the tube and also the lowermost point to which the bottom of the cork extends.

Disconnect the test-tube and wash out the brown solution. By use of a burette measure the volume of water required to fill the test-tube, first to the lower mark, or that volume representing the oxygen absorbed (*1*), and second to the upper mark, or that volume representing the inclosed air (*2*).

Calculate the percentage of oxygen by volume in the inclosed volume of air (*3*).

That volume determined by difference represents the nitrogen (together with small quantities of the rarer gases) in the atmosphere.

84. Other Components of the Atmosphere

a. Expose a piece of calcium chloride on a watch-glass to the air. Note the appearance of the salt after two or three hours and explain (*1*).

b. Pour a few cc. of barium hydroxide solution into a watch-glass and expose to the air for an hour or more; explain [R. 39] (*2*).

c. Repeat *b*, blowing air from the lungs over the watch-glass containing the barium hydroxide solution (*3*).

85. Preparation of Nitrogen and a Nitride. [Two Students Working Together]

a. Fit a 250 cc. flask with a safety tube and delivery tube, as shown in Fig. 4. By means of a clamp about the neck attach the flask to a ring-stand. If *b* is to be performed insert between the flask and delivery tube a U-tube containing calcium chloride for drying the gas.

(*1*)

(*2*)

(*3*)

(*1*)

(*2*)

(*3*)

Place in the flask about 10 g. of sodium nitrite and about 8 g. of ammonium chloride; add 12–15 cc. of water and warm gently. In order to prevent a too rapid evolution of nitrogen it will be necessary to have a dish of cold water close at hand. As soon as the reaction begins bring the dish of water close under the flask, thus immersing the lower part of the flask in the water. After a few seconds remove the dish but return it at any time the evolution of gas is not proceeding uniformly. When sufficient time has elapsed for the displacement of air from the apparatus fill a bottle, previously inverted over a pneumatic trough, with the gas. Remove the bottle and note if this gas possesses an odor (*1*).

Insert a lighted splint into the bottle of nitrogen and state whether or not the gas supports combustion (*2*).

b. Fit a piece of hard glass tubing with two one-hole corks and glass tubing, as shown in Fig. 5. Slide a porcelain boat, about one third filled with powdered magnesium, to the center of this tube and connect the dry nitrogen supply from *a* to one end of the tube. Strongly heat the tube just under the boat, using two Bunsen burners. When all action is over note the color of product in the boat (*3*).

Does nitrogen support combustion in this case (*4*)? If so, construct an equation for the action (*5*).

What may be expected to result when magnesium burns in air (*6*)?

Account for any dark spots appearing on the inside walls of the glass tubing near the boat [R, 40] (*7*).

Transfer the porcelain boat, when cooled, to a dry test-tube, close the tube with a cork, and reserve for **86** *a*.

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

86. Ammonia

a. Add a few drops of water to the magnesium nitride prepared in **85** *b*. Note the odor evolved (*1*).

Construct an equation for the formation of ammonia from a nitride and water (*2*).

b. Strongly heat a small piece of gelatin in a test-tube and note the odor evolved (*3*).

c. Fit a 250 cc. flask with cork and exit tube and connect the latter directly to a U-tube containing just sufficient water to close the bend. The apparatus should be tested for air-tightness. Place in the flask a mixture of about 10 g. each of powdered lime and ammonium chloride, and warm gently [Hood]. As ammonia is evolved it will dissolve in the water in the U-tube. Construct the equation for this action (*4*).

Save the solution for **87** *a*, *b*, *c*, and *d*.

87. Ammonium Salts

a. Test the solution prepared in **86** *c* with litmus and account for the presence of the ion thus identified (*1*).

Hold a glass rod moistened with hydrochloric acid over this solution and construct an equation for the action (*2*).

b. Heat a few cc. of this same solution in a test-tube for a few minutes. Note odor, effect upon litmus, and reaction with hydrogen chloride as the warming proceeds (*3*).

c. Expose a few cc. of the solution to the air in a watch-glass for a few hours. Note, finally, its odor and action to litmus and reactivity towards hydrogen chloride (*4*).

In this respect does the solution of ammonia resemble an aqueous solution of hydrogen chloride, hydrogen sulphide, or sulphur dioxide (*5*)?

(*1*)

(*2*)

(*3*)

(*4*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

d. Neutralize the remaining portion of the ammoniacal solution with dilute sulphuric acid and evaporate this to dryness over a water-bath. Illustrate by reference to the ionic hypothesis the course of this neutralization of ammonium hydroxide (*6*).

Scrape the residue, left upon evaporation, toward the middle of the dish and invert over it a small funnel (the stem of which should be closed with a paper plug). Heat the dish with a small flame directly beneath its center, and observe the formation of a sublimate on the inside walls of the funnel. Examine this sublimate and test it for the presence of the ammonium and sulphate radicals (*7*).

Is the sublimate identical with the original product (*8*)?

e. Into a test-tube containing 1–2 cc. of an ammonium chloride solution pour 1–2 cc. of a sodium hydroxide solution. Note odor (*9*).

Explain the formation of this inactive base by reference to the ionic hypothesis (*10*).

This evolution of ammonia, by the action of a strong base upon an ammonium salt, as just determined, constitutes a distinctive test for the presence of the ammonium radical.

88. Dissociation of an Ammonium Salt

Place a little ammonium chloride into the middle region of an open hard glass tube, and, clasping this tube near one end by means of a clamp, support it at a slightly inclined angle (5°) upon a ring-stand. Insert moistened litmus paper of both colors in each end of the tube and heat the tube strongly at the middle. Observe carefully the effect of the issuing vapors upon the litmus paper (*1*).

What is the action of heat upon ammonium chloride (*2*)?

(*6*)

(*7*)
(*8*)

(*9*)

(*10*)

(*1*)
(*2*)

Formulate equilibrium which is here to be considered (*3*).

What gas appeared first at the ends of the tube (*4*)?

Why does the same gas appear first at both upper and lower ends [R. 41] (*5*)?

Has gravity any influence upon these results (*6*)?

How do you reconcile this action of ammonium chloride with that of ammonium sulphate in **87** *d* (*7*)?

Would ammonium sulphate undergo a dissociation similar to that of ammonium chloride if heated in the tube (*8*)?

What ammonium salt already studied undergoes complete decomposition before dissociation is apparent (**85** *a*) (*9*)?

Compare here also another salt of ammonium (see **94** *a*) which gives practically no ammonia upon heating (*10*).

May we assume that the presence of ammonia in a decomposition product necessarily indicates the presence of the ammonium radical (see **86** *b*) (*11*)?

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

CHAPTER XIV

OXIDES AND OXYGEN ACIDS OF NITROGEN

89. Preparation of Nitric Acid. [Hood]

Procure a 125 cc. distilling flask [Storeroom] and place in it about 10–12 g. of sodium nitrate. Pour into the flask through a funnel about 10 cc. of concentrated sulphuric acid and support the flask by a clamp to a ring-stand; then cork the flask. Fill a small beaker with cold water, hold a test-tube in this water and allow the mouth of the test-tube to extend over the end of the side-arm of the distilling flask; it will be supported in this position by the buoyancy of the water in the beaker.

When the acid has permeated the entire mass of nitrate heat the flask gently until a few cc. of nitric acid have been collected in the test-tube receiver. Then remove this test-tube, close it with a cork, and set aside for **90**. Use extreme care to prevent any of this acid coming in contact with the skin. How does this acid distillate differ from the concentrated nitric acid of the laboratory [R. 42] (*1*)?

Is the reaction between sodium nitrate and sulphuric acid reversible [R. 43] (*2*)?

May other acids replace sulphuric acid in the preparation of nitric acid from a nitrate [R. 44] (*3*)?

90. Properties of Nitric Acid

a. Blow moist air from the breath across the mouth of the tube containing the distillate from **89** (or a little of the concentrated nitric acid from the desk) (*1*).

(*1*)

(*2*)

(*3*)

(*1*)

Lower a glass rod moistened with ammonium hydroxide solution into the mouth of test-tube containing the acid (*2*).

Test also the reaction of this acid to litmus (*3*).

b. Heat a few cc. of the acid prepared in **89** (or a sample of the concentrated acid from the desk) in a test-tube to gentle boiling and note change in color (*4*).

Construct an equation for this decomposition of nitric acid [R. 45] (*5*).

c. Drop a disk of copper into 1–2 cc. of fairly dilute nitric acid and note the appearance of brown vapors of nitrogen tetroxide (*6*).

Is this a reaction of the molecular nitric acid or of the nitrate radical upon copper? Determine by adding a copper disk to each of two test-tubes, — one containing a little sodium nitrate in solution and the other a pinch of sodium nitrate and 1–2 cc. of concentrated sulphuric acid (*7*).

Was nitric acid present in the reaction mixture prepared in **89** before distillation (*8*)?

91. Nitric Oxide

a. Arrange an apparatus as in Fig. 4 and place in it about 10 g. of copper disks, 10 cc. of water, and then 10 cc. of concentrated nitric acid. The gas evolved is to be collected over water in a pneumatic trough. Fill in this way two wide-mouthed bottles and one test-tube and reserve them for use in *b*, *c*, and *d*. Note the color of the gases as they issue from the flask (*1*).

Account for the absence of color of the pure gas finally collected over water (*2*).

Construct equation for decomposition of nitric acid (*3*).

Formulate the action of copper in this connection (*4*).

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*1*)

(*2*)

(*3*)

(*4*)

Finally construct the combined equation for the production of cupric nitrate and nitric oxide (*5*).

b. Introduce a lighted splint into one bottle of nitric oxide (*6*).

Observe the color developed in the bottle when this gas comes in contact with air and explain (*7*).

c. Into the second bottle of nitric oxide introduce a deflagrating spoon containing a little red phosphorus previously ignited by a flame. Account for the result (*8*).

d. Fill a small beaker with water, invert it over water in a pneumatic trough, and then transfer the nitric oxide from the test-tube (collected in *a*) to this beaker. Fill the test-tube next with oxygen, either prepared especially or taken from the laboratory supply, and transfer this volume of oxygen also to the same beaker. Allow the equal volumes of nitric oxide and oxygen thus to interact and when no further change in the total volume of the product is observed transfer the remaining gas back into the test-tube, which has been again filled with water and held over the trough. Record the volume of gas thus collected in the test-tube and apply tests to determine whether it is nitric oxide or oxygen (*9*).

Construct an equation to show the molecular volumes of nitric oxide and oxygen required for interaction (*10*).

e. Prepare a few cc. of a concentrated solution of ferrous ammonium sulphate (consider as ferrous sulphate), divide into two portions, and save one portion for *f*. Into the other portion pass a gentle stream of nitric oxide. What is the product thus obtained (*11*)?

Boil the brown solution and explain result (*12*).

f. Dissolve a crystal of sodium nitrate (or any nitrate)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

in 1–2 cc. of water and add this solution to the other portion of the ferrous ammonium sulphate solution prepared in *e*. Then pour a few cc. of concentrated sulphuric acid very cautiously down the inner walls of the test-tube and observe the brown ring that forms between the layer of concentrated acid at the bottom and the aqueous solution above (*13*).

The formation of this brown ring constitutes a delicate test for the presence of nitric acid or a nitrate. A considerable mixing of the two layers interferes with the test.

The presence of bromide, bromate, iodide, iodate, or nitrite radicals, especially when in high concentration, interferes with this brown ring test, owing to liberation of colored products.

g. Place 2–3 cc. of concentrated nitric acid in a test-tube, warm gently, and lead through it a stream of nitric oxide. After allowing sufficient time for the air in the test-tube to be displaced note whether there is a continued production of these brown fumes, in the interaction of nitric oxide and nitric acid (*14*).

Construct equation for decomposition of nitric acid (*15*).

Construct equation for the oxidation of nitric oxide (*16*).

Combine these equations for the complete reaction between nitric oxide and nitric acid (see **93** *g*) (*17*).

92. Nitrogen Tetroxide

Place 9–10 g. of lead nitrate in a hard glass test-tube, tightly fit the tube with a one-hole cork and delivery tube, and, by means of a clamp about the neck, attach the tube in a horizontal position to a ring-stand. Dissolve about 2 g. of sodium hydroxide in 7 cc. of water in a test-tube and introduce the end of the delivery tube to the bottom of

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

this concentrated alkaline solution. Strongly heat the lead nitrate until the absorption of the brown fumes driven over has practically rendered the alkaline solution no longer soapy to the touch. Test the escaping bubbles of unabsorbed gas for oxygen (*1*).

Finally cork the solution and set aside for **96**.

Formulate the decomposition of lead nitrate (*2*).

The residue, after complete decomposition, is lead oxide. In general, this behavior is typical of all nitrates of the heavy metals. Certain of these nitrates, however, will give the pure metal itself upon further decomposition of the oxide [R. 46].

93. Oxidizing Action of Nitric Acid

a. Place about 0.5 g. of sulphur in a test-tube containing 2–3 cc. of concentrated nitric acid and boil the mixture for a few minutes [Hood]. Is there evidence of action (*1*)?

Pour off the clear part of the mixture into another test-tube, dilute with water, and test for sulphate radical (*2*).

Construct an equation for decomposition of nitric acid (*3*).

Construct an equation for the oxidation of sulphur to sulphur trioxide (*4*).

Combine these two equations for the complete action studied (*5*).

The oxidation of sulphur takes place only slowly and is not effective in reducing much of the nitrogen tetroxide (from decomposition of nitric acid) to nitric oxide. Dilute nitric acid is almost without action upon sulphur.

b. Place about 1 cc. of dilute nitric acid in a test-tube, dilute with 10 to 15 times its volume of water, and drop into

(*1*)

(*2*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

R

the test-tube a little powdered magnesium. Note the evolution of gas and test it with a lighted splint (*6*).

[*Instructions:* This action of magnesium upon very dilute nitric acid is comparable with the action of many metals upon other acids. The position of this metal in the electromotive series makes possible the ready displacement of hydrogen from nitric acid even when the acid is extremely dilute, thus avoiding complicated reactions due to the oxidizing action of nitric acid. Aluminium and zinc can scarcely displace hydrogen from a nitric acid so dilute. When, however, the concentration of the nitric acid reaches a point where one of these metals or another metal lower down in the series can appreciably displace hydrogen, this hydrogen is at once oxidized at the expense of a portion of the acid, and the degree of this reduction of the acid is dependent upon its concentration, the concentration of the active hydrogen, and the temperature. With metals further down in the electromotive series, for example copper, the displacement of hydrogen is nil, and there is presented for study only that action of nitric acid which proceeds from its total decomposition.]

c. Drop a granule of zinc into a test-tube containing 1–2 cc. of dilute nitric acid. Note the rapid evolution of gases. The appearance of brown fumes, however, will indicate a decomposition of acid rather than the displacement of hydrogen as a chief factor. Pour off the clear solution and evaporate it to dryness upon the water-bath. Test the residue for the presence of ammonium radical (*7*).

Construct an equation for the displacement of hydrogen from nitric acid by the action of zinc (*8*).

Construct an equation for the reduction of nitric acid to ammonia by the action of hydrogen (*9*).

Combine the two equations for the complete reaction of zinc upon dilute nitric acid (*10*).

d. Repeat *c,* using concentrated nitric acid in place of the dilute acid. The decomposition of the acid is here at once accomplished through the heat of the reaction and at the same time hydrogen is evolved by simple displace-

(6)

(7)

(8)

(9)

(10)

ment. The presence of a large quantity of hydrogen is sufficient to reduce the nitrogen tetroxide to nitric oxide and also to nitrous oxide and nitrogen. Pour off the clear solution and evaporate to dryness over the water-bath. Test here for the presence of the ammonium radical (***11***).

Has the reduction of nitric acid in this case progressed as far as in the preceding experiment (*c*) where a more dilute acid was employed (***12***)?

e. Place a few granules of tin in a test-tube containing 1–2 cc. of dilute nitric acid. Note if nitric oxide or nitrogen tetroxide is formed (***13***).

From the position of tin in the electromotive series may we infer that a reduction of nitric acid is effected here by displaced hydrogen (***14***)?

Pour out the clear reaction mixture into an evaporating dish and allow it to evaporate upon a water-bath. Test the residue for the ammonium radical (***15***).

Construct the equation for the displacement of hydrogen from nitric acid by the action of tin (***16***).

Construct the equation for the reduction of nitric acid as noted (***17***).

Combine the two equations for the complete reaction of tin upon dilute nitric acid (***18***).

f. Place a few granules of tin in a test-tube containing 1–2 cc. of concentrated nitric acid and note the decomposition of the acid by the heat of reaction (***19***).

Construct equation for decomposition of nitric acid (***20***).

Construct an equation for the oxidation of tin to stannic oxide (***21***).

Construct an equation for the formation of stannic nitrate from the corresponding oxide (***22***).

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)
(*20*)

(*21*)

(*22*)

Combine these equations for the complete reaction of tin upon concentrated nitric acid (*23*).

Finally construct an equation for the hydrolysis of stannic nitrate [R. 47] (*24*). This latter action may be shown by adding considerable water to the stannic nitrate solution and boiling.

g. Drop a few disks of copper into a test-tube containing 1–2 cc. of concentrated nitric acid. Is nitric oxide or nitrogen tetroxide evolved (*25*)?

Is there any reduction of the nitric acid in this case by hydrogen (*26*)?

[*Instructions:* Unless hydrogen is evolved in these reactions with nitric acid the decomposition of the acid proceeds regularly to nitrogen tetroxide, water, and oxygen. The nitrogen tetroxide may further be reduced to nitric oxide, but this step is due primarily to the action of water itself upon the nitrogen tetroxide when the mixture is slightly warmed; nitric oxide and nitric acid are hereby formed simultaneously and they, in turn, may exist in equilibrium with the nitrogen tetroxide and water.

Thus when an excess of concentrated nitric acid is present in the reaction mixture the production of any possible nitric oxide is hindered by reason of its immediate oxidation to nitrogen tetroxide at the expense of the concentrated nitric acid (see **91** *g*).]

h. Construct the equation for the action of copper upon concentrated nitric acid, as determined in *g* (*27*).

Construct the equation for the action of nitrogen tetroxide upon warm water (*28*).

Combine these equations for the complete reaction of copper upon dilute nitric acid, as determined in **91** *a* (*29*).

i. Dip a small piece of wool into a few drops of concentrated nitric acid, or note the appearance of product formed when nitric acid comes in contact with the skin or clothing. Will ammonium hydroxide solution remove these stains (*30*)?

(*23*)

(*24*)

(*25*)

(*26*)

(*27*)

(*28*)

(*29*)

(*30*)

Cotton and many other products are not attacked in this way but give directly nitro derivatives.

j. Place 1–2 cc. of concentrated nitric acid in a test-tube and add to it 3–4 cc. of concentrated hydrochloric acid. Note the appearance of colored fumes (*31*).

Note, also, the odor of chlorine (*32*).

Do nitric or hydrochloric acids singly attack all metals (*33*)?

What metals are attacked by this mixture (*34*)?

Is this mixture more effective in its action upon noble metals than either hydrochloric acid or chlorine (*35*)?

In what form of combination is the noble metal thus brought into solution [R. 48] (*36*)?

Construct an equation which will indicate the reaction between hydrochloric acid and nitric acid (*37*).

94. Nitrous Oxide

a. Arrange an apparatus as in Fig. 4. Place in it about 10 g. of ammonium nitrate and heat gently over a small flame. Do not apply more heat than is necessary to cause a slow evolution of gas. Fill two wide-mouthed bottles with this gas by collection over water. Has the gas an odor (*1*)?

State, also, its common name (*2*).

Construct the equation for this decomposition of ammonium nitrate (*3*).

b. Lower a glowing splint into one bottle of the gas from *a.* Does the gas support this combustion (*4*)?

c. Ignite a little red phosphorus in a deflagrating spoon and lower this spoon into the second bottle of nitrous oxide (*5*).

Account for this marked combustion (*6*).

(31)
(32)
(33)
(34)

(35)

(36)

(37)

(1)
(2)

(3)

(4)

(5)
(6)

Compare it with the combustion of phosphorus in nitric oxide (*7*).

If phosphorus were burned in a closed vessel containing 100 cc. of nitrous oxide show by molecular equations what volume of nitrogen would remain (temperature and pressure constant) (*8*).

95. Nitrous Acid

a. Place in a hard glass test-tube 2–3 g. of sodium nitrate and heat the salt slightly above its melting point over a free flame. Note the formation of gas bubbles in the molten mass as the heating proceeds. Test with a glowing splint for the production of oxygen in this decomposition (*1*).

Continue the heating of the molten mass for 10 to 15 minutes or until the evolution of gas has ceased; then upon cooling add 2–3 cc. of water to the test-tube and shake until all is dissolved. Divide the solution into three portions for use in *b*, *c*, and *d*.

Construct an equation for the decomposition of sodium nitrate by heat (*2*).

Compare this class of nitrates (nitrates of the alkalies) with nitrates of the heavy metals (see **92**) (*3*).

What nitrate falls into a special class (see **94**) (*4*)?

b. To one portion of the solution from *a* add a few cc. of dilute sulphuric acid and account for the result (*5*).

Formulate this decomposition of nitrous acid (*6*).

Does a nitric acid solution undergo this change when treated with dilute sulphuric acid (see **89**) (*7*)?

c. Pour out about 5 cc. of a starch emulsion into a test-tube and add to this a single drop of potassium iodide

(7)

(8)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

[redacted]

solution and a little dilute sulphuric acid. Into this mixture pour the second portion of the sodium nitrite solution from *a* (***8***).

Construct the equation to show the oxidizing action of nitrous acid upon hydrogen iodide (***9***).

d. Into a test-tube containing about 1 cc. of a potassium permanganate solution and 5–10 cc. of water add a few cc. of dilute sulphuric acid; then add the third portion of the sodium nitrite solution from *a* (***10***).

Construct an equation to show the reducing action of nitrous acid upon acidified potassium permanganate (***11***).

96. Identification of Nitrites and Nitrates

a. Examine the solution of sodium salts from **92**. Acidify a few cc. of the solution with dilute sulphuric acid (***1***).

Add a few drops of this acidified solution to about 1 cc. of potassium permanganate solution diluted with ten times its volume of water (***2***).

Add a few drops of the same acidified solution to a few drops of starch emulsion containing a drop of potassium iodide solution (***3***).

The presence of what substance in the original solution from **92** is hereby identified (***4***)?

b. In order to determine whether the solution from **92** contains a nitrate in the presence of a nitrite it is first necessary to remove all of the nitrite. Transfer the remaining portion of the solution from **92** to a small flask and add about 5 g. of ammonium chloride [Hood] and heat to boiling. Explain the evolution of ammonia (***5***).

What other gas is given off simultaneously (see **85** *a*) (***6***)?

When the action is over add about 10 cc. of water to the

(*8*)

(*9*)

(*10*)

(*11*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)
(*6*)

[redacted]

flask and shake. Prepare about 2–3 cc. of a concentrated solution of ferrous ammonium sulphate and to this add 1–2 cc. of the solution just freed from nitrites; then pour a little concentrated sulphuric acid down the inside walls of the test-tube and note if a nitrate is present (*7*).

Construct, finally, the equation for the reaction of nitrogen tetroxide upon sodium hydroxide (*8*).

c. Construct also the equation for the reaction of nitrogen tetroxide upon water when the temperature of the solution is below the point of decomposition of nitrous acid (see **95** *b*) (*9*).

Compare this latter equation with the equation for the action of nitrogen tetroxide upon warm water (**93** *g*, *h*) (*10*).

97. Active Hydrogen

a. The activity of hydrogen when just liberated has been shown in a number of the preceding experiments. Draw a comparison between this active hydrogen and the ordinary molecular hydrogen in the following experiments.

Dilute 1–2 drops of a potassium permanganate solution with 15–20 cc. of water and pour about 5 cc. of this solution into a test-tube containing a few cc. of dilute sulphuric acid and a granule of zinc (*1*).

b. Try now the effect of passing hydrogen from the Kipp generator, or laboratory supply, through another 5 cc. of this same potassium permanganate solution slightly acidulated with dilute sulphuric acid (*2*).

c. Repeat *b*, but in this case drop a few copper disks into the test-tube containing the acidulated potassium permanganate solution. Explain the result [R. 49] (*3*).

(*7*)

(*8*)

(*9*)

(*10*)

(*1*)

(*2*)

(*3*)

CHAPTER XV

PHOSPHORUS

98. Phosphine. [Hood]

a. Drop a fragment of calcium phosphide into a small beaker containing 10–15 cc. of water (*1*).

Hold moistened strips of litmus paper of both colors in the vapor evolved (*2*).

After the experiment test the aqueous solution also for its reaction to litmus (*3*).

Construct an equation for this hydrolysis (*4*).

Compare the hydrolysis with that of magnesium nitride and state a few points of difference between phosphine and ammonia (*5*).

b. Repeat *a,* adding a few cc. of dilute hydrochloric acid to the beaker of water (*6*).

Construct the equation for the action (*7*).

Account for the difference in rate of action in these two experiments (*8*).

99. Metaphosphoric Acid

a. Place about 15 cc. of cold water in a small beaker, drop into it, in small portions, 1–2 g. of phosphorus pentoxide. When the solution becomes clear test with litmus paper (*1*).

Reserve the solution for *b*, *c*, and **100**.

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(1)

s

b. To a small portion of the metaphosphoric acid solution from *a* add a silver nitrate solution, a drop at a time, and shake after each addition (*2*).

Construct the equation for the action (*3*).

Ascertain if the reaction is reversible by diluting 1 cc. of ammonium hydroxide solution tenfold and then adding a little of this diluted ammonium hydroxide solution, a drop at a time. Note if further precipitation occurs (*4*).

What component of the system in equilibrium is removed by the ammonium hydroxide (*5*)?

c. Prepare 1–2 cc. of a solution of albumin in water and to this solution add a few drops of metaphosphoric acid solution from *a* (*6*).

The reaction is characteristic of the undissociated metaphosphoric acid.

100. Orthophosphoric Acid

a. Transfer the remaining portion of the metaphosphoric acid solution (prepared in **99** *a*) to a small flask, previously fitted with a one-hole cork, through which passes a piece of glass tubing 3–5 cm. long. Support the flask on a ring-stand and boil the contents over a free flame for an hour or more; the glass tubing here serves as a reflux condenser for the vapors. When the solution has cooled remove about 1 cc. of it and test this as in **99** *c* for the presence of any unchanged metaphosphoric acid (*1*).

How may this conversion of metaphosphoric acid to orthophosphoric acid be hastened [R. 50] (*2*)?

To 1–2 cc. of the solution add a silver nitrate solution a drop at a time (*3*).

Construct an equation for the reaction possible (*4*).

(2)

(3)

(4)

(5)

(6)

(1)

(2)

(3)

(4)

Bearing in mind that this reaction is reversible, add now a drop or two of highly diluted ammonium hydroxide solution (1 part dilute : 10 water) and account for result (*5*).

Note also the effect of a further addition of this diluted ammonium hydroxide solution (*6*).

To the clear solution finally obtained add a drop or two of dilute nitric acid (*7*).

b. Place about 0.5 g. of red phosphorus in a test-tube containing 5–6 cc. of dilute nitric acid, support the test-tube by a clamp upon a ring-stand and heat the contents to boiling. When the action is over filter the solution (if necessary), transfer it to an evaporating dish, and evaporate to dryness upon a water-bath [Hood]. Moisten the sirup thus obtained with a few drops of concentrated nitric acid and again evaporate it upon the water-bath. When all traces of nitric acid are finally removed dissolve the sirup in a few cc. of water and test the solution with litmus (*8*).

Test a small portion of this aqueous solution with a silver nitrate solution, but first add a drop or two of highly diluted ammonium hydroxide solution (1 dilute : 10 water) (*9*).

The incomplete oxidation of the phosphorus may have led to the production of some phosphorous acid which, in this test, would serve to reduce a portion of the silver nitrate to metallic silver (black).

c. Further test the solution from *b* for orthophosphoric acid by adding 1–2 drops of it to a test-tube containing about 5 cc. of ammonium molybdate solution in nitric acid and warming the mixture gently (*10*).

This test — the production of an ammonium phosphomolybdate — constitutes a delicate test for the orthophosphate radical.

(5)

(6)

(7)

(8)

(9)

(10)

101. Phosphates

a. Dissolve 1–2 g. of sodium phosphate (disodium orthophosphate) in a little water and account for the action of this solution to litmus (*1*).

Reserve the solution for *b* and *c*.

What is the action to litmus of an aqueous solution of monosodium orthophosphate [R. 51] (*2*)?

b. To one portion of the sodium phosphate solution add a drop or two of silver nitrate solution (*3*).

Drop litmus paper into this reaction mixture and account for the presence of the ion thus identified (*4*).

Construct an equation for the reaction (*5*).

c. To a test-tube containing about 1 cc. of magnesium sulphate solution add a few drops of ammonium hydroxide solution, and then 3–4 cc. of ammonium chloride solution. To this mixture ("magnesia mixture") now add a few cc. of the sodium phosphate solution from *a* and shake (*6*).

Construct the equation for this reaction as between sodium phosphate, magnesium sulphate, and ammonium hydroxide (the ammonium chloride is present only to prevent any precipitation of magnesium hydroxide) (*7*).

This constitutes a delicate test for the presence of the orthophosphate radical.

d. Place about 2 g. of sodium phosphate in a porcelain crucible and strongly heat this salt over a blast lamp for 15 to 20 minutes, or until no further change is observed. When cool dissolve the mass in water and test a sample of this solution with silver nitrate solution (*8*).

How does this precipitate differ from that obtained from orthophosphoric acid and silver nitrate (see **100** *a*) (*9*)?

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

How does it differ from that obtained from metaphosphoric acid and silver nitrate (see **99** *b*) (***10***)?

Construct the equation for the decomposition of sodium phosphate by the action of heat (***11***).

Acidify a portion of the sodium pyrophosphate solution with acetic acid and try the action of this acidulated solution upon 1–2 cc. of albumin solution (***12***).

e. Construct a table showing the action of the three phosphoric acids upon silver nitrate and also upon albumin solution (***13***).

Acetic acid is without action upon albumin, consequently the coagulating power of the free phosphoric acids may be determined at once by liberating these acids from their salts through the action of acetic acid.

f. Place about 2 g. of microcosmic salt (sodium ammonium hydrogen phosphate) in a porcelain crucible and strongly heat the salt over a blast lamp till no further action is observed. Note the odor of vapor evolved (***14***).

When cool dissolve the residue in a little water and apply the tests as in *e* to learn what salt has been produced in this decomposition (***15***).

Construct an equation to show this decomposition (***16***).

g. Make a bead on a platinum wire by fusing a little microcosmic salt upon it. Bring this colorless bead in contact with a minute fragment of some metallic oxide, such, for example, as cupric oxide, and reheat the bead in the oxidizing portion of the flame (***17***).

Construct the equation for the action of cupric oxide upon this bead (***18***).

Reheat the bead in the reducing portion of the flame (***19***).

Repeat *g*, using manganese dioxide as in **1** *d* and *e* (***20***).

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)
(*16*)

(*17*)

(*18*)
(*19*)
(*20*)

102. The Halides of Phosphorus

a. Place 2–3 cc. of phosphorus trichloride in a test-tube. Does this halide fume in moist air (*1*)?

Add water to the test-tube a drop at a time and, when about 5 cc. have been added, heat the mixture to boiling (*2*).

Test the vapor with litmus paper (*3*).

Apply also to the mouth of the tube a glass rod moistened with ammonium hydroxide solution (*4*).

What volatile product is liberated in this hydrolysis (*5*)?

Evaporate the solution to a sirup upon the water-bath and reserve for *b*.

b. Transfer the sirup from *a* to a small test-tube and heat this product over the free flame until gas is no longer evolved. Note the odor of the vapor (*6*).

Apply tests as in **101** *e* to ascertain which of the phosphoric acids is present in the residue (*7*).

Construct an equation for this decomposition of phosphorous acid (*8*).

c. Place 1–2 g. of phosphorus pentachloride in a test-tube containing 2–3 cc. of water and boil (*9*).

Test the vapor with litmus paper (*10*).

Apply also a glass rod moistened with ammonium hydroxide solution (*11*).

What volatile product is liberated in this hydrolysis (*12*)?

Pour out not more than 1 cc. of this solution into another test-tube, add to it an equal volume of silver nitrate solution, and filter off the precipitate of the silver halide. Now add to the filtrate a little highly diluted ammonium hydroxide solution (1 dilute : 10 water) a drop at a time. Explain (*13*).

Construct an equation for the complete hydrolysis of phosphorus pentachloride (*14*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

[redacted]

CHAPTER XVI

CARBON

103. Charcoal

a. Place a pinch of powdered wood charcoal in a test-tube, pour upon it 5–6 cc. of litmus solution, and boil the mixture for about a minute. Filter the solution and note the adsorptive properties of this charcoal (*1*).

b. Repeat *a*, using a pinch of animal charcoal (bone black) and the same quantity of litmus solution. Boil for the same length of time, filter, and compare the adsorptive properties of this charcoal with that used in *a* (*2*).

Account for any difference found (*3*).

Of what does bone black chiefly consist [R. 52] (*4*)?

c. Hold a cold porcelain dish at the top of a luminous flame. What is the common name for this deposit (*5*)?

Has this product greater or less adsorptive properties than wood charcoal (*6*)?

104. The Reducing Action of Carbon

a. Fit a hard glass test-tube with a one-hole cork and delivery tube. Place in the tube an intimate mixture of cupric oxide and an equal bulk of powdered wood charcoal. Strongly heat the mixture over a free flame and allow the gases evolved to bubble through a few cc. of lime-water in a test-tube (*1*).

What product of this reaction may now be identified in the residue in the tube (test as in **90** *c* and **93** *g*) (*2*)?

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*1*)

(*2*)

Construct an equation for the reduction of cupric oxide by means of carbon and the consequent oxidation of the carbon to carbon dioxide (*3*).

Construct an equation for the formation of calcium carbonate through the action of carbon dioxide upon calcium hydroxide (lime-water) (*4*).

[*Instructions:* The formation of this precipitate in lime-water or baryta-water is used as a test for the presence of carbon dioxide. Sulphur dioxide forms a similar precipitate of calcium sulphite (or barium sulphite). The addition of dilute hydrochloric acid will again decompose these precipitates, but a few drops of bromine-water first added will oxidize a sulphite to a sulphate (see **78** *f*) and thus only the carbon dioxide will be liberated upon the further addition of acid.]

b. Recall the reduction of sulphates to sulphides (see **81**). Construct an equation for the reduction of sodium sulphate to sodium sulphide by means of carbon (*5*).

105. Preparation of Carbon Dioxide

a. Blow air from the lungs into a test-tube containing a little lime-water and note whether or not carbon dioxide is present in the exhaled air (*1*).

b. Hold an inverted wide-mouthed bottle above a small nonluminous flame for a few seconds, thus collecting some of the hot gaseous products of the combustion. Remove the bottle, quickly add a few cc. of lime-water, close at once with the hand, and shake. Is carbon dioxide present in the combustion products (*2*)?

c. Place a few cc. of lime-water in a wide-mouthed bottle, close the bottle with the hand, and shake (*3*).

Is carbon dioxide present in the air of the laboratory (*4*)?

What are some of the sources of carbon dioxide in air (*5*)?

(*3*)

(*4*)

(*5*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

d. Place a few pieces of magnesite (magnesium carbonate) in a hard glass test-tube fitted with a one-hole cork and delivery tube. Attach a small piece of rubber tubing to this delivery tube and allow the other end of it to dip beneath a few cc. of lime-water in a test-tube. Strongly heat the magnesite and note the formation of a precipitate in the test-tube (*6*).

If all of the carbon dioxide were thus driven from the magnesite, of what would the residue consist [R. 53] (*7*)?

e. Arrange an apparatus as in Fig. 4. Interpose between the end of rubber delivery tube and flask a U-tube containing sufficient water to cover the bend and thus afford a means of washing the gas free from any hydrogen chloride that may be liberated from the hydrochloric acid to be employed. Place in the flask a few pieces of marble and pour into the funnel a little dilute hydrochloric acid (*8*).

Construct the equation for the reaction (*9*).

Collect two wide-mouthed bottles of carbon dioxide by the upper displacement of air and cover each bottle with a glass plate. Pass the gas also through a few cc. of water in a test-tube and cork the tube. Reserve all for **106.**

If no regular laboratory supply of this gas is at hand this supply of carbon dioxide may be used at once for **107.**

106. Properties of Carbon Dioxide

a. Open one of the bottles of carbon dioxide from **105** *e* and transfer a portion of the gas to a test-tube containing a little lime-water (*1*).

Is the gas heavier than air (*2*)?

b. Invert an empty wide-mouthed bottle over the second bottle of this gas (from **105** *e*), withdraw the glass

(6)

(7)

(8)

(9)

(1)

(2)

T

plate, and allow the carbon dioxide and air to intermingle. After ten minutes replace the glass plate between the two bottles, remove the upper bottle, add a little lime-water to it, and shake (*3*).

Does the heavier gas diffuse into the lighter (*4*)?

c. Test the aqueous solution of carbon dioxide, as collected in the test-tube in **105** *e*, with litmus (*5*).

Boil the solution and again test with litmus (*6*).

Does the aqueous solution of this gas resemble a solution of hydrogen sulphide, sulphur dioxide, ammonia, or hydrogen chloride (*7*)?

107. Carbonates

a. Pass a current of carbon dioxide from the apparatus arranged in **105** *e*, or from a laboratory supply, into a test-tube containing 4–5 cc. of sodium hydroxide solution until this solution is saturated [Test]. Test the solution with litmus paper (*1*).

Pour the solution into an evaporating dish and allow evaporation to take place spontaneously. Construct an equation for the formation of this product (*2*).

b. Heat the dry residue from *a* in a test-tube and determine what two products are driven off (*3*).

Dissolve the residue in a few cc. of water and divide into three portions for use in *c*, *d*, and *e*.

c. To one portion of the solution from *b* add a few drops of hydrochloric acid and note what gas is evolved (*4*).

Is the residue in *b* thus shown to be a carbonate (*5*)?

d. To the second portion of the solution add a few drops of dilute nitric acid or dilute sulphuric acid (*6*).

From the standpoint of the ionic hypothesis account for

(3)
(4)

(5)
(6)

(7)

(1)

(2)

(3)

(4)
(5)

(6)

the readiness with which carbonates are decomposed by many acids (*7*).

e. Test the third portion of the solution from *b* with litmus and account for this action (*8*).

What is the action to litmus of that solution prepared in *a* when no decomposition has taken place [R. 54] (*9*)?

Construct an equation for the action of heat upon the carbonate prepared in *a* (*10*).

108. Carbon Monoxide. [Hood]

a. Arrange an apparatus as in Fig. 4. Interpose a U-tube in the delivery circuit as described in **105** *e* and fill the bend of this U-tube with sodium hydroxide solution. Now place in the flask about 10 g. of crystallized oxalic acid, pour upon this acid through the funnel 20–25 cc. of concentrated sulphuric acid, and heat the mixture gently. Collect two wide-mouthed bottles of the gas over water in the pneumatic trough and reserve them for *b* and *c*. Test the solution in U-tube for a carbonate (*1*).

b. Add a few cc. of lime-water to one of the bottles collected in *a* and note if any carbon dioxide is still present in the gas (*2*).

c. Bring a lighted splint to the mouth of the other bottle and note the color of the burning gas (*3*).

Now add a few cc. of lime-water to this bottle, close with a glass plate, and note what gas is formed in this combustion (*4*).

Formulate this decomposition of oxalic acid into water, carbon dioxide, and carbon monoxide [R. 55] (*5*).

What are the relative volumes of carbon dioxide and carbon monoxide produced in this decomposition (*6*)?

(*7*)

(*8*)

(*9*)

(*10*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

Construct an equation for the combustion of carbon monoxide (*7*).

What would result upon passing a stream of carbon monoxide over heated cupric oxide in a hard glass test-tube (*8*)?

Construct an equation for this reaction (*9*).

109. Methane

a. Grind together in a mortar 5–6 g. of fused sodium acetate and about 15 g. of soda-lime (a mixture of calcium oxide and sodium hydroxide). Place the mixture in a hard glass test-tube fitted with a one-hole cork and delivery tube. By means of a clamp about its neck attach the tube in a nearly horizontal position to a ring-stand (the test-tube should be inclined a few degrees toward its mouth in order to avoid contact of condensed vapors with the hotter portions of the tube). Slip over the test-tube a cylinder of wire gauze and, beginning at the rear end, heat the contents very gently at first till a uniform evolution of gas is secured. When all the air is displaced collect one bottle and one test-tube of this gas over water in a pneumatic trough. Reserve these for use in *b* and *c*.

Attach a glass nozzle to the end of the delivery tube and ignite the gas. Note the color and degree of luminosity of the flame (*1*).

Hold over the jet of burning gas a dry inverted beaker and note one of the products of this combustion (*2*).

b. Hold the bottle of methane from *a*, mouth downward, and apply a flame to the mouth (*3*).

Quickly right the bottle, pour into it a few cc. of limewater, and shake (*4*).

What other product of this combustion is identified (*5*)?

(7)

(8)

(9)

(1)

(2)

(3)

(4)

(5)

Construct an equation for the complete combustion of methane with oxygen (*6*).

What ratio will the resulting volume of gases in this combustion bear to the original volume of methane when a temperature of 100° is constant throughout (*7*)?

State, also, this approximate ratio when a temperature of 0° is constant (*8*).

c. Into the test-tube of methane from *a* add a few drops of bromine-water and shake. Does this gas readily absorb bromine (*9*)?

Does bromine act slowly upon methane [R. 56] (*10*)?

110. Acetylene

a. Invert a test-tube full of water over an evaporating dish also filled with water. Grasp a piece of calcium carbide in the tongs and quickly insert it under the mouth of the test-tube (*1*).

Test the reaction of the water in the dish to litmus (*2*).

Construct, now, an equation for the action of water upon calcium carbide (*3*).

When the test-tube is filled with gas quickly remove it from the water and ignite the gas at mouth of tube (*4*).

Compare the color of flame and degree of luminosity with that of burning methane (*5*).

Construct an equation for this combustion (*6*).

b. Repeat *a*, and, after collecting another test-tube of acetylene, quickly pour into the tube not more than 1 cc. of bromine-water. Close the tube with the thumb and shake. Is bromine readily absorbed by acetylene (*7*)?

Compare here the action of methane toward bromine (**109** *c*) and account for the difference [R. 57] (*8*).

(6)

(7)

(8)

(9)

(10)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

111. Flames

a. Recall the experiments on the Bunsen burner outlined in **1**, and account for the presence of carbon in the luminous flame (*1*).

b. Does hydrogen burn with luminosity (see **16**) (*2*)? Compare here a jet of burning methane (see **109** *a*) and also one of acetylene (see **110** *a*) (*3*).

What is the action of heat alone upon the carbon hydrides (hydrocarbons) [R. 58] (*4*)?

c. Open the air holes of a Bunsen burner supplying a luminous flame and apply a glowing splint close to one of these air holes. What substance is found to be entering in large quantities (*5*)?

Attach a piece of rubber tubing to the laboratory supply of carbon dioxide and insert the other end of this tubing into one of the air holes at the base of a Bunsen burner supplying a nonluminous flame. Close the other air hole with the finger and then introduce into this nonluminous flame a gentle stream of carbon dioxide (*6*).

What is the cause of this action (*7*)?

Would nitrogen serve the same purpose (*8*)?

What is the double effect of air in this connection (*9*)?

112. Ethyl Alcohol

a. Place 15–20 g. of glucose sirup in a 125 cc. flask, drop in a few small pieces of yeast, and nearly fill the flask with water. Cork the flask with a plug of cotton, and set aside in a warm place for two or three days. After this time remove the cotton plug from the flask and filter the liquid. Transfer the clear filtrate to a larger flask fitted with a one-hole cork and glass delivery tube bent through a little more

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

than 90°. Connect the other end of this delivery tube with a condenser just as shown with the distilling flask in Fig. 6. Heat the contents of the flask to gentle boiling. By means of a test-tube containing a little lime-water test the gas which first issues at the further end of the condenser (*1*).

Finally, as the vapors condense, collect 40–50 cc. of the distillate. Transfer this distillate to a small distilling flask (125 cc.) provided with thermometer and connected with a condenser exactly as described in Fig. 6. Now heat the contents of the flask to boiling and collect that portion distilling over between 78° and 85°. Note the odor of this final distillate (*2*).

Has the product any effect upon litmus (*3*)?

Reserve it for use in *b* and *c*.

b. Pour a portion of the distillate from *a* into an evaporating dish and ignite it. Hold an inverted wide-mouthed bottle over this flame and note at once one of the products of the combustion (*4*).

Quickly right this wide-mouthed bottle, add a few cc. of lime-water to it, and state what other product of the combustion is detected (*5*).

Formulate the complete combustion of ethyl alcohol (*6*).

c. Pour a few drops of the distillate from *a* into a test-tube, add a small crystal of iodine, and then add 1–2 cc. of sodium hydroxide solution. Shake the mixture well and warm gently. Note the formation of a yellow precipitate of iodoform (CHI_3) with its characteristic odor (*7*).

The production of iodoform by this means may be used as a test for the presence of alcohol and similar products.

d. Repeat *c*, substituting a few drops of glucose sirup, or a pinch of sugar, in place of the alcohol (*8*).

Is sugar an alcohol (*9*)?

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

(5) [illegible]

(6) [illegible]

(7) [illegible]

(8) [illegible]

(9) [illegible]

e. Repeat *c*, substituting a few drops of glycerol in place of the alcohol. Is glycerol an alcohol (*10*)?

113. Acetic Acid

Place 1–2 g. of sodium acetate in a test-tube, add a few cc. of dilute sulphuric acid, and warm. Note the odor (*1*).

Test the action of the vapors upon litmus (*2*).

114. Esterification: Formation of an Ester

a. Place 1–2 g. of sodium acetate in a test-tube, add 1–2 cc. of ethyl alcohol, and then about 1 cc. of concentrated sulphuric acid. Gently warm the mixture and note odor of vapor (an ester) (*1*).

What acid is liberated in the action of sulphuric acid upon sodium acetate (*2*)?

Sulphuric acid further serves the purpose of withdrawing a molecule of water from this organic acid and the base, — ethyl alcohol. What is the name of the resulting salt (*3*)?

Apply litmus paper to the mouth of the tube and note if this ester is acid or basic (*4*).

b. Repeat *a*, substituting amyl alcohol for the ethyl alcohol. Note odor of ester produced (*5*).

What is the name of this ester (*6*)?

The formation of an ester may serve as a test for the presence of acetic acid or an acetate.

115. Saponification: Hydrolysis of an Ester

a. Place about 0.5 cc. of ethyl acetate in a test-tube, drop in a few pieces of litmus of both colors, and then add about 10 cc. of water. Shake the mixture and note effect upon litmus from time to time (*1*).

(10)

(1)

(2)

(1)

(2)

(3)

(4)

(5)

(6)

(1)

How do you interpret this result (*2*)?

Construct an equation for the hydrolysis of an ester (saponification) (*3*).

[*Instructions:* If ethyl acetate is not at hand **114** *a* may be repeated on a slightly larger scale and the mixture distilled. The ester thus obtained as a distillate may be used to illustrate the saponification just described.]

b. Soap. Place about 2 g. of sodium hydroxide in a test-tube, add about 4 cc. of water, and when solution is effected add about 4 cc. of alcohol and shake. Allow the mixture to settle, then pour off the alcoholic (upper) layer into another test-tube, and add to this a little less than an equal volume of cottonseed oil. Shake the mixture well, then pour it into an evaporating dish, and set this dish upon a wire gauze on a ring-stand. Warm the dish, gently stirring the contents during the heating. Ignite the alcohol at surface of liquid and continue the heating and stirring until the alcohol (as detected by the flame) is driven off. The residue is chiefly the sodium salts of the acids which were present in the ester (cottonseed oil) used. Rub a little of this soap with water on the hands (*4*).

Dissolve a large part of this soap in 15–20 cc. of water and divide the clear solution into three portions for use in *c*, *d*, and **116** *b*.

[*Instructions:* The acids present are principally stearic and oleic and the alcohol with which they are associated in these esters is glycerol. The alcohol used in the experiment serves only as a solvent for the fat or oil and the alkali and thus facilitates the saponification. As sodium stearate the formula of soap is $C_{17}H_{35}COONa$.]

c. To one portion of the soap solution from *b* add a little dilute hydrochloric acid and shake. Note the appearance of the organic acids thus liberated (*5*).

(*2*)

(*3*)

(*4*)

(*5*)

U

Withdraw a trace of this coagulum by means of a glass rod, suspend it in a test-tube containing a little water, and then add a few drops of sodium hydroxide solution. Warm if necessary and note whether a soap is again formed (*6*).

d. To another portion of the clear soap solution add a little calcium chloride solution and note the properties of the calcium salts of these organic acids (*7*).

116. Cleansing Action of Soap

a. Pour about 1 cc. of cottonseed oil into each of two test-tubes, then add 5–10 cc. of water to each and shake well. Allow the tubes to stand for a few minutes (*1*).

b. To one of these test-tubes now add a little soap solution, — a portion of that clear solution prepared in **115** *b*, — and again shake. Allow the test-tube to stand for a few minutes, and note result (*2*).

Account for the difference in this case, and state the general action of cleansing solutions upon foreign substances (*3*).

(6)

(7)

(1)

(2)

(3)

[redacted]

CHAPTER XVII

SILICON AND BORON

117. Silica and Silicic Acid

a. Place 1–2 cc. of sodium silicate solution (waterglass) in a test-tube, dilute with an equal volume of water, and add concentrated hydrochloric acid, drop by drop, until the solution is strongly acid (*1*).

Construct an equation for the formation of this jelly-like substance from sodium silicate (here considered as metasilicate) (*2*).

Evaporate the mixture to dryness upon a sand-bath and wash the product with water. Test its solubility in acids and alkalies (*3*).

Formulate this dehydration of the silicic acid (*4*).

b. Place about 1 cc. of sodium silicate solution in a test-tube, dilute with an equal volume of water, and then add a drop or two of this solution to a few cc. of concentrated hydrochloric acid in another test-tube (*5*).

If silicic acid is liberated here what form is it in (*6*)?

Evaporate the mixture to dryness upon a sand-bath [Hood] and compare product with that obtained in *a* (*7*).

118. Analysis of a Silicate

a. Prepare a "fusion mixture" by grinding together in a mortar 1–2 g. each of dry potassium carbonate and anhydrous sodium carbonate. Mix with this not more than 0.5 g. of powdered talc and then, by means of a plat-

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

inum wire coiled in watch-spring form, fuse a portion of the final mixture in the flame of a blast lamp. When all action has ceased remove the wire and bead from the flame and break off the bead into a test-tube. Repeat this operation till five or six beads are obtained; then heat these beads with a little boiling water, until completely disintegrated. Filter the mixture through a small filter paper, washing the precipitate with 1–2 cc. of water. Now puncture the filter paper and wash the precipitate into another test-tube and reserve for *b*. Acidify the filtrate with concentrated hydrochloric acid (*1*).

Proceed as in **117** *a* to identify the precipitate thus produced. What radical was present in the original talc (*2*)?

b. Add a little dilute hydrochloric acid to the test-tube from *a*, containing the insoluble portion of the disintegrated fusion mixture. Filter the solution thus formed, if necessary, and add ammonium hydroxide solution to alkaline reaction, — a precipitate is aluminium hydroxide (*3*).

Boil the contents of the tube and again filter. To the filtrate now add a few drops each of ammonium hydroxide solution and ammonium chloride solution; finally add a few drops of sodium phosphate solution, and shake well (*4*).

Compare the precipitate with that obtained in **101** *c*, and state what metallic radical is thus identified in talc (*5*).

119. Silicon Tetrafluoride

Mix in a test-tube about 1 g. each of sand and pulverized calcium fluoride and then moisten the mixture with concentrated sulphuric acid. Apply a gentle heat and hold in the vapors a glass rod previously moistened with water (*1*).

Construct an equation for the formation of silicon tetrafluoride from the fluorspar above (*2*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*1*)

(*2*)

Formulate the hydrolysis of silicon fluoride (*3*).

Construct also an equation for the action of hydrogen fluoride upon silicon fluoride (*4*).

120. Boric Acid

a. Dissolve about 5 g. of borax in 10–15 cc. of hot water in a test-tube, add concentrated hydrochloric acid (5–7 cc.) until the solution is strongly acid; then set the tube aside to cool. Filter off the crystals and wash with only 1–2 cc. of cold water. Dissolve the crystals in the smallest possible amount of boiling water and again set the solution aside to cool; filter off the purified crystalline product and wash with a few cc. of cold water.

b. Dissolve a portion of the boric acid from *a* in hot water and test the solution with litmus (*1*).

Dip a strip of turmeric paper in this solution and wrap this moistened turmeric around the neck of this same test-tube. Boil the solution until the turmeric paper has become dry and taken on a red color (*2*).

Touch this dry turmeric paper with a glass rod previously dipped in sodium hydroxide solution, thus obtaining a color reaction which may be used as a test for boric acid (*3*).

c. Place about 1 cc. of alcohol on a watch-glass, drop into the alcohol a few crystals of boric acid (or add a few drops of the aqueous solution of this acid prepared in *b*). Bring a flame to the surface of this boric acid solution (*4*).

The color imparted to the flame constitutes a delicate test for the presence of boric acid (*5*).

121. Borates

a. Dissolve about 1 g. of borax in a little water and test the solution with litmus (*1*).

(3)

(4)

(1)

(2)

(3)

(4)

(5)

(1)

Account for any hydrolysis, if noted (*2*).

Reserve the solution for *b*.

b. Place 1–2 drops of the borax solution from *a* into one test-tube and about 5 cc. of it into a second test-tube. Add to the first test-tube 15–20 cc. of water (warm water is best) and then to each of the tubes add a few drops of silver nitrate solution (*3*).

Account for this difference in action and state the effect of a continued dilution of an aqueous borax solution (*4*).

Construct an equation for the action of silver nitrate upon a concentrated solution of borax (*5*).

Construct an equation for the action of silver nitrate upon a very dilute solution of borax (*6*).

c. Heat a platinum wire in a nonluminous Bunsen flame and, while yet glowing, dip the hot end into a little borax. Return the wire to the flame and note the changes which the borax undergoes upon heating (*7*).

Remove the borax bead from the flame and bring it in contact with a trace of cupric oxide; then return the bead to the oxidizing portion of the flame (*8*).

Repeat the experiment, using ferric oxide, and state in what form these metals exist in the final beads (*9*).

d. In testing for borates it is necessary simply to liberate the boric acid present and then apply the tests described in **120** *b* or *c*.

Dissolve a small crystal of borax in 1–2 cc. of water in a test-tube, add a drop of concentrated sulphuric acid, and 2–3 cc. of alcohol. Heat the mixture till the vapors may be ignited (*10*).

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

[redacted]

CHAPTER XVIII

IDENTIFICATION OF NEGATIVE RADICALS

122. Analytical Reactions

The same outline as given in **82** will serve in general for the study of all acid radicals present in the "unknown" substances. This outline and additional tests will be considered in full, and the classification of all analytical reactions will be based upon the special characteristics exhibited by each of the following named negative radicals:

Hydroxide
Chloride
Bromide
Iodide
Chlorate
Bromate
Iodate

Peroxide
Sulphides
Sulphites
Sulphates
Thiosulphate
Nitrite

Nitrate
Phosphates
Carbonates
Acetate
Silicate
Borate

The positive radicals should include only the strongly electropositive elements; the salts themselves may be soluble or insoluble. Ammonium salts should receive special consideration.

Examine the unknown as directed and record each observation. If the unknown substance is in solution, *a*, *b*, and *c* necessarily must be omitted and *d*, *e*, and *f* can be applied only under *A*. Evaporation of the solution to dryness

would permit, of course, the application of all tests as herein described.

a. Appearance: Form, color, and odor (*1*).

b. Solubility: Dissolve about 0.5 g. of the substance in water in a test-tube, warming if necessary. If the compound is practically insoluble reserve for *g* (*2*).

Test the aqueous solution with litmus and reserve for *d* (*3*).

c. Stability: Strongly heat about 1 g. of the substance in a dry hard glass test-tube and observe changes as they occur, noting carefully the evolution of gas or vapor.

Continue the heating till all action has ceased (*4*).

If water vapor alone is evolved this vapor will react neutral to litmus and thus indicate water of hydration or some form of a hydro or hydroxy salt. Certain hydrated salts of weak bases will give off acid vapors due to hydrolysis (*5*).

A COLORLESS, ODORLESS GAS may be oxygen from a peroxide, chlorate, bromate, iodate, or alkali nitrate, or carbon dioxide from a hydrocarbonate (or nitrous oxide from ammonium nitrate or nitrogen from ammonium nitrite) (*6*).

A COLORLESS GAS with MARKED ODOR may be sulphur dioxide from a hydrosulphite, hydrogen sulphide from a hydrosulphide (or ammonia from ammonium salts) (*7*).

A COLORLESS GAS FUMING in MOIST AIR may be sulphur trioxide from a hydrosulphate (*8*).

A COLORED GAS with ODOR may be nitrogen tetroxide from certain nitrates or nitrites (*9*).

A SUBLIMATE may be sulphur from a polysulphide (possibly also a sublimed ammonium salt) (*10*).

The residue left after heating should be taken up in warm

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

water and the solution treated exactly as outlined in *d*, *e*, and *f*, for a solution of the original or undecomposed substance. Differentiation in the tests as noted between solutions of the decomposed and undecomposed salt will be highly indicative of the nature of the negative radical.

d. Reaction to Diluted Sulphuric Acid (1 part concentrated acid : 1 part water).

A = original substance.	*B = residue from decomposition by heat, in c.*
Use the solution from *b* or dissolve a small quantity of the substance in a little water, add diluted sulphuric acid, and warm, noting the positive and negative tests below.	Dissolve the residue in a small quantity of water, add diluted sulphuric acid, and warm, noting the positive and negative tests below.

Colorless Gas, Fuming in Moist Air: A Hydrogen Halide.

	A Indicating		*B* Indicating
Positive (*11*)	Chloride, bromide, or iodide	→ Positive (*12*)	Chloride, bromide, or iodide in original substance.
Negative (*13*)	None of these present.	↗ Now Positive (*14*)	**Chlorate, bromate, or iodate in original.**
		↘ Still Negative (*15*)	**Compounds of chlorine, bromine, and iodine absent.**

(11)

(12)

(14)

(13)

(15)

x

[redacted]

Colorless Gas, Nonfuming but of Marked Odor: Hydrogen Sulphide, Sulphur Dioxide, or Hydrogen Acetate.

A		B	
Positive (*16*)	Sulphide, polysulphide, sulphites, thiosulphate, or acetate.	Positive (*17*)	Sulphites, sulphides, thiosulphate, or acetate in original.
Negative (*18*)	None of these present.	Still Negative (*19*)	None of these present.

Colorless, Odorless Gas: Oxygen or Carbon Dioxide.

A		B	
Positive (*20*)	Peroxide or carbonates.	Positive (*21*)	Carbonates in original substance.
		Now Negative (*22*)	Peroxide (or alkaline earth carbonate) in original substance.
Negative (*23*)	None of these present.	Negative (*24*)	None of these present.

Colored Gas: Bromine or Iodine or Nitrogen Tetroxide.

A		B	
Positive (*25*)	Possibly bromide or iodide; or nitrite.	Positive (*26*)	Bromide or iodide possibly present.
		Now Negative (*27*)	Heavy metal nitrite in original substance (or ammonium nitrite).
Negative (*28*)	Nitrite absent: probably bromide or iodide absent.	Now Positive (*29*)	Alkali nitrate in original substance.
		Still Negative (*30*)	None of these present.

(*16*)

(*17*)

(*18*)

(*19*)

(*21*)

(*20*)

(*22*)

(*23*)

(*24*)

(*25*)

(*26*)

(*29*)

(*28*)

(*27*)

(*30*)

NO GAS EVOLVED

	A		B
Positive (*31*)	Hydroxide, chlorate, bromate, or iodate, sulphate, nitrate, phosphate, silicate, or borate. →	Positive (*32*)	Hydroxide, sulphate, phosphate, silicate, or borate in original.
	↘	Negative: NOW EVOLVING GAS (*33*)	Chlorate, bromate, iodate, or nitrate in original.

FORMATION of PRECIPITATE: Sulphur or Silicon Dioxide.

	A		B
Positive (*34*)	Polysulphide, thiosulphate, or silicate. →	Positive (*35*)	Polysulphide, thiosulphate, or silicate.
Negative (*36*)	None of these present. →	Negative (*37*)	None of these present.

e. Reaction to Silver Nitrate, in Presence of Dilute Nitric Acid.

Dissolve a few particles of each substance (*A* and *B*) in 1–2 cc. of water and add to the solution a few drops of dilute nitric acid, and then about 1 cc. of silver nitrate solution.

WHITE to YELLOW PRECIPITATE (Insoluble in Cold Dilute Nitric Acid): Silver Halides or Silver Iodate; (or silver bromate if in sufficient concentration).

	A		B
Positive (*38*)	Chloride, bromide, iodide, iodate (or bromate) present. →	Positive (*39*)	Chloride, bromide, iodide, iodate (or bromate) present.

(*31*)

(*32*)

(*33*)

(*34*)

(*35*)

(*36*)

(*37*)

(*38*)

(*39*)

A			*B*	
Negative (*40*)	Chloride, bromide, iodide, iodate (or considerable bromate) absent.	↗	Now Positive (*41*)	Chlorate (or a little bromate) present in original.
		↘	Negative (*42*)	Compounds of chlorine, bromine, and iodine absent.

Black Precipitate (Insoluble in cold dilute Nitric Acid, but soluble upon heating): Silver Sulphide.

A			*B*	
Positive (*43*)	Sulphides or thiosulphate.	→	Positive (*44*)	Sulphides or thiosulphate.
Negative (*45*)	None of these present.	→	Negative (*46*)	None of these present.

f. Reaction to Barium Chloride in Presence of Dilute Hydrochloric Acid.

Dissolve a few particles of the substance in water and add to the solution a few drops of dilute hydrochloric acid, and then a few drops of barium chloride solution.

White Precipitate: Barium Sulphate.

A			*B*	
Positive (*47*)	Sulphate.	→	Positive (*48*)	Sulphate, sulphide, sulphite, or thiosulphate present in original.
Negative (*49*)	Sulphate absent.	→	Negative (*50*)	Sulphate, sulphide, sulphite, or thiosulphate absent.

(*40*)

(*41*)

(*42*)

(*43*)

(*44*)

(*45*)

(*46*)

(*47*)

(*48*)

(*49*)

(*50*)

g. When the substance is more or less insoluble its reduction by means of a "fusion mixture" or carbon is to be recommended. Proceed exactly as described in **118** ***a.*** Treat product with warm water. Examine solution and insoluble material. Acidify, note odor of any gas evolved, and examine according to directions in *d.*

h. Nonreactivity.

When no positive tests are furnished in the reactions just outlined a partial indication of a phosphate or borate seems apparent.

It will be necessary, therefore, to apply the individual tests for these negative radicals, as discussed under their several headings. In the case of a phosphate, distinction should be made as to which one of the three may be present.

123. Classification

For the classification of these reactions just presented it is advisable to consider the acid radicals with respect to their actions toward the most important reagents, — namely, silver nitrate, barium chloride, and sulphuric acid. Under each group or reagent-column insert the formula of any compound which may be precipitated or set free from the reaction mixture in which the particular acid radical is concerned. Practically all of the data necessary for this table (on opposite page) may be gathered from preceding experiments and especially from this chapter. The table should serve as a guide in the study of unknowns.

Apply [Instructor] for the remaining unknowns; six in all should constitute the least requirement of the student in the recognition of negative radicals.

ANIONS	SILVER NITRATE [IN PRESENCE OF DILUTE NITRIC ACID]	BARIUM CHLORIDE [IN PRESENCE OF DILUTE HYDROCHLORIC ACID]	SULPHURIC ACID [1 ACID : 1 WATER]
✓Hydroxide . .			
✓Peroxide . . .			
Chloride . . .			
Bromide . . .			
Iodide			
✓Chlorate . . .			
Bromate . . .			
Iodate			
Sulphide . . .			
Polysulphide. .			
Sulphate . . .			
Sulphite . . .			
Thiosulphate. .			
Nitrate . . .			
Nitrite. . . .			
Phosphate . .			
Carbonate . .			
Acetate . . .			
✓Silicate . . .			
✓Borate . . .			

CHAPTER XIX

THE ALKALI METALS AND AMMONIUM

124. Potassium Hydroxide

a. Dissolve 20–25 g. of potassium carbonate in 200–300 cc. of water in a beaker and heat the solution to boiling. Slake 15–20 g. of quicklime in another beaker and, when slaked, add more water until a thin paste is obtained. Pour this paste, slowly and with constant stirring, into the hot potassium carbonate solution, and continue the boiling for a few minutes. Allow the mixture to settle and then decant off the clear liquid, reserving for use in *b.*

By reference to Appendix IV compare the solubilities of calcium hydroxide and calcium carbonate (*1*).

Construct an equation for the reaction above (*2*).

Does the reaction proceed to completion? If so, explain from the standpoint of the ionic hypothesis (*3*).

b. [Two students working together.] Pour into a burette a portion of the alkaline solution prepared in *a.* Into another burette pour a quantity of normal hydrochloric acid [Special]. See that the nozzles of both burettes are completely filled with the corresponding solutions. Measure into a small flask about 10 cc. of the alkaline solution (*4*).

Add a drop of phenolphthalein solution to the flask and then run in the acid cautiously until the red color of the "indicator" just disappears (*5*).

(1)

(2)

(3)

(4)

(5)

If the acid solution is exactly normal the number of cc. of acid required for the neutralization of 1 cc. of the alkali will give directly the normality of the alkali (*6*).

If the acid is not exactly normal determine, by means of the factor, the equivalent of the volume used in cc. of normal acid, and then determine as before the volume of normal acid required for the neutralization of 1 cc. of this alkali, *i.e.* the normality of the alkali (*7*).

c. When the normality of the alkali is thus determined, calculate the weight of potassium hydroxide per liter (*8*).

If the alkaline solution is above normal calculate the volume of solution which must be diluted to 100 cc. in order to give a normal alkali (*9*).

125. Potassium Nitrate

a. Dissolve 17 g. of sodium nitrate and 15 g. of potassium chloride in 40–50 cc. of water, and evaporate the solution on a sand-bath to one half its volume. Decant the hot solution from the crystals which have appeared during the evaporation and wash the crystals with a few cc. of cold water. Examine these crystals as to form and compare with crystals of sodium nitrate and potassium chloride (*1*).

Compare them also with crystals of potassium nitrate and sodium chloride (*2*).

As the hot solution cools a further separation of crystals will occur. Again decant off the liquor and wash this second crop of crystals with a few cc. of cold water. Compare them with the first drop of crystals (*3*).

By reference to Appendix V note which one of the four compounds, possible of existence in a solution where potas-

(6)

(7)

(8)

(9)

(1)

(2)

(3)

sium chloride and sodium nitrate are mixed, is least soluble at 100° (*4*).

If this least soluble salt separates out from the hot solution what other salt must be left in large quantity in the hot mother liquor (*5*)?

Will there be a greater or less tendency for this other salt to separate as the solution cools (*6*)?

Test a small sample of each crop of crystals and note the relative amount of impurity present (*7*).

Recrystallize portions of the first and second crops of crystals from small quantities of water in test-tubes and apply tests to prove the purity of each (*8*).

Account for the purification of potassium nitrate by the method of crystallization (*9*).

b. Mix together on a paper 2–3 g. of pulverized potassium nitrate and 1 g. of powdered charcoal. Drop a pinch of this mixture into a red hot crucible and note results (*10*).

Allow the residue in the crucible to cool, test with dilute sulphuric acid, and note the gases evolved (*11*).

Reserve the mixture for *d.*

c. Mix together on a paper 2–3 g. of pulverized potassium nitrate and 1 g. of flowers of sulphur. Drop a pinch of this mixture into a red hot crucible and note gas evolved (*12*).

Allow the residue to cool. Dissolve it in water and test with barium chloride solution (*13*).

Reserve the mixture for *d.*

d. Bring together on a paper a pinch of the mixture from *b* and one also from *c.* Drop a little of this final mixture into a red hot crucible [Caution] (*14*).

Explain the explosive power of gunpowder (*15*).

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)
(*15*)

126. Potassium Thiocyanate. [Hood]

Warm upon a sand-bath 1–2 cc. of potassium cyanide solution in an evaporating dish. Now add yellow ammonium sulphide solution till the yellow color remains. Finally evaporate the mixture completely to dryness. Dissolve the residue in a few cc. of water and add a drop of the solution to one drop of ferric chloride solution diluted with 10 to 15 times its volume of water (*1*).

This production of ferric thiocyanate constitutes a delicate test for ferric ion.

What kind of ionic chemical change is here illustrated (*2*)?

127. Reactions of Potassium Salts

a. Heat a little solid potassium nitrate upon a clean platinum wire and observe color of flame produced (*1*).

Examine this flame with a spectroscope and note position of the lines of potassium in respect to the yellow D line of sodium. The latter is always observed unless precautions are taken to purify the various salts and even the air of the laboratory from traces of sodium compounds (*2*).

b. Saturate 5–7 cc. of warm water (at about 40°) with potassium nitrate and add the solution to an equal volume of tartaric acid solution in a beaker. Cool the final solution and stir constantly (*3*).

Filter off the precipitate and wash it with 1–2 cc. of cold water. Would you classify this product as soluble or only slightly soluble in water (*4*)?

Reserve the product for *c* and *d*.

c. Dissolve a few particles of the precipitate from *b* in warm water and test reaction of solution to litmus (*5*).

(*1*)

(*2*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

Y

What class of salt is shown to be present (potassium is a strong base and tartaric acid a dibasic acid) (*6*)?

d. Strongly heat the remaining portion of the precipitate fr[illegible] *b* in an open porcelain crucible. Extract the cooled mass with hot water and acidify the solution with hydrochloric or sulphuric acid (*7*).

The ignition of all alkali salts of organic acids gives a similar result.

e. Try the action of 1–2 cc. of potassium chloride solution upon a few cc. of picric acid solution (*8*).

Repeat the experiment diluting the potassium chloride solution tenfold with water (*9*).

Is potassium picrate soluble or slightly soluble (*10*)?

128. Ammonium Salts

a. What is the general effect of heat upon ammonium salts (*1*)?

Ascertain by trial whether or not ammonium phosphate behaves in this manner. Dissolve the residue in water and test the solution to litmus (*2*).

Recall an experiment (**85** *a*) in which certain ammonium salts failed to give ammonia upon heating (*3*).

Recall also an experiment (**86** *b*) in which ammonia was evolved from a substance containing no ammonium salt (*4*).

b. Add a few drops of sodium hydroxide solution to a few drops of a solution of any ammonium salt and warm (*5*).

Is this a distinctive characteristic of ammonium salts? If so, explain by reference to the ionic hypothesis (*6*).

c. Add a few drops of a solution of any ammonium salt to 1–2 cc. of tartaric acid solution and shake (*7*).

(6)

(7)

(8)

(9)

(10)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

Classify ammonium hydrogen tartrate as to solubility (***8***).

d. Repeat *c,* substituting 1–2 cc. of picric acid solution for the tartaric acid (***9***).

Classify ammonium picrate as to solubility (***10***).

e. Compare the salts prepared in *c* and *d* with the similar compounds prepared in **127** *b, c, d,* and *e* (***11***).

Test the reaction of potassium chloride or ammonium chloride solution to litmus and explain (***12***).

129. Sodium Hydrogen Carbonate. [Solvay Process]

a. Place about 75 cc. of ammonium hydroxide solution and 25 cc. of water in a 250 cc. flask, add about 30 g. of powdered salt, and shake the mixture until the ammoniacal solution is thoroughly saturated with the sodium chloride. Filter the solution and place it in a wide-mouthed bottle fitted with a two-hole cork. Through one of these holes lead almost to the bottom of the bottle a glass delivery tube connected at its upper end with a laboratory supply of carbon dioxide (or Kipp's generator). When the air in the bottle is displaced by carbon dioxide close the second hole by a glass rod and allow the carbon dioxide to be absorbed slowly by the solution in the bottle. If after an hour no appreciable precipitation has taken place disconnect the carbon dioxide supply and close the glass delivery tube with a cap of rubber tubing plugged with a glass rod. Set the closed bottle aside for a day or two and filter off the deposit which slowly accumulates. Dry the product between filter papers and reserve for *b* and *c* and **130.** Construct equations for the formation of sodium hydrocarbonate from salt (***1***).

b. Dissolve a little of the product prepared in *a* in water and test the reaction of the solution to litmus (***2***).

(*8*)

(*9*)

(*10*).

(*11*)

(*12*)

(*1*)

(*2*)

If the hydrocarbonate is present why is there no acid reaction (*3*)?

c. To a few cc. of this solution of sodium hydrocarbonate add any dilute mineral acid and note gas evolved (*4*).

130. Sodium Carbonate

a. Place a portion of the solid sodium hydrogen carbonate from **129** *a* in a test-tube, clamp this tube near its neck to a ring-stand so that the mouth of tube is inclined slightly downward. Then heat the salt strongly and note gas and vapor evolved (*1*).

Construct an equation for this reaction (*2*).

When the action has ceased cool the tube, dissolve the residue in a little water, and reserve for *b*, *c*, and *d*.

b. Test the solution of this salt from *a* with litmus (*3*).

Relate this action to that of the sodium hydrogen carbonate in **129** *b* and explain (*4*).

c. Test a few drops of the aqueous solution from *a* with a little dilute mineral acid and explain (*5*).

d. Allow the rest of the solution to evaporate spontaneously to point of crystallization. Remove one or two crystals and expose them to the air on a watch-glass (*6*).

131. Reactions of Sodium Salts

a. Heat any salt of sodium upon a platinum wire and note color of flame (*1*).

Examine this flame with a spectroscope (*2*).

b. To a few drops of a concentrated solution of any sodium salt add 1–2 cc. of tartaric acid and shake (*3*).

Compare result with that obtained in **127** *b* and **128** *c* (*4*).

c. Repeat *b*, substituting 1–2 cc. of picric acid solution for the tartaric acid (*5*).

(3)

(4)

(1)

(2)

(3)

(4)

(5)

(6)

(1)

(2)

(3)

(4)

(5)

Compare result with that obtained in **127** *e* and **128** *d* (*6*).

d. Which salts of potassium, ammonium, and sodium are the least soluble (*7*)?

e. How could you distinguish the salts of potassium, ammonium, and sodium from each other (*8*)?

132. Ionic Equilibrium. [R. 59]

a. Fill a test-tube with water, add a few drops of methyl orange solution, and distribute the solution between three test-tubes. To one tube add a few drops of an acid, to the second a few drops of a base, and note the colors shown by this indicator in neutral, acid, and alkaline solutions (*1*).

b. Fill again a test-tube with water containing 2–3 drops of methyl orange solution. Distribute the solution between three test-tubes and add to each of two tubes a few drops of acetic acid. To the third tube add a drop of hydrochloric acid. To one of the tubes containing acetic acid add a little solid sodium chloride and shake (*2*).

The addition here of an ionogen furnishing no common ion should not affect the concentration of either ion present in acetic acid.

To the second tube containing acetic acid add a little solid sodium acetate and shake (*3*).

The addition here of an ionogen furnishing a common ion has what effect upon the equilibrium between this common ion, when uniting with any other ion, and the ionogen possible of formation (*4*)?

To the third tube containing hydrochloric acid add a little solid sodium chloride and shake (*5*).

The addition here of an ionogen likewise furnishing a common ion must have the same effect as just noted in

(*6*)

(*7*)

(*8*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

the case of acetic acid and sodium acetate. If, however, no appreciable change is observed in the acidity of the solution, wherein must lie the reason for this variance (*6*)?

133. Ion-Product Constant

Ionic equilibrium is now to be referred to saturated solutions of ionogens. Fill a test-tube with water, drop in a little potassium chlorate, and shake till saturation is effected. Distribute the clear solution between three test-tubes.

To one test-tube add a saturated sodium chloride solution, shake, and allow to stand for 1–2 minutes (*1*).

The addition here of an ionogen furnishing no common ion should not affect the ionic equilibrium for the ionogen concerned.

To the second test-tube add a saturated solution of potassium chloride, shake, and allow to stand (*2*).

The addition now of an ionogen furnishing a common ion (potassium ion) must at once disturb the equilibrium between the ionogen concerned (potassium chlorate) and its ions. If the solution, however, is saturated in respect to this ionogen (as expressed by the ion-product constant for potassium chlorate), what must occur (*3*)?

To the third test-tube add a saturated solution of sodium chlorate, shake, and allow to stand (*4*).

Again the addition of an ionogen furnishing a common ion (chlorate ion) will have what effect upon the ionic equilibrium between potassium chlorate and its ions (*5*)?

What must result if the ion-product constant is overstepped (*6*)?

The slight dilution of original solutions by addition of other solutions is here to be disregarded.

(6)

(1)

(2)

(3)

(4)

(5)

(6)

134. Application of Ion-Product Constant

a. Purification of Sodium Chloride. The impurities in common salt consist chiefly of chlorides and sulphates of magnesium and calcium. Place about 25 g. of crude common salt in a flask, pour upon it a little water, and shake; then decant the liquid together with all suspended impurities. Pour upon this washed salt about 100 cc. of water and shake until the solution is saturated. Decant clear solution into a beaker and pass into it a current of hydrogen chloride (*1*).

Prepare a hydrogen chloride generator as described in **38** (Fig. 12), and in order to avoid frothing pour 25–30 cc. of concentrated hydrochloric acid upon the salt in this flask. Attach the small end of the thistle tube to the exit tube of the flask and allow the hydrogen chloride to be delivered into the salt solution through the open or larger end, thus avoiding any stoppage of the delivery tube by small crystals.

When considerable precipitation has occurred filter off the crystals of purified sodium chloride and dry them by pressing between filter papers. Expose a few of these crystals to moist air and note if moisture is absorbed (*2*).

Why is sodium chloride precipitated (*3*)?

Why are not magnesium and calcium chlorides also precipitated (*4*)?

Are these latter salts in any way affected (*5*)?

Are the sulphates of magnesium and calcium at all affected in this operation (*6*)?

b. Liberation of Hydrogen Chloride from Hydrochloric Acid. Explain the evolution of hydrogen chloride from a concentrated hydrochloric acid solution when a little concentrated sulphuric acid is dropped into the latter (*7*).

(1)

(2)

(3)

(4)

(5)

(6)

(7)

CHAPTER XX

THE ALKALINE EARTH METALS

135. Calcium Oxide

Place a small piece of marble upon the wire gauze and heat it strongly with a Bunsen flame for 10–15 minutes. Break off a fragment from the heated product and treat it with a few drops of dilute hydrochloric acid in a test-tube (*1*).

Determine in similar manner the action of this acid upon a small fragment of marble that has not been heated (*2*).

Construct an equation to show the effect of heat upon marble (*3*).

Is this a reversible reaction [R. 60]? If so, what conditions are necessary for complete decomposition of marble (*4*)?

Reserve the remaining portion of the quick lime for **136.**

136. Calcium Hydroxide

Place the quick lime, prepared in **135**, in a test-tube, moisten with a few drops of water, and note effect (*1*).

Add now 10–15 cc. of water to the tube and shake. Filter the mixture and collect the clear filtrate in a small flask. Ascertain whether or not calcium hydroxide is very soluble in water by pouring out a few drops of the solution upon a watch-glass and allowing the solution to evaporate (*2*).

Determine the reaction of this lime-water to litmus (*3*).

Reserve the solution in the flask for use in **137.**

(1)

(2)

(3)

(4)

(1)

(2)
(3)

[redacted]

137. Calcium Carbonate and Calcium Hydrocarbonate

Into the flask from **136**, containing the solution of calcium hydroxide, pass a current of carbon dioxide from the laboratory supply (or Kipp's apparatus). Note the formation of a precipitate and formulate the reaction (*1*).

Continue passing this stream of carbon dioxide through the mixture and note finally the disappearance of the precipitate. Construct an equation for this action (*2*).

Transfer a portion of this clear solution to a test-tube and heat it to boiling (*3*).

Explain the result (*4*).

Into the remaining portion of the clear solution in the flask pour a few cc. of lime-water (*5*).

Construct an equation for this action (*6*).

"Temporary hardness" in water is due to the presence of certain of the more soluble hydrocarbonates, especially that of calcium. In what two ways may it be removed (*7*)?

138. Reactions of Calcium Salts

a. Heat any salt of calcium upon a clean platinum wire and note color of flame (*1*).

Examine this flame with a spectroscope and indicate, by a diagram, the positions of the calcium lines with reference to the D line of sodium (*2*).

b. To a test-tube containing 1–2 cc. of calcium chloride solution add an excess of ammonium oxalate solution (*3*).

Filter off the precipitate and divide it into two portions.

Treat one portion of the precipitate with a little dilute hydrochloric acid in a test-tube (*4*).

Treat the second portion of the precipitate with diluted acetic acid (1 part acid : 3 or 4 parts water) (*5*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

z

Explain the behavior of calcium oxalate towards hydrogen ion of varying concentration (see **133**) (*6*).

c. Ascertain if oxalic acid may be used in place of the ammonium oxalate in *b*. Add a slight excess of oxalic acid to 1–2 cc. of calcium chloride solution in a test-tube (*7*).

In order to determine whether or not this reaction is reversible filter off the precipitate of calcium oxalate and add a few drops of ammonium hydroxide solution to the clear filtrate. Note the additional amount of calcium oxalate precipitated and compare this with the entire volume of precipitate as first obtained when oxalic acid and calcium chloride were mixed (*8*).

Place the precipitated calcium oxalate in a test-tube, add a little water and just sufficient dilute hydrochloric acid to dissolve this precipitate. Now add considerable sodium acetate solution and explain the effect of sodium acetate upon the hydrogen ion [R. 61] (*9*).

d. Place 2–3 cc. of calcium chloride solution in a test-tube, add a slight excess of ammonium carbonate solution, and warm the mixture slightly. Filter off the precipitate and divide it into two portions. Test a small sample of the filtrate from this precipitated carbonate, with a few drops of ammonium oxalate solution, and note if the filtrate still holds calcium salt (*10*).

Is calcium carbonate more soluble than the oxalate (*11*)?

Treat one portion of the precipitate with dilute hydrochloric acid and note action (*12*).

Treat the second portion of the precipitate with diluted acetic acid (1 acid : 3 or 4 water) and note action (*13*).

Explain this difference in behavior of calcium carbonate and calcium oxalate towards dilute acetic acid (*14*).

(6)

(7)

(8)

(9)

(10)

(11)

(12)

(13)

(14)

e. To a test-tube containing 2–3 cc. of calcium chloride solution add an excess of dilute sulphuric acid (***15***).

Filter off the precipitate and treat a very small portion of it with a little concentrated hydrochloric acid in a test-tube. Explain the result (***16***).

Divide the clear filtrate from this precipitated calcium sulphate into three portions. To one portion add an equal volume of alcohol and shake. Note difference of solubility of calcium sulphate in water and in dilute alcohol (***17***).

Neutralize the second portion of the filtrate with ammonium hydroxide solution and then add ammonium oxalate solution and explain (***18***).

Is the sulphate of calcium more or less soluble than the oxalate (***19***)?

To the third portion of the filtrate add sodium carbonate solution, both for neutralization of acid present and precipitation of carbonate (***20***).

Is the carbonate more or less soluble than the sulphate of calcium (***21***)?

"Permanent hardness" in water is due chiefly to the presence of sulphate of calcium (and magnesium) and cannot be removed by boiling the solution. What method may be recommended for its removal (***22***)?

f. To 1–2 cc. of calcium chloride solution add a little potassium dichromate solution (***23***).

A precipitate may be obtained if the calcium salt is in sufficient concentration (see **140** *f*).

139. Reactions of Strontium Salts

Dilute 3–4 cc. of strontium chloride solution with twice its volume of water and use in *a*, *b*, *c*, *d*, and *e*.

(15)

(16)

(17)

(18)

(19)

(20)

(21)

(22)

(23)

a. Dip a platinum wire into the strontium chloride solution and introduce the wire into a flame. Note color of flame (*1*).

Examine this colored flame with the spectroscope, draw a diagram of the strontium spectrum and compare it with a spectrum of calcium (**138** *a*) (*2*).

b. Add a little ammonium carbonate solution to one portion of the strontium chloride solution (*3*).

Construct the equation for this action (*4*).

c. To the second portion of the strontium chloride solution add ammonium oxalate solution (equation) (*5*).

Is strontium oxalate more or less soluble than strontium carbonate (see Appendix IV) (*6*)?

d. Add to the third portion of the strontium chloride solution a little dilute sulphuric acid (equation) (*7*).

Is strontium sulphate more or less soluble than strontium carbonate (see Appendix IV) (*8*)?

e. To the last portion of the strontium chloride solution add calcium sulphate solution (prepared by shaking a little powdered calcium sulphate with water and filtering the mixture in order to obtain the clear solution) (*9*).

Is strontium sulphate more or less soluble than calcium sulphate (*10*)?

f. To a few cc. of strontium chloride solution add a little potassium dichromate solution and note the precipitation of a slight amount of strontium chromate (*11*).

Test the reaction mixture with Congo red paper, to detect free mineral acid if present in sufficient quantity (*12*).

Construct an equation for the reaction (*13*).

Compare this result with that obtained for calcium chromate in **138** *f* (*14*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

Add a little acetic acid to the test-tube and note the solubility of strontium chromate in this reagent (*15*).

Recall these results for comparison in **140** *f*.

140. Reactions of Barium Salts

Dilute 3–4 cc. of barium chloride solution with twice its volume of water and use in *a*, *b*, *c*, *d*, *e*, and *f*.

a. Try the flame test with this solution (*1*).

Examine the colored flame with the spectroscope, draw a diagram of the spectrum and compare it with the spectra of calcium (**138** *a*) and strontium (**139** *a*) (*2*).

b. Add a little ammonium carbonate solution to one portion of the barium chloride solution (*3*).

c. Add ammonium oxalate solution to the second portion of the barium chloride solution (*4*).

Is barium oxalate more or less soluble than barium carbonate (see Appendix IV) (*5*)?

d. Add a little dilute sulphuric acid to the third portion of the barium chloride solution (*6*).

Is barium sulphate more or less soluble than barium carbonate (see Appendix IV) (*7*)?.

e. To the fourth portion of the barium chloride solution add strontium sulphate solution (prepared by shaking a little powdered strontium sulphate with water and filtering off the clear solution) (*8*).

Is barium sulphate more or less soluble than strontium sulphate (*9*)?

Compare the solubilities of the sulphates of calcium, strontium, and barium (*10*).

May these differences in solubility serve as a means for the identification of the alkaline earth metals (*11*)?

(*15*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

[redacted]

f. To the last portion of the barium chloride solution add a little potassium dichromate solution (*12*).

Test the reaction mixture with Congo red paper, rinse the paper with water, and note if mineral acid is present in appreciable quantity (*13*).

Construct an equation for the formation of barium chromate (*14*).

Compare the solubilities of calcium chromate (**138** *f*), strontium chromate (**139** *f*), and barium chromate (see also Appendix IV) (*15*).

Add a little acetic acid to the test-tube containing barium chromate and note the insolubility of this chromate (*16*).

May this reaction serve for the separation of barium from calcium and strontium (see **139** *f*) (*17*)?

141. Identification of Positive Radicals

The positive radicals so far studied include the elements potassium, sodium, calcium, strontium, and barium, and the group ammonium. Methods for the recognition of each have been given in the text proper. When, however, an "unknown" is presented, the student should first determine the analytical group to which the cation belongs. For this purpose certain well-selected precipitants have found universal use. One cannot do better, therefore, than to adopt the system which, based upon these precipitants, serves so admirably for the separation of the cations into distinctive groups.

In general the salts of the alkali metals constitute a "soluble class" and these cations, therefore, fail of precipitation by the more common reagents.

The alkaline earth metals, on the other hand, may give

(12)

(13)

(14)

(15)

(16)

(17)

a number of almost insoluble compounds and, as has just been observed, the carbonates constitute the most acceptable form for their precipitation. Of the soluble carbonates the most serviceable for this precipitation is ammonium carbonate. The presence of an ammonium salt, such as ammonium chloride, is also required since an excess of ammonium salt prevents the formation of the more or less soluble hydroxides. The use of other carbonates does not necessarily eliminate the formation of these hydroxides through hydrolysis, but with ammonium carbonate the precipitation of the alkaline earth metals in the form of carbonates is the only possible result. The mother liquor left after the removal of these carbonates is usually freed of the last traces of alkaline earth metals by further treatment with ammonium sulphate and oxalate.

When the alkali and alkaline earth metals are together present in a solution, we must first rid the solution of acid by its neutralization with ammonium hydroxide and then add the precipitant, — ammonium carbonate. If no acid is present, hydrochloric acid should be added and then ammonium hydroxide solution used for its neutralization. In this way we are assured of the presence of an excess of ammonium chloride in the solution. A precipitate obtained by the use of ammonium carbonate indicates at once calcium, strontium, or barium carbonates, which should be filtered off and dissolved at once in dilute acetic acid.

This acetic acid solution may now be examined for the presence of calcium, strontium, or barium in accordance with the reactions outlined in this chapter.

The mother liquor left after the separation of the insoluble carbonates of the alkaline earth metals is next to be ex-

[redacted]

amined for the presence of potassium or sodium; the latter of course is always present in minute quantities.

If ammonium salts are present, recognition of this fact must be made in the original solution by warming it with a strong alkali and testing for the evolution of ammonia.

The identification of other positive radicals will be considered under the general scheme for their classification, discussed at the end of each of the following chapters.

Apply [Instructor] for two unknown solutions (A and B) containing salts of calcium, strontium, barium, potassium, and sodium.

The student may be required to determine also what negative radicals are present; in this matter reference should be made to **122** and **123**.

Place the results found for each unknown in the table on the opposite page.

Solution containing Salts of
Ca, Sr, Ba, K, and Na

Acidify solution with hydrochloric acid, then make alkaline with ammonium hydroxide and add ammonium carbonate solution

Unknown	*Precipitate* $CaCO_3$, $SrCO_3$, $BaCO_3$ Dissolve in acetic acid. Apply individual tests for Ca, Sr, and Ba.	*Filtrate* $K^{\cdot}$ and $Na^{\cdot}$
A		
B		

[redacted]

CHAPTER XXI

COPPER AND SILVER

142. Cuprous Chloride

a. Dissolve about 2 g. of cupric chloride in 10–15 cc. of water in a small flask, add 2–3 cc. of concentrated hydrochloric acid and 4–5 g. of copper disks, and then boil the mixture till the green color has disappeared. If a few drops of this yellowish brown solution are mixed with a few cc. of water in a test-tube, there should be an absence of blue color (and hence of cupric ion). When this stage is reached, divide the solution into two portions, reserve one for **143**, and pour the second into a beaker of water (*1*).

Filter off the precipitate thus formed and construct the equation for its formation (*2*).

Reserve this cuprous chloride for *b*, *c*, and *d*.

b. Place a small quantity of the cuprous chloride from *a* in a test-tube, add a little concentrated hydrochloric acid to effect a solution, and explain [R. 62] (*3*).

Compare the concentration of cuprous ion in cuprous chloride with its concentration in this complex ion (*4*).

Construct an equation for the formation of the complex chloride (*5*).

Pour this acid solution into considerable water in a test-tube. Is the complex chlorocuprous acid easily hydrolyzed by water (*6*)?

(1)

(2)

(3)

(4)

(5)

(6)

c. Repeat *b*, dissolving a small amount of cuprous chloride in concentrated hydrochloric acid. To this solution now add a little chlorine-water (*7*).

What ion is identified at once by its color (*8*)?

Pour the solution into considerable water in a test-tube and note if the oxidation is complete (*9*).

Construct an equation for the action (*10*).

Define this form of oxidation and also the reduction as shown in *a* by reference to the ionic hypothesis (see **64**) (*11*).

d. Expose a portion of moist cuprous chloride to direct sunlight and observe effect [R. 63] (*12*).

143. Cuprous Oxide

a. To that reaction mixture from **142** *a* containing cuprous chloride and hydrochloric acid, add sufficient sodium hydroxide solution for complete precipitation of hydrated cuprous oxide and warm gently (*1*).

Construct an equation for the formation of cuprous oxide from cuprous chloride (*2*).

Reserve the mixture for *b*, *c*, and *d*.

b. Pour a small portion of this mixture from *a* into a test-tube and add a little concentrated hydrochloric acid (*3*).

Compare the concentration of cuprous ion in cuprous oxide with that in cuprous chloride (*4*).

c. To a second portion of this mixture of cuprous oxide add ammonium hydroxide solution (*5*).

Note color of ammonio-cuprous ion(*6*).

Shake the contents of this tube with air and note change to blue ammonio-cupric ion (see **144**) (*7*).

d. Boil the last portion of the mixture and observe the slow oxidation of cuprous oxide (*8*).

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

[redacted]

144. Cupric Hydroxide

a. Dilute 3–4 cc. of cupric sulphate solution with twice its volume of water and add an excess of sodium hydroxide solution (*1*).

Construct the equation for the reaction (*2*).

Divide the mixture into three portions and reserve for *b*, *c*, and *d*.

b. Heat one portion of the mixture from *a* to boiling. Note color change and formation of new product [R. 64] (*3*).

c. To the second portion of the cupric hydroxide suspension add ammonium hydroxide solution and shake (*4*).

What complex ion is formed (*5*)?

Explain the formation of this soluble complex base from the almost insoluble cupric hydroxide (*6*).

What class of ionic change is thus represented (see **64**) (*7*)?

d. Add a little diluted glucose syrup to the third portion of the mixture from *a*; warm the two gently. Compare the final precipitate with that prepared in **143** *a* (*8*).

145. Cuprous Iodide

Dilute in a test-tube a few cc. of cupric sulphate solution with twice its volume of water and add a little potassium iodide solution (*1*).

Filter off the precipitate, place it in a test-tube with a few drops of concentrated sulphuric acid, and observe if it reacts as an iodide (see **76** *f*) (*2*).

Shake the filtrate with chloroform and note what free substance is thus extracted (*3*).

Construct a series of equations to show the formation of this product from a cupric salt (*4*).

(1)
(2)

(3)

(4)
(5)

(6)
(7)

(8)

(1)

(2)

(3)

(4)

146. Reactions of Cupric Salts

Dilute 3–4 cc. of cupric sulphate solution with twice its volume of water and use in *a*, *b*, *c*, and *d*.

a. Test the reaction of a cupric sulphate solution to litmus and explain (*1*).

b. Pass a current of hydrogen sulphide into one portion of the cupric sulphate solution and construct an equation for the reaction (*2*).

Is this action reversible? Ascertain by adding dilute sulphuric acid to the test-tube containing the cupric sulphide in suspension (*3*).

c. To another portion of the cupric sulphate solution add a little potassium ferrocyanide solution (*4*).

Construct the equation for this reaction (*5*).

d. To another portion of the cupric sulphate solution add sodium carbonate solution (*6*).

Is a normal carbonate precipitated [R. 65] (*7*)?

e. Recall the action of zinc upon cupric ion (see **64**) (*8*).

f. Make a borax bead, moisten the bead with a solution of any copper salt, and heat in the oxidizing flame (*9*).

Reheat the bead in the reducing flame (*10*).

Compare results with those in **101** *g* and **121** *c* (*11*).

g. Mix a little anhydrous sodium carbonate with a small quantity of any copper salt. Place a portion of this mixture upon a charred splint and heat it in the reducing portion of a small Bunsen flame. Now break off the charred portion of the splint in a mortar, add a little water to wash away the lighter particles, and examine the residue (*12*).

Drop the residue into a test-tube containing about one cc. of dilute nitric acid (*13*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

Add now an excess of ammonium hydroxide solution and note distinctive reaction for cupric ion (*14*).

147. Ammonio-Cupric Compounds

a. Into a test-tube containing a few drops of cupric sulphate solution add a drop of ammonium hydroxide solution (*1*).

State the nature of the precipitate first formed [R. 66] (*2*).

Add now a slight excess of ammonium hydroxide solution to the test-tube and note formation of ammonio-cupric sulphate. State how ammonio-cupric hydroxide might have been prepared (see **144** *c*) (*3*).

Reserve the blue solution for *b*, *c*, and *d*.

Does the formation of the ammonio-cupric ion constitute a delicate test for copper? Ascertain by highly diluting one cc. of cupric sulphate solution in a test-tube and adding ammonium hydroxide solution (*4*).

Is the colorless ammonio-cuprous ion readily oxidized into this colored complex ion (see **143** *c*) (*5*)?

b. Pour a little of the blue ammonio-cupric solution into a test-tube and drop into it a few pieces of zinc. Do you observe the disappearance of blue color and slow separation of copper as in **146** *e* (*6*)?

Does this prove the presence of cupric ion in the complex ammonio-cupric ion (see **64** *a*) (*7*)?

c. Into the second portion of the ammonio-cupric sulphate solution pass a current of hydrogen sulphide (*8*).

Does cupric sulphide give a greater or less concentration of cupric ion than this ammonio-cupric ion (*9*)?

d. To the last portion of ammonio-cupric sulphate solution add potassium ferrocyanide solution (*10*).

(14)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

Compare the relative concentrations of cupric ion in cupric ferrocyanide and in ammonio-cupric ion (*11*).

Should we expect cupric sulphide or cupric ferrocyanide to dissolve in ammonium hydroxide solution (*12*)?

148. Cuprocyanides

a. Dilute 3–4 cc. of cupric sulphate solution with twice its volume of water, add a few drops of potassium cyanide solution, and note the formation of a precipitate of cupric cyanide, which immediately loses cyanogen to give the insoluble cuprous cyanide. Add now a considerable excess of potassium cyanide solution (*1*).

Construct a series of equations to express each step leading to the final potassium cuprocyanide (*2*).

Does the solution show the color of the cupric ion (*3*)?

Place a small portion of the solution in a test-tube and pass into it hydrogen sulphide (*4*).

Into another test-tube containing a little of this potassium cuprocyanide solution drop a few pieces of zinc. Is there a separation of copper due to the discharge of any cuprous ion possibly present (see **147** *b*) (*5*)?

b. Does the cuprocyanide ion give a greater or less concentration of cuprous ion than cuprous sulphide (*6*)?

Would cuprous sulphide dissolve in potassium cyanide solution (*7*)?

Should one be able to obtain the bead test for copper when using the potassium cuprocyanide solution (*8*)?

Write the following salts in the order of their decreasing ability to give free copper ions: cupric hydroxide, cupric sulphate, cupric sulphide, cuprocyanide ion, ammonio-cupric ion, cupric ferrocyanide (*9*).

(*11*)

(*12*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

149. Potassium Cupric Sulphate. [A double salt]

a. Dissolve 5 g. of powdered potassium sulphate in about 25 cc. of warm water (at 60–70°) in a small flask. Calculate the weight of crystallized cupric sulphate which corresponds, in equi-molecular proportions, to 5 g. of potassium sulphate. Dissolve this weight of the hydrated cupric sulphate in its own weight of water and pour the solution into the flask containing the potassium sulphate. After mixing the solutions set the flask aside. Examine the form of the crystals which appear and compare them with those of blue vitriol (*1*).

b. Dissolve a little of this double salt in a few cc. of water and apply a few tests for the presence of cupric ion. Does hydrogen sulphide precipitate cupric sulphide (*2*)?

Does potassium ferrocyanide give the brown cupric ferrocyanide (*3*)?

Does ammonium hydroxide give ammonio-cupric ion (*4*)?

How do double salts differ from the complex compounds as illustrated in **147** and **148** and the simple compounds such as cupric sulphate itself (*5*)?

150. The Silver Halides

a. The Chloride. Dilute a few cc. of silver nitrate solution with an equal volume of water and add a slight excess of dilute hydrochloric acid (*1*).

Construct an equation for the reaction and note that no complex ion is formed here (as with cuprous chloride) (*2*).

Filter off the precipitate and wash it with water upon the filter. Divide the precipitate into four portions and note the color of this chloride (*3*).

Expose one portion to direct sunlight and note change (*4*).

(1)

(2)

(3)

(4)

(5)

(1)

(2)

(3)

(4)

Place the second portion in a test-tube and add ammonium hydroxide solution a little at a time and shake (*5*).

Give name and formula of complex salt formed (*6*).

To this same test-tube, containing the complex salt, add cautiously a little dilute nitric acid and express by an equation the action noted (*7*).

To the third portion of the silver chloride precipitate in a test-tube add sodium thiosulphate solution and shake (*8*).

Construct the equation for the action (*9*).

b. The Bromide. Dilute a few cc. of silver nitrate solution with an equal volume of water and add a slight excess of potassium bromide solution (*10*).

Filter off the precipitate, wash with water, and divide it into three portions. Note color of the bromide (*11*).

Expose one portion to direct sunlight. Is there a visible change of color in this compound (*12*)?

To the second portion of the precipitate in a test-tube add a little ammonium hydroxide solution and shake (*13*).

Does silver bromide give a greater or less concentration of argentic ion than ammonio-argentic ion (*14*)?

Has the concentration of the ammonium hydroxide present much to do in determining this factor (*15*)?

To the third portion of the precipitate add a little sodium thiosulphate solution and shake (*16*).

c. The Iodide. Dilute a few cc. of silver nitrate solution with an equal volume of water and add a slight excess of potassium iodide solution (*17*).

Filter off the precipitate, wash with water, and divide it into three portions. Note color of the iodide (*18*).

Expose one portion to direct sunlight. Compare the result with those for the two other halides (*19*).

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

[redacted]

To the second portion of the precipitate in a test-tube add a little ammonium hydroxide solution and shake (*20*).

Does silver iodide give a greater or less concentration of argentic ion than ammonio-argentic ion (*21*)?

Compare here the silver halides and this complex ammonio-argentic ion in the order of their decreasing ability to give argentic ion (*22*).

Relate this order to the order of their respective solubilities as noted in Appendix IV (*23*).

151. Reactions of Silver Salts

a. Test the reaction of silver nitrate solution to litmus (*1*).

b. Place a drop of silver nitrate solution upon the skin. Examine the spot after an hour or more and explain (*2*).

c. Pass a current of hydrogen sulphide through 1–2 cc. of silver nitrate solution diluted with 4–5 cc. water (*3*).

Construct the equation for this action (*4*).

Is the reaction reversible? Ascertain by adding dilute nitric acid to the test-tube (*5*).

d. Dilute one drop of silver nitrate solution in a test-tube with 3–4 cc. of water and add a drop of sodium carbonate solution (*6*).

Pass a current of carbon dioxide through the mixture and explain (*7*).

e. To a test-tube containing 1–2 cc. of silver nitrate solution add slight excess of sodium hydroxide solution (*8*).

Construct an equation for the formation of an intermediate product (*9*).

Formulate the decomposition of the latter (*10*).

(*20*)

(*21*)

(*22*)

(*23*)

(*1*)

(*2*)

(*3*)
(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)
(*10*)

Does the excess of sodium hydroxide lead to the production of a complex compound (*11*)?

Filter off the precipitate, wash with water, and place a small portion of it in a test-tube. To this test-tube now add a little ammonium hydroxide solution (*12*).

What complex base is now present? Relate the same to similar complex salts studied in **150** (*13*).

Place a small quantity of the silver oxide in a test-tube and add sodium chloride solution (*14*).

Compare the concentration of argentic ion in silver oxide with that in silver chloride (*15*).

Transfer the rest of the oxide to a porcelain crucible and heat it strongly over a free flame (*16*).

Compare this oxide with other oxides in its reaction to heat (*17*).

Try the action of nitric acid upon the residue in the crucible (*18*).

f. To a few drops of silver nitrate solution add a single drop of potassium cyanide solution (*19*).

Add now a slight excess of the potassium cyanide solution and construct equations for the complete action (*20*).

Compare the concentration of argentic ion in silver cyanide with that in the argenticyanide ion (*21*).

g. Prepare a little silver chloride by adding dilute hydrochloric acid to 1–2 cc. of silver nitrate solution and decanting off the clear liquid. Wash the insoluble silver chloride with water and again decant the liquid. Now add a granule of zinc and a little dilute hydrochloric acid. Shake and observe the result (*22*).

When all traces of the silver chloride have disappeared, remove any unchanged zinc and decant off the liquid. Now

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

(*20*)

(*21*)

(*22*)

add ammonium hydroxide solution to the test-tube and note if pure silver is dissolved by this reagent (*23*).

h. To 1–2 cc. of silver nitrate solution add a few drops of potassium dichromate solution (*24*).

Test the reaction mixture with Congo red paper for the presence of free mineral acid (*25*).

Construct an equation for the reaction (*26*).

152. The Argentic Ion

Prepare, as in **151** *g*, a little silver chloride and distribute the moist product between four test-tubes for use in *a*, *b*, *c*, and *d*.

a. Into one of the tubes containing the silver chloride pass a current of hydrogen sulphide (*1*).

Construct the equation for the reaction (*2*).

Does silver sulphide give a greater or less concentration of argentic ion than silver chloride (and the other silver halides) (*3*)?

b. To the second test-tube add sufficient ammonium hydroxide solution to dissolve the silver chloride and then pass into this solution a current of hydrogen sulphide (*4*).

Does silver sulphide give a greater or less concentration of argentic ion than ammonio-argentic ion (*5*)?

c. Add sufficient sodium thiosulphate solution to the third test-tube to dissolve the silver chloride. Then pass a current of hydrogen sulphide through this solution (*6*).

Compare the concentration of argentic ion in this complex salt with that in silver sulphide (*7*).

d. To the fourth test-tube add just sufficient potassium cyanide solution to dissolve the silver chloride and then pass into the solution a current of hydrogen sulphide (*8*).

(*23*)

(*24*)

(*25*)

(*26*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

Does silver sulphide give a greater or less concentration of argentic ion than argenticyanide ion (*9*)?

Is the precipitated silver sulphide soluble in a large excess of potassium cyanide solution (*10*)?

Will hydrogen sulphide precipitate silver sulphide from a solution of a silver salt containing a large excess of potassium cyanide (*11*)?

e. Arrange the following named salts of silver in the order of their decreasing ability to give argentic ion: silver chloride, silver oxide, silver iodide, silver bromide, silver cyanide, silver sulphide, argenticyanide ion, ammonio-argentic ion, and argentithiosulphate ion (*12*).

153. Classification of Copper and Silver in an Analytical Scheme

The experimental work in this chapter would naturally point to hydrogen sulphide as the best precipitant for these two metals. The use of a carbonate, as in the preceding chapter, would not lead to complete precipitation, and furthermore if ammonium carbonate were to be used the resulting soluble complex ammonio derivatives would only carry these metals over into the group of the alkalies.

The sulphides of these metals can be formed most readily and from all copper and silver solutions save a very few containing complex ions. The reactions concerned are practically non-reversible, hence we may, with impunity, employ acids to decompose any of the complex ions into simple ions for combination with the sulphide ion. Of the acids best adapted for this purpose hydrochloric acid is much to be preferred.

The insoluble compounds formed by the use of hydro-

(*9*)

(*10*)

(*11*)

(*12*)

chloric acid are few and quite distinct. Their removal, therefore, will constitute the first step in this analytical scheme. Though both cuprous chloride and silver chloride are insoluble in water, the former dissolves in hydrochloric acid of sufficient strength. Consequently, when these two elements are present in a solution, the silver chloride alone will be removed in the acidification by hydrochloric acid. This acidification, however, should proceed somewhat beyond mere acidity; the solution in fact should be about one fourth normal hydrochloric acid.

We may place silver, therefore, in the group of insoluble chlorides and for convenience shall describe it as in Group I.

After the removal of the silver, cupric sulphide may be precipitated from the mother liquor by the action of hydrogen sulphide. Copper, therefore, falls in the next group (Group II) or among those elements whose sulphides are formed in acid solution and which on the other hand do not form insoluble chlorides.

Neither the alkaline earths nor the alkalies are affected by [illegible] introduction of sulphide ions. The sulphides of these metals are completely hydrolyzed. The mother liquor, therefore, after the removal of the copper (Group II), may at once be neutralized with ammonium hydroxide. An excess of ammonium chloride and also ammonium sulphide will thus be formed (the former is in fact required). Ammonium carbonate may then be added for the precipitation of the carbonates of the alkaline earths as noted in the preceding chapter.

Apply [Instructor] for one unknown solution (C) containing salts of silver, copper, calcium, strontium, or barium.

SOLUTION CONTAINING SALTS OF
Ag, Cu, Ca, Sr, AND Ba

Acidify solution with hydrochloric acid

Unknown	*Precipitate* AgCl	*Filtrate* $Cu^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$ Pass H_2S into solution	
		Precipitate CuS	*Filtrate* $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$
C			

CHAPTER XXII

MAGNESIUM, ZINC, CADMIUM, AND MERCURY

154. Reduction by Magnesium

Mix thoroughly in a mortar about 1 g. of calcium carbonate and an equal bulk of magnesium powder. Place the mixture in a test-tube and attach this test-tube by a clamp to a ring-stand. By means of a free flame (applied along the sides of the tube) cautiously heat the upper portion of the mixture and, when the reaction begins, remove the heat supply. Guard against hot particles flying out of the tube. When the action is over, cool the tube, add a little water, and then concentrated hydrochloric acid (*1*).

In addition to the hydrogen and carbon dioxide, which arise from the action of hydrochloric acid upon any unchanged magnesium or calcium carbonate, note the peculiar odor of the hydrocarbon (*2*).

Explain and write an equation for the formation of that compound which yields this hydrocarbon (*3*).

Both the magnesium oxide and calcium oxide formed in this experiment will be dissolved by the excess of hydrochloric acid. Filter off any undissolved material and test it for carbon (by heating it with a few particles of potassium nitrate and examine the gases for carbon dioxide) (*4*).

Account for the production of carbon in this reduction of calcium carbonate (*5*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

155. Properties of Magnesium Compounds

a. Test a solution of magnesium chloride with litmus and account for the action (*1*).

b. Evaporate 2–3 cc. of magnesium chloride solution to dryness in a test-tube by the aid of a gentle heat. Finally heat the tube strongly (*2*).

Test the action of the vapor upon litmus (*3*).

Remove as much of this condensed vapor as is possible (absorption by strips of filter paper) and then add a little water to the cooled residue. Does the entire mass dissolve in the water (*4*)?

Explain this change and construct the equation for any hydrolysis that may have occurred (*5*).

c. Pour equal amounts of magnesium sulphate solution (1–2 cc.) into each of three test-tubes. To one of these tubes add a little sodium hydroxide solution and construct an equation for the reaction (*6*).

To the second tube add a little ammonium hydroxide solution (*7*).

Is there any difference in the quantity of precipitate here from that where sodium hydroxide was used (*8*)?

Mix in a test-tube one cc. of ammonium hydroxide solution and 3–4 cc. of ammonium chloride solution and add this mixture to the third tube containing the magnesium sulphate solution (*9*).

What is the effect of the ammonium salt upon the ionization of ammonium hydroxide (*10*)?

Compare the concentration of hydroxide ion in magnesium hydroxide with that in ammonium hydroxide, with and without the presence of an ammonium salt (*11*).

Does magnesium hydroxide dissolve in ammonium chlo-

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

ride? Ascertain by adding ammonium chloride solution to one of the test-tubes containing this precipitate and explain the result in terms of the ion-product constant (*12*).

d. Place 1–2 cc. of magnesium sulphate solution in a test-tube, add to it a little ammonium carbonate solution, and warm (*13*).

Repeat the experiment, adding 2–3 cc. of ammonium chloride solution before adding the ammonium carbonate (*14*).

Explain the solubility of magnesium carbonate in ammonium chloride solution (*15*).

Compare here the action of ammonium carbonate upon salts of calcium, strontium, and barium (*16*).

e. To a few cc. of magnesium sulphate solution add sodium phosphate solution and formulate the reaction (*17*).

Repeat the experiment but first add a little ammonium chloride solution and then ammonium hydroxide solution before adding the sodium phosphate (*18*).

Explain the formation of this final crystalline precipitate and state the purpose of the two ammonium compounds (*19*).

f. Pass a current of hydrogen sulphide through a few cc. of magnesium sulphate solution diluted with water (*20*).

Magnesium sulphide resembles what other sulphides in this respect (*21*)?

g. Place in an evaporating dish 10–15 cc. of tap water, acidify with hydrochloric acid, and evaporate to a small volume over a water-bath. Transfer the concentrated solution to a test-tube and add ammonium chloride and ammonium hydroxide solutions. Now add ammonium carbonate solution to precipitate calcium, strontium, and barium if present. After the removal of these carbonates, test the filtrate for the presence of magnesium (*22*).

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

(20)

(21)

(22)

156. Reactions of Zinc Salts

a. Test the reaction of a zinc sulphate solution to litmus and explain (*1*).

b. Dilute 2–3 cc. of zinc sulphate solution with an equal volume of water, add sodium carbonate solution, and heat the contents of the tube to boiling (*2*).

Filter off the precipitate, wash it with water, and set aside to dry. Test a small sample of it with hydrochloric acid. Is it a normal carbonate [R. 67] (*3*)?

Place the dry zinc carbonate in a porcelain crucible and heat to redness for a few minutes. Remove small portions of the heated product and test again with dilute hydrochloric acid (*4*).

What is the color of the final product in the crucible both when cold and hot (*5*)?

Reserve for **157** *a.*

c. Dilute 3–4 cc. of zinc sulphate solution with an equal volume of water and pass into it a current of hydrogen sulphide (see **72** *c*) (*6*).

Shake the mixture and distribute it equally between three test-tubes.

In the first test-tube ascertain if the reaction is reversible by adding dilute sulphuric acid a drop at a time and shaking after each addition (*7*).

Now add to this acid solution a little powdered sodium sulphate and again pass hydrogen sulphide into the tube (*8*).

Explain the effect of sodium sulphate upon the concentration of the hydrogen ion present (*9*).

To the second test-tube add just sufficient dilute sulphuric acid to dissolve the precipitate and then add an equal

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

volume of sodium acetate solution. Pass into the tube a current of hydrogen sulphide and explain the result (*10*).

To the third tube add a little ammonium hydroxide solution and pass into it a current of hydrogen sulphide (if desired, ammonium sulphide solution may be added) (*11*).

Is the precipitation practically complete in each of the three test-tubes as finally arranged (*12*)?

Filter off the precipitates and reserve for use in **157** *b*.

d. To 2–3 cc. of zinc sulphate solution add a few drops of potassium cyanide solution (*13*).

Now add a slight excess of this cyanide solution (*14*).

Construct equations for the reactions concerned (*15*).

Pass a current of hydrogen sulphide into the solution of this complex salt and state the relative ability of the complex ion and zinc sulphide to give zinc ion (*16*).

e. To 2–3 cc. of zinc sulphate solution add a few drops of ammonium hydroxide solution (*17*).

Add now a slight excess of the ammonium hydroxide and state name and formula for the complex salt thus formed (*18*).

Compare this complex ion of zinc with that of copper of similar structure (*19*).

157. Zincates

a. Drop into the crucible from **156** *b*, containing the zinc oxide, a drop of cobalt chloride solution and again heat the crucible. Note color of product, — a cobalt zincate (*1*).

b. Roll up the filter paper from **156** *c*, containing the zinc sulphide, and coil the platinum wire tightly around it. Roast the mass in a Bunsen flame; then remove and moisten the ash with cobalt chloride solution and roast again. Note color of product and compare with *a* (*2*).

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

(*1*)

(*2*)

c. To 2–3 cc. of zinc sulphate solution add a little water and then a few drops of sodium hydroxide solution (*3*).

Filter off the precipitate and distribute it between three test-tubes, each containing 1–2 cc. of water. To one tube add a slight excess of sodium hydroxide solution (*4*).

Explain the formation of the soluble zincate and state in what way the zinc hydroxide here functions (*5*).

Pass a current of hydrogen sulphide into the zincate solution and compare the relative ability of zincate ion and zinc sulphide to give zinc ion (*6*).

To the second test-tube add dilute hydrochloric acid (*7*).

In what way does the zinc hydroxide now function (*8*)?

To the third tube add ammonium hydroxide solution (*9*).

What complex base is thus formed? Compare the action here with that observed in **156** *e* and in **144** *c* (*10*).

Pass a current of hydrogen sulphide into the ammoniacal solution and compare the relative ability of this complex ion and zinc sulphide to give zinc ion (*11*).

158. Relative Activity of Certain Acids

The relative amounts of zinc sulphide precipitated from solutions of zinc salts of certain acids may serve as a means of comparing the relative activity of the acids concerned.

Place in three test-tubes equal volumes (2–3 cc.) of zinc chloride solution, zinc sulphate solution, and zinc acetate solution. Compare first the relative activity of these solutions toward litmus and toward Congo red paper (*1*).

Now pass into each solution a current of hydrogen sulphide to saturation (*2*).

(*3*)

(*4*)

(*5*)

(*6*)
(*7*)
(*8*)
(*9*)

(*10*)

(*11*)

(*1*)

(*2*)

[redacted]

The greatest precipitation will occur in that test-tube where the acid liberated by the action of hydrogen sulphide can function least in reversing the reaction. Do hydrochloric, sulphuric, and acetic acids have here the same tendency to react with zinc sulphide precipitated (*3*)?

If not, state which acid is most active, which next, and which least (*4*).

(If this comparison cannot be made from an observation of the precipitates just obtained, the contents of each test-tube should be filtered and each filtrate made alkaline with ammonium hydroxide. Compare now the precipitates of zinc sulphide obtained in the several cases and thus determine the relative amounts of zinc held in solution in each of the three original test-tubes by the acids liberated through the action of hydrogen sulphide.)

159. Reaction of Cadmium Salts

a. Place 1–2 cc. of cadmium sulphate solution in a test-tube, test its reaction to litmus, and explain (*1*).

b. Add to this solution from *a* a little sodium carbonate solution (*2*).

Filter off the precipitate and test portions of it with hydrochloric acid (*3*).

Is this a normal carbonate [R. 68] (*4*)?

c. Dilute 2–3 cc. of cadmium sulphate solution with an equal volume of water and pass hydrogen sulphide into it (*5*).

Divide the contents of the tube into two portions.

Ascertain if the reaction is reversible by adding to one of the tubes a diluted sulphuric acid (1 part concentrated acid : 1 part water), drop by drop (*6*).

(3)

(4)

(1)

(2)

(3)

(4)

(5)

(6)

To this same test-tube then add powdered sodium sulphate or powdered sodium acetate and note the effect upon the concentration of hydrogen ion (*7*).

Filter the contents of a second test-tube containing the cadmium sulphide suspension and add a little ammonium hydroxide solution to the filtrate (*8*).

Does this indicate complete precipitation of cadmium sulphide by the action of hydrogen sulphide (*9*)?

Is cadmium sulphide soluble in ammonium hydroxide solution (*10*)?

d. Dilute 2–3 cc. of cadmium sulphate solution with an equal volume of water and then add a few drops of sodium hydroxide solution (*11*).

Distribute the mixture between three test-tubes.

To one test-tube add a slight excess of sodium hydroxide solution. Does cadmic hydroxide function as an acid (*12*)?

To another test-tube add a little dilute hydrochloric acid and note if the hydroxide functions as a base (*13*).

To the third test-tube add ammonium hydroxide solution and state what complex ion is here formed (*14*).

Pass into this latter solution a current of hydrogen sulphide and compare the concentration of cadmic ion in cadmic sulphide with that in this ammonio-cadmic ion (*15*).

e. To 2–3 cc. of cadmium sulphate solution add a few drops of potassium cyanide solution (*16*).

Now add a slight excess of the potassium cyanide and state what complex salt is formed (*17*).

Divide the solution into two portions.

Pass a current of hydrogen sulphide into one portion and compare the concentration of cadmic ion in cadmic

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

sulphide with its concentration in this complex cadmicyanide ion (*18*).

To the second portion of the solution add sodium hydroxide solution and note if any cadmic hydroxide is precipitated. If not, what can be said of the relative concentrations of cadmic ion in cadmic hydroxide and in this complex cadmicyanide ion (*19*)?

f. Arrange the following salts of cadmium in the order of their decreasing ability to give cadmic ion: cadmic sulphate, cadmic hydroxide, cadmic cyanide, cadmic sulphate, cadmicyanide ion, and ammonio-cadmic ion (*20*).

160. Reactions of Mercuric Salts

Dilute 4–5 cc. of mercuric chloride solution with an equal volume of water and distribute between six test-tubes.

a. Test the reaction of this solution to litmus (*1*).

b. Add dilute hydrochloric acid to a few drops of this solution (other mercuric salts are equally unreactive) (*2*).

c. To a second portion of the solution add sodium hydroxide solution and construct an equation for the formation of mercuric oxide (*3*).

d. Add a little ammonium hydroxide solution to the third portion (*4*).

Construct an equation for the formation of ammono-basic mercuric chloride (*5*).

e. Pass a current of hydrogen sulphide into the fourth portion and construct an equation for the reaction (*6*).

f. To the fifth portion add a few drops of potassium iodide solution (*7*).

Add now a slight excess of the iodide solution and construct an equation for the formation of the complex salt (*8*).

(18)

(19)

(20)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

Into this solution of the complex salt pass a current of hydrogen sulphide and ascertain if the complex ion gives a greater or less concentration of mercuric ion than mercuric sulphide (*9*).

g. Drop a copper disk into the sixth portion of the solution and ascertain if cupric ion enters the solution (see Appendix III) (*10*).

h. Add a globule of mercury to the last portion of the solution of mercuric chloride and shake. Note the formation of a precipitate (*11*).

Compare this reduction by mercury with that obtained by the use of copper in *g* (*12*).

161. Reactions of Mercurous Salts

Dilute 4–5 cc. of mercurous nitrate solution with an equal volume of water and distribute between six test-tubes.

a. Test the reaction of this solution to litmus (*1*).

b. Add dilute hydrochloric acid to a small portion of the solution (*2*).

Decant off the liquid and add ammonium hydroxide solution to the precipitate. Formulate the reaction (*3*).

Compare the result here with that obtained in **160** *b* (*4*).

c. To the second portion of the solution add sodium hydroxide solution [R. 69] (*5*).

Heat the contents of the test-tube and compare the final product with the precipitate obtained in **160** *c* (*6*).

d. Add a little ammonium hydroxide solution to the third portion (*7*).

Compare the result with that obtained in **160** *d* (*8*).

Construct an equation for the reaction (*9*).

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)

(*2*)

(*3*)
(*4*)

(*5*)

(*6*)

(*7*)
(*8*)
(*9*)

Compare the formula for this final product with that of the product finally obtained in *b* (*10*).

e. Pass a current of hydrogen sulphide into the fourth portion. In what way does the precipitate readily decompose [R. 70] (*11*)?

f. Add a few drops of potassium iodide solution to the fifth portion of the solution and state what two products result upon the spontaneous decomposition of this precipitate (*12*).

What is the action of an excess of the iodide solution upon this final mixture (*13*)?

g. Drop a few disks of copper into the last portion of the mercurous nitrate solution and ascertain if cupric ion enters the solution (*14*).

h. State several ways by which one may distinguish between mercurous and mercuric salts (*15*).

162. Couples

Freshly clean four small granules of zinc by shaking them for a few minutes in a test-tube with a little dilute hydrochloric acid. Pour off the acid and wash the granules repeatedly with water. Now place a granule in each of four test-tubes, and into one test-tube pour 1–2 cc. of mercurous nitrate solution; into the second test-tube pour 1–2 cc. of silver nitrate solution, and into the third test-tube pour 1–2 cc. of cupric sulphate solution. After a few minutes decant off the liquid from each of the three test-tubes and wash the granules with water. Finally pour upon these three granules and also upon the fourth granule of pure zinc in the fourth test-tube, an equal volume (about 2 cc.) of dilute sulphuric acid (*1*).

(*10*)

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*1*)

Which granule acts upon the acid most vigorously and why [R. 71] (*2*)?

163. Classification of Magnesium, Zinc, Cadmium, and Mercury in an Analytical Scheme

With the precipitants, hydrochloric and hydrosulphuric acids, already decided upon, it becomes a comparatively simple task to fit the elements of this chapter into the scheme already proposed. Magnesium sulphide, however, is easily hydrolyzed; hence this element will fall into the groups of the alkaline earths and alkalies. Mercury, as already noted, offers two distinct and well-known classes of salts for consideration. The mercurous salts give an insoluble chloride (**161** *b*) and hence mercurous ion, together with argentic ion, will be removed as chlorides (Group I) upon the original acidification of the unknown solution.

When the filtrate, after the separation of Group I, is treated with hydrogen sulphide, cadmic sulphide and mercuric sulphide will be precipitated. These sulphides, therefore, resemble cupric sulphide and hence cadmic ion and mercuric ion fall into Group II.

The filtrate, left after the separation of Group II, is now to be neutralized with ammonium hydroxide. In this way one secures an excess of ammonium sulphide and, in fact, the proper conditions for the complete precipitation of those sulphides soluble to a greater or less extent in acids. Zinc sulphide is just such a sulphide (**156** *c*) and the zinc ion, therefore, falls into a separate group completely precipitated by alkali sulphides.

After the removal of any zinc as sulphide, ammonium chloride and ammonium carbonate are next added to the

(2)

filtrate and the carbonates of the alkaline earths thus removed. The large excess of ammonium salts will, of course, prevent any precipitation of magnesium carbonate (**155** *d*). The filtrate from the alkaline earth carbonates has now only to be treated with sodium phosphate when the highly insoluble magnesium ammonium phosphate (**155** *e*) will be precipitated. Any of the alkalies present may be identified in the final filtrate.

Apply for two unknowns containing salts of calcium, strontium, barium, copper, silver, magnesium, zinc, cadmium, and mercury.

SOLUTION CONTAINING SALTS OF
Ag, Cu, Cd, Hg, Zn, Ca, Sr, Ba, AND Mg
Acidify with hydrochloric acid

	Precipitate AgCl, HgCl	*Filtrate* $Cu^{\cdot\cdot}$ $Cd^{\cdot\cdot}$ $Hg^{\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ Pass H_2S into solution			
		Precipitate CuS, CdS, HgS	*Filtrate* $Zn^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ Neutralize with NH_4OH		
			Precipitate ZnS	*Filtrate* $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ Add $NH_4Cl + (NH_4)_2CO_3$	
Unknown				*Precipitate* $CaCO_3$, $SrCO_3$ $BaCO_3$	*Filtrate* $Mg^{\cdot\cdot}$ Add Na_2HPO_4 *Precipitate* = $MgNH_4PO_4$
D					
E					

[redacted]

CHAPTER XXIII

ALUMINIUM, TIN, AND LEAD

164. Aluminium

a. Drop a little aluminium into each of three test-tubes, one containing a few cc. of dilute hydrochloric acid, the second dilute sulphuric acid, and the third dilute nitric acid (*1*). Compare and explain the results (*2*).

b. Drop a little aluminium into a test-tube containing 2–3 cc. of sodium hydroxide solution. Warm the mixture and note result (*3*).

Test the escaping gas for hydrogen and construct an equation for the reaction (*4*).

Dilute the contents of the tube with an equal volume of water and filter. To the clear solution add a few drops of dilute hydrochloric acid, stopping short of acidity (*5*).

Construct an equation for the reaction (*6*).

165. Reactions of Aluminium Salts

a. Test the reaction of an aluminium sulphate solution to litmus and explain (*1*).

b. Dilute 1–2 cc. of aluminium sulphate solution with an equal volume of water, add one drop of sodium hydroxide solution, and shake (*2*).

Distribute the contents of the tube between three test-tubes and apply the following tests to the precipitate now held in suspension.

(*1*)
(*2*)

(*3*)

(*4*)

(*5*)
(*6*)

(*1*)

(*2*)

To one of these tubes add a little dilute hydrochloric acid and state what type of hydroxide is present (*3*).

To another tube add a few drops of sodium hydroxide solution. State again what type of hydroxide is present (*4*).

Add now an excess of ammonium chloride solution to this same test-tube and heat to boiling. Account finally for the re-formation of the precipitate (*5*).

To the third tube add ammonium hydroxide solution and note if a soluble complex salt is formed (*6*).

c. Dilute 1–2 cc. of aluminium sulphate solution with an equal volume of water, and add a little sodium carbonate solution (*7*).

Filter off the precipitate and wash well with water till free from any excess of sodium carbonate. Then test the precipitate with dilute hydrochloric acid and note if a carbonate is present (*8*).

Construct an equation for the formation of product (*9*).

d. Pass a current of hydrogen sulphide through 2–3 cc. of aluminium sulphate solution slightly diluted with water and explain (*10*).

Now add to the tube a little ammonium sulphide solution and note result (*11*).

Filter off the precipitate, wash it well with water upon the filter, and apply a test to a small portion of it in order to ascertain if a sulphide is present (*12*).

Construct an equation for the formation of product (*13*).

Reserve the major portion of the precipitate for *e*.

e. Roll up the filter paper from *d*, containing the precipitate, and coil a platinum wire tightly around it. Roast the mass in the Bunsen flame, remove it for a moment,

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)
(*9*)

(*10*)

(*11*)

(*12*)
(*13*)

moisten with cobalt chloride solution, and again roast. State color of cobalt aluminate here formed (*14*).

166. Alum

a. Prepare a saturated solution of 5 g. of hydrated aluminium sulphate. Calculate the amount of ammonium sulphate which corresponds in equi-molecular proportions to this weight of the aluminium salt. Dissolve this weight of ammonium sulphate in a small quantity of water and mix the two solutions. Set the mixture aside and note form and taste of the crystals (larger crystals may be obtained by suspending a thread in the beaker containing the mixture) (*1*).

b. Dissolve a few of the small crystals from *a* in water and apply tests as in **165** *b* to ascertain if the solution contains the aluminium ion (*2*).

To another portion of the solution add sodium hydroxide solution in excess and heat the mixture to boiling. Account for the odor evolved (*3*).

Is the compound a double salt or a complex salt (*4*)?

167. Dyeing

a. Prepare six strips of cotton cloth by immersing them first in a beaker of boiling water containing a few cc. of concentrated hydrochloric acid and then again immersing them in another beaker of boiling water containing a few drops of ammonium hydroxide solution. Rinse the strips well and thus secure samples of cotton cloth free from sizing.

b. An Insoluble Dye: Indigo. Pour about 5 cc. of the indigo suspension into a beaker. Add 15–20 cc. of water and a pinch of sodium hyposulphite (so-called sodium "hydrosulphite"). Gently warm the solution till the color has

(14)

(1)

(2)

(3)
(4)

disappeared and then immerse in it two strips of cotton cloth. Remove the strips, wring out the excess of moisture, and set them aside to dry (*1*).

When one of the strips is sufficiently dry immerse it again in the "indigo white" solution and again remove the moist cloth and set it aside to dry (*2*).

Finally wash the two strips in running water and compare the depths of color in each (*3*).

NOTE: If sodium hyposulphite is not at hand reduce the blue insoluble indigo by warming the diluted suspension with the addition of a little glucose and 1–2 cc. of sodium hydroxide solution.

c. A Direct Dye: Congo Red. Pour 3–4 cc. of Congo red solution into a beaker containing 10–20 cc. of water. Add a pinch of sodium carbonate to neutralize any effect of acid from the air and heat to boiling. Dip a strip of the prepared cotton cloth and also a piece of wool into the hot solution for a few minutes. Remove these strips and wash them in running water. Is this a direct dye for both cotton and wool (*4*)?

d. A Direct Dye: Picric Acid. Place 3–4 cc. of picric acid solution in a small beaker, add about 10 cc. of water, and immerse in this solution a strip of cotton cloth and a piece of wool. Remove these pieces after a few minutes' stirring and wash well in running water. Is this dye fast to washing on both cotton and wool (*5*)?

e. An Indirect Dye (Non-basic): Cochineal. A free insoluble "lake" may be made by adding a few drops of ammonium hydroxide solution to 2–3 cc. of the cochineal solution in a test-tube and then adding 1–2 cc. of aluminium sulphate solution.

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

In order that cloth may be impregnated with this lake, soak a strip of cotton cloth in 1–2 cc. of aluminium sulphate solution diluted with a little water, and then immerse this moist cloth in a beaker containing 2–3 cc. of cochineal solution and a few drops of ammonium hydroxide solution (*6*).

In this operation the cloth is first mordanted with the aluminium hydroxide which in turn takes up the dye to form the insoluble lake.

f. An Indirect Dye (Non-basic): Alizarin. Dilute 2–3 cc. of aluminium sulphate solution with 10 cc. of water in a test-tube and heat the solution to boiling. Immerse a strip of cotton cloth in the boiling solution. After a few minutes transfer this cloth to a small beaker of boiling water containing a few drops of ammonium hydroxide solution. Remove the cloth at once and wring out the moisture. Aluminium hydroxide thus remains as a precipitate within the fibers of the cloth.

Place in an evaporating dish 4–5 cc. of alizarin suspension and 30–40 cc. of water, and heat to boiling. Immerse in the dish the strip of cloth "mordanted" as above and also a fresh strip of this cotton cloth which has not been so treated. After about 10 minutes' stirring in the hot solution remove the strips and wash well in running water. Is the dye fast to washing on both strips (*7*)?

168. Tin

a. Place a few granules of tin in a test-tube containing 2–3 cc. of dilute nitric acid. Set the tube aside for **170 *f*** (*1*).

b. Place a few granules of tin in a test-tube containing 2–3 cc. of concentrated nitric acid and warm (*2*).

When the action is complete dilute the contents of the

(6)

(7)

(1)

(2)

tube with a little water and filter. Wash the precipitate on the filter with considerable water and set it aside to dry. When dry place the product in a test-tube and heat strongly. Is it a nitrate (*3*)?

Construct an equation for the hydrolysis which is here to be considered (*4*).

c. Place a few granules of tin in a test-tube containing 2–3 cc. of concentrated hydrochloric acid and warm. Make sure that an excess of tin is present and then set the tube aside for **170** *f* (*5*).

d. Warm a few granules of tin with 2–3 cc. of concentrated hydrochloric acid and then remove any excess of tin still present. Now add bromine-water till the color is no longer destroyed. Finally heat the solution to boiling, to liberate excess of bromine, and reserve for **169** *b* (*6*).

169. Reactions of Stannic Salts

a. Pass a current of hydrogen sulphide through 2–3 cc. of stannic chloride solution in a test-tube (*1*).

Remove a small portion of the mixture to another test-tube and add to it a little dilute hydrochloric acid to ascertain if the reaction is reversible (*2*).

What class of sulphides is thus identified (*3*)?

Filter the major portion of the mixture and treat the precipitate in a test-tube with warm ammonium sulphide solution (*4*).

To this final solution add dilute hydrochloric acid and construct an equation for the reaction (*5*).

b. Pass a current of hydrogen sulphide into the solution prepared in **168** *d* and note if the precipitate resembles the sulphide obtained where stannic ion is present (*6*).

(3)

(4)

(5)

(6)

(1)

(2)
(3)

(4)

(5)

(6)

c. To 3–4 cc. of stannic chloride solution in a test-tube add a very little sodium hydroxide solution (*7*).

Filter off the precipitate and distribute it between three test-tubes each containing a few cc. of water.

To one of these tubes add a little sodium hydroxide solution and construct an equation for the reaction (*8*).

To the second tube add dilute hydrochloric acid and construct an equation for this action (*9*).

To the third portion add ammonium hydroxide solution and explain (*10*).

What type of hydroxide is here identified (*11*)?

d. Drop a few granules of tin into a test-tube containing 2–3 cc. of stannic chloride solution and heat to boiling. Reserve the mixture for **170** *e*.

170. Reactions of Stannous Salts

a. Saturate 2–3 cc. of stannous chloride solution with hydrogen sulphide (*1*).

Test a small portion of the mixture in a separate test-tube with dilute hydrochloric acid and note if the reaction is reversible (*2*).

Filter the remaining portion and warm the precipitate in a test-tube with ammonium sulphide solution. If solution is not effected add a minute portion of flowers of sulphur (*3*).

State the function of this sulphur [R. 72](*4*).

Construct an equation for the final reaction (*5*).

Add a little dilute hydrochloric acid to the clear ammonium sulphide solution and note if stannic sulphide (see **169** *a*) is precipitated (*6*).

Construct an equation for this reaction (*7*).

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

b. To a test-tube containing 3–4 cc. of stannous chloride solution add a very little sodium hydroxide solution (*8*).

Filter off the precipitate and treat separate portions as outlined in **169** *c* (*9*).

What type of hydroxide is here identified (*10*)?

c. Place about 1 cc. of mercuric chloride solution in a test-tube and add to this tube one drop of stannous chloride solution (*11*).

Filter off the precipitate and moisten it on the filter with ammonium hydroxide solution (*12*).

What class of mercury salt is at once identified (*13*)?

Construct an equation from the standpoint of the ionic hypothesis for this reduction of mercuric chloride and the consequent oxidation of stannous to stannic ion. Stannic chloride is without action upon mercuric chloride (*14*).

d. Repeat *c*, adding now an equal volume (an excess) of stannous chloride solution and note gradual disappearance of the white insoluble mercurous salt (*15*).

Finally complete the reaction by warming, then filter off the precipitate, moisten with ammonium hydroxide solution, and state if any trace of mercurous salt is present (*16*).

What is the precipitate unacted upon by the ammonium hydroxide (*17*)?

Construct an equation from the standpoint of the ionic hypothesis for this reduction of a mercurous salt by means of stannous chloride (*18*).

e. Add a few drops of mercuric chloride solution to one portion of the solution prepared in **169** *d* and note if stannous ion can be identified (*19*).

Construct an equation from the ionic standpoint to explain this reduction of stannic ion (*20*).

(8)

(9)

(10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

(20)

[redacted]

To the second portion of the solution from **169** *d* add bromine-water till the color no longer disappears; then boil the solution to remove the excess of bromine and finally add a drop of mercuric chloride solution to ascertain if stannous or stannic ion is present (*21*).

f. Treat each of the solutions prepared in **168** *a* and *c* with a few drops of mercuric chloride solution and ascertain if stannous or stannic ion is present (*22*).

171. Reactions of Plumbous Salts

a. Test the reaction of plumbous nitrate solution to litmus (*1*).

b. Dilute 1–2 cc. of plumbous nitrate solution with several times its volume of water and saturate with hydrogen sulphide (*2*).

Test a portion of the mixture with dilute nitric acid and ascertain if the reaction is reversible (*3*).

What class of sulphides is thus identified (*4*)?

c. Add a few drops of dilute hydrochloric acid to a test-tube containing about 1 cc. of plumbous nitrate solution (*5*).

Filter off the precipitate, transfer it to a test-tube containing 4–5 cc. of water, heat the mixture to boiling, and allow the clear solution to stand. Note solubility of this chloride (*6*).

Dilute the filtrate, as obtained above, with 5–10 cc. of water and pass into it a current of hydrogen sulphide (*7*).

What further indication is given in regard to the solubility of this chloride (*8*)?

d. Place 2–3 cc. of plumbous nitrate solution in a test-tube and add a very little sodium hydroxide solution (*9*).

Filter off the precipitate and treat separate portions of it as outlined in **169** *c* (*10*).

(21)

(22)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

What type of hydroxide is thus identified (*11*)?

e. Dilute about 1 cc. of plumbous nitrate solution with several times its volume of water and add a few drops of potassium iodide solution (*12*).

Boil the contents of test-tube and filter. Examine filtrate upon cooling and note solubility of plumbous iodide (*13*).

f. Dilute about 1 cc. of plumbous nitrate solution with several times its volume of water and add a few drops of potassium dichromate solution (*14*).

Test the reaction mixture with Congo red paper and explain (*15*).

Construct equation for the formation of precipitate (*16*).

How may one proceed to dye a strip of cotton cloth with an insoluble color (see **167** *b*) such as this plumbous chromate (*17*)?

g. Dilute about 1 cc. of plumbous nitrate solution with 3–4 times its volume of water and add a few drops of dilute sulphuric acid (*18*).

Transfer a portion of this mixture to another test-tube and add dilute hydrochloric acid (warming if necessary) (*19*).

Compare the solubility of this sulphate with that of barium (see **75** *c*) (*20*).

172. Lead Dioxide

a. Mix together in a test-tube about 1 g. of minium and 5–6 cc. of dilute nitric acid and warm the mixture till the color change is complete (*1*).

Filter off the precipitate and reserve it for *b*. Reserve the filtrate for *c*.

b. Place the precipitate from *a* in a test-tube, add about 1 cc. of concentrated hydrochloric acid, and warm. Apply

(*11*)

(*12*)

(*13*)

(*14*)

(*15*)

(*16*)

(*17*)

(*18*)

(*19*)

(*20*)

(*1*)

[redacted]

to the mouth of the tube a strip of paper moistened with a starch-potassium iodide emulsion (*2*).

What kind of oxide is thus identified (see **34**) (*3*)?

c. Test small portions of the filtrate from *a* with potassium iodide solution (see **171** *e*) and with potassium dichromate solution (see **171** *f*) and ascertain if plumbous ion is present (*4*).

What is the constitution of red lead as determined by these reactions (*5*)?

173. Classification of Aluminium, Tin, and Lead in an Analytical Scheme

Tin and lead form sulphides insoluble in acids. These metals therefore fall into Group II of the analytical scheme. Plumbous chloride, however, is somewhat insoluble and hence the greater portion of the lead will be precipitated as chloride upon the initial acidification of the "unknown" solution. The plumbous chloride thus removed may be separated from the other insoluble chlorides of Group I by its solubility in hot water.

When hydrogen sulphide is introduced into the filtrate from Group I the precipitation of lead (that portion left unprecipitated as chloride) and tin as sulphides will be complete. That property of stannic sulphide (and also of stannous sulphide in the presence of sulphur) of dissolving in ammonium sulphide solution offers a simple means for the separation of tin from those metals classified in this group. The filtrate from these sulphides insoluble in the alkali sulphide contains ammonium sulphostannate and again yields stannic sulphide upon acidification. Stannic sulphide therefore falls into a special class of sulphides (class *b*) among

(2)

(3)

(4)

(5)

those sulphides insoluble in acids; class *a* is made up of those sulphides of this group which do not dissolve in ammonium sulphide.

The ease with which aluminium sulphide is hydrolyzed by water makes impossible the precipitation of aluminium as such, though indeed the final production of aluminium hydroxide serves as the best means of its separation. This hydroxide is soluble both in strong bases and acids but ammonium hydroxide is without action upon it. It is well to boil the filtrate from Group II until all traces of hydrogen sulphide have disappeared and then to add ammonium hydroxide solution in excess. The neutralization first of the hydrochloric acid present introduces an excess of an ammonium salt, — a condition not unfavorable for the complete precipitation of the highly insoluble aluminium hydroxide. This precipitation of an hydroxide in the presence of ammonium salts presents a separate group, known as Group III, of the analytical scheme.

Immediately upon the removal of aluminium hydroxide the filtrate is again treated with hydrogen sulphide and the ammonium sulphide, thereby formed, accomplishes the complete precipitation of zinc sulphide and those sulphides generally known as soluble in dilute acids (Group IV).

The next group (Group V) comprises those metals whose carbonates are precipitated in the presence of ammonium salts. Group VI is made up of magnesium only and Group VII comprises the metals of the alkalies.

Apply for two unknowns containing salts of silver, mercury, lead, cadmium, copper, tin, aluminium, zinc, and magnesium.

SOLUTION CONTAINING SALTS OF

Ag, Cu, Cd, Hg, Pb, Sn, Al, Zn, AND Mg

Acidify with HCl

<table>
<tr><td rowspan="4">Unknown</td><td rowspan="4"><i>Precipitate</i>
AgCl, HgCl, $PbCl_2$</td><td colspan="5"><i>Filtrate</i>
$Cu^{\cdot\cdot}$ $Cd^{\cdot\cdot}$ $Hg^{\cdot\cdot}$ $Pb^{\cdot\cdot}$ $Sn^{\cdot\cdot}$ $Sn^{\cdot\cdot\cdot\cdot}$ $Al^{\cdot\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$
Pass H_2S into Solution</td></tr>
<tr><td colspan="2"><i>Precipitate</i>
CuS, CdS, HgS, PbS, SnS, SnS_2
Boil with Yellow $(NH_4)_2S$</td><td colspan="3"><i>Filtrate</i>
$Al^{\cdot\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$
Boil off H_2S and add NH_4OH</td></tr>
<tr><td rowspan="2"><i>Precipitate</i>
CuS, CdS, HgS, PbS</td><td rowspan="2"><i>Filtrate</i>
$(NH_4)_2SnS_3$</td><td rowspan="2"><i>Precipitate</i>
$Al(OH)_3$</td><td colspan="2"><i>Filtrate</i>
$Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$
Pass in H_2S</td></tr>
<tr><td><i>Precipitate</i>
ZnS</td><td><i>Filtrate</i>
$Mg^{\cdot\cdot}$</td></tr>
<tr><td>F</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>G</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

[redacted]

CHAPTER XXIV

ARSENIC, ANTIMONY, AND BISMUTH

174. Arsenic

a. Mix a pinch of pulverized arsenious oxide with a little powdered charcoal. Place the mixture in a test-tube, heat strongly over a free flame, and note the odor (*1*).

Construct an equation for the reaction (*2*).

b. Place about 0.5 g. of pulverized arsenic in a test-tube, pour upon it 2–3 cc. of concentrated nitric acid, and heat to boiling [Hood] (*3*).

Compare the action with that in **100** *b* (*4*).

Reserve the solution for **176** *f*.

175. Arsenious Compounds

a. Boil a pinch of arsenious oxide with a little water and test the reaction of the solution to litmus (*1*).

Now add to the test-tube a little sodium hydroxide solution and again heat to boiling (*2*).

Construct an equation for the action and state what type of oxide is thus identified (*3*).

b. Boil a pinch of arsenious oxide with a few cc. of concentrated hydrochloric acid (*4*).

Construct an equation for the action and state again what type of oxide is identified (*5*).

Set the clear solution aside and examine later for crystals of arsenious oxide [R. 73] (*6*).

(*1*)
(*2*)

(*3*)
(*4*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

Is the reaction between arsenious oxide and hydrochloric acid reversible (*7*)?

Set the tube and its contents aside for *c*.

c. Pour a portion of the clear solution from *b* into a separate test-tube, dilute with water, and pass into it a current of hydrogen sulphide (*8*).

Test a small portion of this mixture with dilute hydrochloric acid to ascertain if the reaction is reversible (*9*).

Filter the remaining portion of the mixture and warm the precipitate with ammonium sulphide solution (*10*).

Construct an equation for the action (*11*).

Add a little dilute hydrochloric acid to the yellow solution and construct an equation for this reaction (*12*).

176. Arsenites

a. Test reaction of sodium arsenite solution to litmus (*1*).

b. Add a few drops of silver nitrate solution to 1–2 cc. of sodium arsenite solution (*2*).

Is the precipitate soluble in ammonium hydroxide solution (*3*)?

c. Add a few drops of cupric nitrate solution to 1–2 cc. of sodium arsenite solution (*4*).

d. Pass a current of hydrogen sulphide into a few cc. of sodium arsenite solution (*5*).

Now add a few drops of dilute hydrochloric acid to this same solution and explain [R. 74] (*6*).

Construct an equation for the reaction (*7*).

177. Arsenates

a. Test the reaction of a sodium arsenate solution to litmus (*1*).

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*1*)

b. Add a few drops of silver nitrate solution to 1–2 cc. of sodium arsenate solution and formulate the reaction (*2*).

Is the precipitate soluble in ammonium hydroxide solution (*3*)?

c. Add a few drops of cupric nitrate solution to 1–2 cc. of sodium arsenate solution (*4*).

d. Add a few cc. of sodium arsenate solution to a test-tube containing a few cc. of "magnesia mixture" and compare the result with that in **101** *c* (*5*).

e. Add a few drops of dilute hydrochloric acid to a few cc. of sodium arsenate solution and pass into this a current of hydrogen sulphide (*6*).

Now add an excess of concentrated hydrochloric acid to the solution, warm and saturate again with hydrogen sulphide (*7*).

Explain the action of the concentrated acid [R. 75] (*8*).

f. Neutralize cautiously the acid solution from **174** *b* with ammonium hydroxide solution and apply tests to identify the arsenate ion (*9*).

178. Arsine [Hood] [Poisonous]

Arrange a small apparatus as shown in Fig. 4. Place in it a sufficient quantity of zinc and dilute hydrochloric acid for the generation of hydrogen and when the air in the apparatus is completely displaced by the hydrogen (use care in testing) ignite the gas at the tip of the exit tube. Hold a crucible lid in the burning hydrogen. If the materials in the flask are pure no deposit will be observed on this cold surface of the crucible lid. Now introduce into the flask, through the safety tube, 1–2 drops of arsenious chloride solution. Note appearance of flame and again hold the crucible cover in it (*1*).

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(1)

Account for this deposition of arsenic and construct an equation for its formation (*2*).

At a point somewhat back of the tip of the exit tube apply a Bunsen flame directly to the tube through which the hydrogen and arsine are passing (*3*).

Dissolve a pinch of bleaching powder in a little water and apply a few drops of this solution to the black deposit of arsenic on the crucible cover (*4*).

When the experiment is completed fill the flask completely with water to stop further action.

179. Antimony

a. Repeat **174** ***a*** using antimonious oxide in place of arsenious oxide (*1*).

b. Heat gently about 1 g. of pulverized antimony with 3–5 cc. of concentrated nitric acid in a test-tube [Hood] (*2*).

When the antimony is completely oxidized dilute the contents of the tube with 3–4 times its volume of water and filter. Wash the insoluble product upon the filter with considerable water, then remove a small portion of it and apply a test to ascertain whether or not a nitrate is present (*3*).

What other metals behaved similarly when treated with concentrated nitric acid (*4*)?

Reserve the white product for **180** ***a.***

180. Antimonious Compounds

a. Boil a very small portion of the product from **179** ***b*** with a little sodium hydroxide solution and state what type of oxide is identified (*1*).

Boil the second portion of the product with a little dilute hydrochloric acid and state again what type of oxide is identified (*2*).

(*2*)

(*3*)

(*4*)

(*1*)

(*2*)

(*3*)

(*4*)

(*1*)

(*2*)

b. Mix about 0.5 g. of antimonious chloride with a little water in a test-tube and test the reaction of this mixture to litmus (*3*).

Now add a little more water to the test-tube and warm, then add to this mixture (4–5 cc. in volume) a little concentrated hydrochloric acid drop by drop (shaking after each addition and using care to avoid excess) and note if this reaction is reversible (*4*).

Again add a little water to the tube and note result (*5*).

Finally add concentrated hydrochloric acid drop by drop (avoiding an excess) and confirm the former result (*6*).

Compare this action of antimonious chloride with that found for phosphorus trichloride (**102** *a*) and arsenious chloride (**175** *b*) under similar conditions (*7*).

Reserve the final solution for *c*.

c. Saturate the final solution from *b* with hydrogen sulphide (*8*).

Test a small portion of the mixture with dilute hydrochloric acid and ascertain if this reaction is reversible (*9*).

Filter the remaining portion of the mixture and warm the precipitate with ammonium sulphide solution (*10*).

Construct an equation for the action (*11*).

Finally add a little dilute hydrochloric acid to this yellow solution and construct an equation for the reaction (*12*).

181. Stibine

Repeat **178** using antimonious chloride in place of arsenious chloride (dilute a minute quantity of this chloride with dilute hydrochloric acid and add only a few drops of the solution to the flask generating the hydrogen) (*1*).

Construct an equation for the decomposition of stibine (*2*).

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

(*1*)

(*2*)

What other hydrides behave like stibine when heated (*3*)?

Prepare a few cc. of bleaching powder solution and note if this will dissolve the black deposit of antimony (*4*).

182. Bismuth

a. Warm about 1 g. of bismuth with 5–7 cc. of dilute nitric acid. When the reaction is practically at an end pour off the clear solution into another tube and reserve for *b* (*1*).

Compare the result with that obtained for arsenic and antimony under similar conditions (*2*).

b. Heat the contents of the tube from *a* to boiling and pour off a little of the clear solution (1–2 cc. of bismuth nitrate solution from the side shelf may be substituted if desired) into a test-tube containing a few cc. of water (*3*).

Now add to this test-tube a little concentrated nitric acid drop by drop (shaking after each addition and using care to avoid excess) and note if this reaction is reversible (*4*).

Reserve the solution for *c*.

c. Saturate the final solution from *b* with hydrogen sulphide (*5*).

Test a small portion of the mixture with dilute nitric acid and ascertain if the reaction is reversible (*6*).

Filter the remaining portion of the mixture, warm the precipitate with ammonium sulphide solution, and filter. To this filtrate add a little dilute hydrochloric acid and note if any black precipitate of bismuth sulphide is formed (*7*).

Compare this result with those obtained for arsenic and antimony sulphides (*8*).

d. Add a little sodium hydroxide solution to a few cc. of bismuth nitrate solution (*9*).

Add now an excess of sodium hydroxide solution and com-

(*3*)

(*4*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

[redacted]

pare this action of hydrated bismuth oxide with that of arsenic and antimony oxides under similar conditions (*10*).

Filter off the precipitate and ignite it in a porcelain crucible. Note the color when hot and when cold (*11*).

183. Classification of Arsenic, Antimony, and Bismuth in an Analytical Scheme

Arsenic, antimony, and bismuth form sulphides insoluble in acids and thus fall into Group II of the analytical scheme. Both arsenic and antimony sulphides dissolve in ammonium sulphide to form sulpho-salts, hence these sulphides will be removed together with stannic sulphide (and stannous sulphide in the presence of sulphur) when the sulphides of Group II are boiled with ammonium sulphide solution. Upon acidification of the solution thus formed the sulphides of arsenic and antimony are again precipitated (constituting class *b* of the sulphides of Group II). Bismuth sulphide is insoluble in alkali sulphides and hence falls into class *a* of the sulphides of Group II.

Apply for two unknown solutions which may contain salts of mercury, lead, copper, bismuth, cadmium, arsenic, antimony, tin, aluminium, zinc, magnesium, calcium, strontium, and barium.

(*10*)

(*11*)

SOLUTION CONTAINING SALTS OF
Hg, Pb, Cu, Cd, Bi, As, Sb, Sn, Al, Zn, Mg, Ca, Sr, Ba
Acidify with HCl

<table>
<tr><td rowspan="5">Unknown</td><td rowspan="5">*Precipitate*
$HgCl$, $PbCl_2$</td><td colspan="6">*Filtrate*
$Cu^{\cdot\cdot}$ $Cd^{\cdot\cdot}$ $Hg^{\cdot\cdot}$ $Pb^{\cdot\cdot}$ $Bi^{\cdot\cdot\cdot}$ $As^{\cdot\cdot\cdot}$ $As^{\cdot\cdot\cdot\cdot\cdot}$ $Sb^{\cdot\cdot\cdot}$ $Sb^{\cdot\cdot\cdot\cdot\cdot}$ $Sn^{\cdot\cdot}$ $Sn^{\cdot\cdot\cdot\cdot}$ $Al^{\cdot\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$
Pass H_2S into the solution</td></tr>
<tr><td colspan="2">*Precipitate*
CuS, CdS, HgS, PbS, Bi_2S_3, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2
Boil with yellow $(NH_4)_2S$</td><td colspan="4">*Filtrate*
$Al^{\cdot\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$
Boil off H_2S and add NH_4OH</td></tr>
<tr><td rowspan="3">*Precipitate*
CuS, CdS, HgS, PbS, Bi_2S_3</td><td rowspan="3">*Filtrate*
As, Sb, Sn, Sulpho-Salts
Acidify with HCl
Precipitate
As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2</td><td rowspan="3">*Precipitate*
$Al(OH)_3$</td><td colspan="3">*Filtrate*
$Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$
Pass H_2S into solution</td></tr>
<tr><td rowspan="2">*Precipitate*
ZnS</td><td colspan="2">*Filtrate*
$Mg^{\cdot\cdot}$ $Ca^{\cdot\cdot}$ $Sr^{\cdot\cdot}$ $Ba^{\cdot\cdot}$
Add $(NH_4)_2CO_3$</td></tr>
<tr><td>*Precipitate*
$CaCO_3$
$SrCO_3$
$BaCO_3$</td><td>*Filtrate*
$Mg^{\cdot\cdot}$</td></tr>
<tr><td>H</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>I</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

CHAPTER XXV

CHROMIUM AND MANGANESE

184. Chromates and Dichromates

a. Dissolve a very small piece (about 0.5 g.) of potassium hydroxide in 8–10 cc. of water. Place about 10 cc. of potassium dichromate solution in an evaporating dish and then add to this a little of the alkaline solution, drop by drop, until the change in color is complete. Concentrate the final solution to small volume on a water-bath and set aside to crystallize. State colors of dichromate and chromate ion (*1*).

Dissolve the final crystalline product in a few cc. of water and divide into three portions for use in *b*, *c*, and *d*.

b. To one portion of the potassium chromate solution from *a* add a few drops of dilute sulphuric acid and state what ion is now identified (*2*).

c. To the second portion of the potassium chromate solution add a few drops of barium chloride solution and test the reaction mixture with Congo red paper for the presence of free mineral acid (*3*).

Construct an equation for the reaction and compare this result with that obtained when potassium dichromate is used (see **140** *f*) (*4*).

d. To the third portion of the potassium chromate solution add a few drops of plumbous nitrate solution and test for the presence of free mineral acid (*5*).

(1)

(2)

(3)

(4)

(5)

Formulate the reaction and compare the result with that obtained when potassium dichromate is used (see **171** *f*) (*6*).

e. Recall the actions of hydrogen peroxide (see **56** *e*), hydrogen sulphide (see **69** *f*), and sulphur dioxide (see **78** *h*) upon acidified potassium dichromate solution (*7*).

f. Add a little ammonium sulphide solution to a few cc. of potassium dichromate solution and construct an equation for the reaction (*8*).

185. Chromic Anhydride

Prepare a cold saturated solution of about 1 g. of potassium dichromate in 6–8 cc. of water, pour off the clear solution into a beaker, and add to it twice its volume of concentrated sulphuric acid (*1*).

When cool filter the mixture through a small plug of asbestos placed in the neck of a funnel. Dry the precipitate on a piece of broken bisque plate and set aside for **186** *a*.

186. Chromic Oxide

a. Place about 1 cc. of alcohol in a test-tube and pour [Caution] a few drops of this alcohol upon the dry chromic anhydride as collected on the bisque plate in **185**. Wash the product into a beaker with water and filter off the insoluble portion. Apply the borax bead test as described in *b* (*1*).

b. Pulverize about 1 g. of potassium dichromate and mix this in a crucible with one fourth its weight of flowers of sulphur. Heat the crucible and its contents over a blast lamp for 10–15 minutes, then grind up the resulting mass in a mortar with a little water and filter; wash the insoluble product upon the filter with water and set aside to dry (*2*).

Prepare a borax bead upon a platinum wire and bring this

(*6*)

(*7*)

(*8*)

(*1*)

(*1*)

(*2*)

[redacted]

bead in contact with a particle of the chromic oxide. Reheat the borax bead in both oxidizing and reducing flames and note effect (*3*).

This action is characteristic of all chromium compounds.

187. Chromyl Chloride

Grind together in a mortar about 1 g. each of potassium dichromate and sodium chloride. Place the mixture in a dry test-tube and add slowly a few drops of concentrated sulphuric acid. Warm the tube gently and pour out the distillate (which condenses in drops upon the inner walls of the tube) into another test-tube containing a few cc. of water. Divide this aqueous solution into two portions. Test one portion with litmus paper (*1*).

To this same portion add a few drops of dilute nitric acid and then a few drops of silver nitrate solution and state what radical is thus identified (*2*).

To the second portion of the solution add a few drops of the silver nitrate solution directly and state again what radical (other than the former) may be identified (*3*).

Construct the equation for the reaction as between chromic acid and hydrochloric acid (*4*).

Is this a reversible reaction (*5*)?

As both chromyl bromide and iodide are unstable (yielding free bromine and iodine respectively) this liberation of chromyl chloride may serve as a means of identification of a solid chloride when in the presence of bromide and iodide.

188. Chrome Alum

Calculate the weight of concentrated sulphuric acid necessary to prepare potassium sulphate and chromic sulphate from 5 g. of potassium dichromate. Dissolve the 5 g.

(*3*)

(*1*)

(*2*)

(*3*)

(*4*)
(*5*)

of potassium dichromate in a small amount of water and slowly add to this solution the calculated quantity of sulphuric acid. To the warm mixture now add alcohol (the reducing agent) drop by drop (5 to 6 cc. may be necessary) until the yellow color has disappeared entirely and the reduction is complete (*1*).

Set aside to evaporate spontaneously and reserve for **189.**

189. Reactions of Chromic Salts

Dissolve a little chrome alum (the crystals obtained in **188** may be employed) in a few cc. of water. Divide the solution into four portions for use in *a*, *b*, *c*, and *d*. Consider only the chromic sulphate present in constructing the equations. State the color of chromic ion (*1*).

a. To one portion of the solution add ammonium hydroxide solution in excess (*2*).

b. To the second portion add a drop of sodium hydroxide solution (*3*).

Now add a slight excess of this same reagent and explain (*4*).

Boil one half of this final solution vigorously [R. 76] (*5*).

To the other half add bromine-water and warm (*6*).

c. To the third portion of the chrome alum solution add ammonium sulphide solution (*7*).

Filter off the precipitate, wash well with water upon the filter and test it to ascertain if a sulphide is present (*8*).

Construct an equation for the reaction (*9*).

d. To the fourth portion of the chrome alum solution add ammonium carbonate solution (*10*).

Filter off the precipitate, wash it well with water and test it to ascertain if a carbonate is present (*11*).

Construct an equation for the reaction (*12*).

(*1*)

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)

(*6*)

(*7*)

(*8*)

(*9*)

(*10*)

(*11*)

(*12*)

[redacted]

190. Manganates and Permanganates

a. Fuse in an iron crucible [Storeroom] a mixture of 3–4 g. of potassium hydroxide and 2–3 g. of potassium chlorate (the oxidizing agent) and into this introduce about 2 g. of powdered manganese dioxide, a little at a time. Stir the fused mass with an iron file during the operation. Finally, when effervescence has ceased, allow the mass to cool somewhat and then treat with a little cold water. Decant off the clear liquid containing the potassium manganate and reserve it for *b* and *c*. What is the color of manganate ion (*1*)? The presence of potassium chloride in this solution is of course to be disregarded.

b. Place 1–2 cc. of the clear green solution from *a* in a small beaker and add to it a large quantity of water (if no color change occurs pass carbon dioxide through the liquid or add to it a few drops of acetic acid). State the color of permanganate ion (*2*).

Construct the equation for the hydrolysis of potassium manganate (*3*).

In what way does the use of an acid facilitate this hydrolysis (*4*)?

c. Dissolve a pinch of sodium sulphite in a few cc. of water and add a little of this solution to a few cc. of the green solution from *a* (*5*).

What precipitate is formed in this reduction (*6*)?

Construct an equation for the reaction (*7*).

d. Add a few drops of the sodium sulphite solution (as prepared in *c*) to a few cc. of potassium permanganate solution acidified with dilute sulphuric acid (*8*).

Is there a precipitate formed in this case (*9*)?

Construct an equation for the reaction (*10*).

(*1*)

(*2*)

(*3*)

(*4*)

(*5*)
(*6*)
(*7*)

(*8*)
(*9*)
(*10*)

e. Repeat *d*, using a potassium permanganate solution made alkaline with sodium hydroxide solution (*11*).

The action of the alkali here reverses the process by which potassium permanganate itself is formed and the oxidation of the sulphite proceeds as in *c*.

f. Recall the action of hydrogen peroxide (see **56** *c*), hydrogen sulphide (see **69** *g*), and sulphur dioxide (see **78** *i*) upon acidified potassium permanganate solution (*12*).

191. Reactions of Manganous Salts

a. Test the reaction of manganous chloride solution to litmus (*1*).

What is the color of manganous ion (*2*)?

b. Add a few drops of sodium hydroxide solution to a few cc. of manganous chloride solution (*3*).

Divide this mixture into two portions.

Shake one in a test-tube with air (*4*).

To the other add a little bromine-water and explain [R. 77] (*5*).

c. Place a few cc. of manganous chloride solution in each of two test-tubes. Add to one of the tubes a few cc. of ammonium chloride solution, then into both tubes pour an excess of ammonium hydroxide solution and explain the difference in action (*6*).

d. Add a little ammonium sulphide solution to a few cc. of manganous chloride solution and construct the equation for the reaction (*7*).

e. Pass a current of hydrogen sulphide into a manganous chloride solution (*8*).

Then add a few drops of ammonium hydroxide solution to alkaline reaction (*9*).

(11)

(12)

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

Filter off the precipitate, wash it well with water, and apply a test for the sulphide radical (*10*).

What class of sulphides is thus identified (*11*)?

f. Prepare a borax bead on a platinum wire and bring this bead in contact with a manganous salt solution. Reheat the bead in both oxidizing and reducing flames (see **1** *d*) (*12*).

192. Classification of Chromium and Manganese in an Analytical Scheme

Salts of chromium and manganese, even those containing these elements in the forms of more or less stable complex anions, are readily converted into the chromic and into the manganous class of compounds respectively. In this event manganese is best precipitated as a sulphide insoluble in alkalies, whereas chromium is best removed as an hydroxide. The precipitation of chromium as chromic hydroxide will occur immediately upon the addition of ammonium hydroxide to the filtrate from Group II (whether or not it is freed of hydrogen sulphide). Chromium, therefore, falls into Group III along with aluminium in the analytical scheme. The simultaneous precipitation here of manganous hydroxide is prevented by the presence of ammonium salts in excess. The precipitation of manganese as manganous sulphide, however, follows directly upon the addition of hydrogen sulphide to the ammoniacal filtrate left after the removal of aluminium and chromium. Manganese and zinc fall, therefore, in Group IV of the analytical scheme.

Apply to the instructor for one unknown containing salts of copper, cadmium, bismuth, arsenic, antimony, tin, aluminium, chromium, manganese, zinc, and magnesium.

(*10*)
(*11*)

(*12*)

SOLUTION CONTAINING SALTS OF
Cu, Cd, Bi, As, Sb, Sn, Al, Cr, Mn, Zn, Mg
Acidify with HCl and pass H_2S into solution

<table>
<tr><td rowspan="3">UNKNOWN</td><td colspan="2"><i>Precipitate</i>
CuS, CdS, Bi_2S_3, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5
SnS or SnS_2
Warm with yellow $(NH_4)_2S$</td><td colspan="3"><i>Filtrate</i>
$Al^{\cdots}$ $Cr^{\cdots}$ $Mn^{\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$
Boil off H_2S and add NH_4OH</td></tr>
<tr><td rowspan="2"><i>Precipitate</i>
CuS, CdS, Bi_2S_3</td><td><i>Filtrate</i>
As, Sb, Sn, Sulpho-Salts
Acidify with HCl</td><td rowspan="2"><i>Precipitate</i>
$Al(OH)_3$, $Cr(OH)_3$</td><td colspan="2"><i>Filtrate</i>
$Mn^{\cdot\cdot}$ $Zn^{\cdot\cdot}$ $Mg^{\cdot\cdot}$
Pass H_2S into solution</td></tr>
<tr><td><i>Precipitate</i>
As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2</td><td><i>Precipitate</i>
MnS, ZnS</td><td><i>Filtrate</i>
$Mg^{\cdot\cdot}$</td></tr>
<tr><td>J</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

CHAPTER XXVI

IRON, COBALT, AND NICKEL

193. The Action of Acids upon Iron

a. Place about 1 g. of pulverized iron in a test-tube and pour upon it 5–6 cc. of dilute hydrochloric acid (*1*).

After 10–15 minutes dilute the contents of the tube with a little water and filter. Reserve the filtrate for **195** *g*.

b. Place about 1 g. of pulverized iron in a test-tube and pour upon it 5–6 cc. of dilute nitric acid (*2*).

After 10–15 minutes dilute the mixture with a little water and filter. Pour the filtrate into an evaporating dish and evaporate it to dryness upon a water-bath [Hood] (*3*).

Reserve the dish and residue for **195** *h*.

194. Reactions of Ferrous and Ferric Salts

Dissolve about 0.5 g. ferrous ammonium sulphate in 8–10 cc. of water. In another test-tube dilute 4–5 cc. of ferric chloride solution with an equal volume of water. Test separate portions of these two solutions with the reagents mentioned in *a*, *b*, *c*, and *d*. Construct the necessary equations but disregard the presence of the ammonium sulphate in the case of the ferrous salt.

a. Reaction to potassium ferrocyanide solution (*1*).

b. Reaction to potassium ferricyanide solution (*2*).

c. Reaction to ammonium thiocyanate solution (*3*).

d. Reaction to ammonium hydroxide solution in excess. Shake the mixtures with air and explain (*4*).

(1)

(2)

(3)

(1)
(2)
(3)

(4)

195. Reduction and Oxidation among Ferrous and Ferric Salts

a. Drop a pinch of pulverized iron into a test-tube containing 10–15 cc. of ferric chloride solution and boil for a few minutes (*1*).

Account for the formation of a precipitate (*2*).

Filter and apply a test to a very small portion of the filtrate to determine whether ferrous ion or ferric ion is present (*3*)

Construct an equation for this reduction from the standpoint of the ionic hypothesis (*4*).

Divide the clear filtrate into four portions and reserve for use in *b*, *c*, *e*, and *f*.

b. Into one portion of the solution from *a* pass a current of hydrogen sulphide and explain (*5*).

Now add a little ammonium hydroxide solution (*6*).

Filter off the precipitate, wash it with water till free of hydrogen sulphide, and apply a test to ascertain if it is a sulphide (*7*).

Construct an equation to explain the formation of this product (*8*).

c. To another portion of the solution from *a* add directly a little ammonium sulphide solution (*9*).

Wash the precipitate and ascertain if it is a sulphide (*10*).

d. Saturate a few cc. of ferric chloride solution with hydrogen sulphide (*11*).

Filter off the precipitate of sulphur and apply a test to one portion of the filtrate to determine whether ferrous ion or ferric ion is present (*12*).

Construct an equation for this reduction from the standpoint of the ionic hypothesis (*13*).

The clear filtrate may be used in *e* and *f*.

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)

(13)

e. To the third portion of the solution from *a* (or a portion of the filtrate from *d*) add a little chlorine-water and shake. Apply a test to ascertain if ferric ion is present (*14*).

Construct an equation for this oxidation from the standpoint of the ionic hypothesis (*15*).

f. Dilute about 1 cc. of potassium permanganate solution in a test-tube with an equal volume of dilute sulphuric acid and add 8–10 cc. of water. To the last portion of the filtrate from *a* (or *d*) add a little of this acidified potassium permanganate solution, drop by drop, till the pink color is permanent. Then apply a test to the solution to determine whether ferrous ion or ferric ion is present (*16*).

Construct an equation to express the ionic changes in the compounds concerned (*17*).

g. Test the filtrate from **193** *a* to ascertain whether ferrous ion or ferric ion is present (*18*).

Account for the presence of this ionic form of iron (*19*).

h. Add a little water to the residue in the evaporating dish from **193** *b* and account for the precipitate formed (*20*).

Determine which ionic form of iron is present in the aqueous solution (*21*).

Explain the difference in action of nitric and hydrochloric acids upon iron (see *g*) (*22*).

196. Iron Ammonium Alum

Dissolve about 5 g. of ferrous ammonium sulphate in 15 cc. of water. Heat the solution to boiling and add a little concentrated nitric acid, drop by drop, until there is no further appearance of a dark brown color (see **91** *e*). Then set the solution aside to cool (*1*).

Filter off the crystals and dry them between filter papers.

(14)

(15)

(16)

(17)

(18)

(19)

(20)

(21)

(22)

(1)

Make a solution of a crystal and determine what ionic form of iron is present (*2*).

197. Ferrocyanides and Ferricyanides

a. Add a little ammonium hydroxide solution to a few cc. of potassium ferrocyanide solution and note if ferrous ion or ferric ion is present (*1*).

b. Add ammonium sulphide solution to a few cc. of potassium ferrocyanide solution and note if any insoluble ferrous sulphide is formed (see **195** *c*) (*2*).

c. Acidify a few cc. of potassium ferrocyanide solution with dilute hydrochloric acid and add also a few cc. of ether and shake vigorously [R. 78] (*3*).

Construct the equation for the formation of the free complex acid (*4*).

d. Add bromine-water to a few cc. of potassium ferrocyanide solution, boil the solution to rid it of excess of bromine, and then add a little ferric chloride solution (*5*).

Compare this result with that obtained in **194** *b* (*6*).

Account for this oxidation of ferrocyanide ion from the standpoint of the ionic hypothesis (*7*).

198. Reactions of Cobalt Salts

a. Test the reaction of cobaltous chloride solution to litmus (*1*).

State the color of cobaltous ion (*2*).

b. Add a few drops of sodium hydroxide solution to a few cc. of cobaltous chloride solution (*3*).

Remove a very small portion of the mixture to another test-tube and try the action of ammonium hydroxide solution upon the precipitate which is held in suspension (*4*).

(2)

(1)

(2)

(3)

(4)

(5)
(6)

(7)

(1)
(2)

(3)

(4)

To the major portion of the mixture add an excess of sodium hydroxide solution and warm (*5*).

Finally shake the mixture with air (*6*).

c. Add ammonium sulphide solution to a few cc. of cobaltous chloride solution and apply a test to ascertain if the reaction is reversible (*7*).

d. Add a few drops of potassium cyanide solution to a few cc. of cobaltous chloride solution (*8*).

Add excess of reagent and formulate reaction (*9*).

Boil the solution for a few minutes (or add to it a little chlorine-water) and formulate the reaction [R. 79] (*10*).

Finally add a little ammonium sulphide solution to the tube and note if cobaltous ion is present (*11*).

e. Prepare a borax bead and bring it in contact with a cobalt salt (either solid or in solution), and study the effect of the oxidizing and reducing flames upon it (*12*).

199. Reactions of Nickel Salts

Place separate portions of nickelous sulphate solution in a series of test-tubes. Apply the same reagents as described in **198** and construct equations for the possible reactions.

a. Reaction to litmus and color of nickelous ion (*1*).

b. Reaction to sodium hydroxide solution (*2*).

Try the action of ammonium hydroxide solution upon the precipitate thus held in suspension (*3*).

c. Reaction to ammonium sulphide solution (*4*).

d. Reaction to potassium cyanide solution (*5*).

Study also the effect of an excess of this reagent (*6*).

Then boil the solution and add chlorine-water and compare with result in **198** *d* [R. 80] (*7*).

e. Apply the borax bead test (*8*).

(*5*)
(*6*)

(*7*)

(*8*)
(*9*)

(*10*)

(*11*)

(*12*)

(*1*)
(*2*)

(*3*)
(*4*)
(*5*)
(*6*)

(*7*)
(*8*)

[redacted]

200. Classification of Iron, Cobalt, and Nickel in an Analytical Scheme

These metals may conveniently be precipitated as sulphides but not in acid solution. The solubility of the complex ammonio salts of both cobalt and nickel will not permit of any separation of these metals as hydroxides in Group III. As sulphides, however, the first possibility for their removal in the analytical scheme will come in Group IV along with the sulphides of manganese and zinc.

Both ferrous and ferric hydroxides are insoluble, hence iron may be removed in Group III along with aluminium and chromium. Ferrous hydroxide, however, is quite soluble in the presence of ammonium salts, consequently the filtrate from Group II, when freed from hydrogen sulphide (which serves as a reducing agent for ferric salts), must be boiled with a little nitric acid in order to reoxidize all ferrous salts to the ferric condition. When ammonium hydroxide is added to the final solution all of the iron will be precipitated as ferric hydroxide.

Apply to the instructor for two unknowns, containing salts of silver, lead, mercury, copper, bismuth, cadmium, arsenic, antimony, tin, aluminium, chromium, iron, cobalt, nickel, manganese, zinc, calcium, strontium, barium, magnesium, and the alkalies.

Solution containing Salts of

Ag, Pb, Hg, Cu, Bi, Cd, As, Sb, Sn, Al, Cr, Fe, Co, Ni, Mn, Zn, Ca, Sr, Ba, Mg, K, Na

Add a few drops of HCl. If a precipitate appears continue the addition till precipitation is complete

<table>
<tr><td rowspan="6">Unknown</td><td rowspan="6"><i>Precipitate</i>
Group I
AgCl
$PbCl_2$
HgCl</td><td colspan="7"><i>Filtrate</i>
$Cu^{\cdot\cdot}\ Bi^{\cdot\cdot\cdot}\ Cd^{\cdot\cdot}\ Hg^{\cdot\cdot}\ As^{\cdot\cdot\cdot}\ As^{\cdot\cdot\cdot\cdot\cdot}\ Sb^{\cdot\cdot\cdot}\ Sb^{\cdot\cdot\cdot\cdot\cdot}\ Sn^{\cdot\cdot}\ Sn^{\cdot\cdot\cdot\cdot}\ Al^{\cdot\cdot\cdot}\ Cr^{\cdot\cdot\cdot}\ Fe^{\cdot\cdot}\ Fe^{\cdot\cdot\cdot}\ Co^{\cdot\cdot}\ Ni^{\cdot\cdot}\ Mn^{\cdot\cdot}\ Zn^{\cdot\cdot}\ Ca^{\cdot\cdot}\ Sr^{\cdot\cdot}\ Ba^{\cdot\cdot}\ Mg^{\cdot\cdot}\ K^{\cdot}\ Na^{\cdot}$
Neutralize filtrate from Group I with dilute NH_4OH and add HCl to solution to make it ½ N acid. Heat and pass H_2S into solution</td></tr>
<tr><td colspan="2" rowspan="2"><i>Precipitate</i>
Group II
CuS, Bi_2S_3,
CdS, HgS,
PbS
As_2S_3, As_2S_5
Sb_2S_3, Sb_2S_5
SnS, SnS_2
Boil with yellow $(NH_4)_2S$</td><td colspan="5"><i>Filtrate</i>
$Al^{\cdot\cdot\cdot}\ Cr^{\cdot\cdot\cdot}\ Fe^{\cdot\cdot}\ Co^{\cdot\cdot}\ Ni^{\cdot\cdot}\ Mn^{\cdot\cdot}\ Zn^{\cdot\cdot}\ Ca^{\cdot\cdot}\ Sr^{\cdot\cdot}\ Ba^{\cdot\cdot}\ Mg^{\cdot\cdot}\ K^{\cdot}\ Na^{\cdot}$
Boil off H_2S from filtrate from Group II. Add a little HNO_3 and boil to oxidize $Fe^{\cdot\cdot}$ to $Fe^{\cdot\cdot\cdot}$. Then add NH_4Cl and finally NH_4OH in excess</td></tr>
<tr><td rowspan="4"><i>Precipitate</i>
Group III
$Al(OH)_3$
$Cr(OH)_3$
$Fe(OH)_3$</td><td colspan="4"><i>Filtrate</i>
$Co^{\cdot\cdot}\ Ni^{\cdot\cdot}\ Mn^{\cdot\cdot}\ Zn^{\cdot\cdot}\ Ca^{\cdot\cdot}\ Sr^{\cdot\cdot}\ Ba^{\cdot\cdot}\ Mg^{\cdot\cdot}\ K^{\cdot}\ Na^{\cdot}$
Pass H_2S into filtrate from Group III</td></tr>
<tr><td rowspan="3"><i>Precipitate</i>
CuS, Bi_2S_3,
CdS, HgS,
PbS</td><td rowspan="3"><i>Filtrate</i>
As,Sb,Sn, Sulpho-Salts. Acidify with HCl to precipitate
As_2S_3
As_2S_5
Sb_2S_3
Sb_2S_5
SnS_2</td><td rowspan="3"><i>Precipitate</i>
Group IV
CoS, NiS,
MnS, ZnS</td><td colspan="3"><i>Filtrate</i>
$Ca^{\cdot\cdot}\ Sr^{\cdot\cdot}\ Ba^{\cdot\cdot}\ Mg^{\cdot\cdot}\ K^{\cdot}\ Na^{\cdot}$
Add $(NH_4)_2CO_3$</td></tr>
<tr><td rowspan="2"><i>Precipitate</i>
Group V
$CaCO_3$
$SrCO_3$
$BaCO_3$</td><td colspan="2"><i>Filtrate</i>
$Mg^{\cdot\cdot}\ K^{\cdot}\ Na^{\cdot}$
Add a few drops of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$
Heat and allow to stand. Filter off precipitate of last traces of Group V. Add to filtrate Na_2HPO_4</td></tr>
<tr><td><i>Precipitate</i>
Group VI
$MgNH_4PO_4$</td><td><i>Filtrate</i>
$K^{\cdot}Na^{\cdot}$
Group VII</td></tr>
<tr><td>K</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>L</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

APPENDIX

I. Correction of Barometric Readings

The barometric readings taken at room temperature (Temp.) must be reduced to the corresponding height of a column of mercury at 0°, by subtracting the proper correction, as placed in the second column (Corr'n), from the observed reading in millimeters.

TEMP.	CORR'N	TEMP.	CORR'N	TEMP.	CORR'N	TEMP.	CORR'N
12°	1.5	17°	2.1	22°	2.7	26°	3.2
13	1.6	18	2.2	23	2.8	27	3.3
14	1.7	19	2.3	23.5	2.9	28	3.4
15	1.9	20	2.5	24	3.0		
16	2.0	21	2.6	25	3.1		

II. Tension of Aqueous Vapor in Millimeters of Mercury

TEMP.	AQ. TENS. IN MM.	TEMP.	AQ. TENS. IN MM.	TEMP.	AQ. TENS. IN MM.	TEMP.	AQ. TENS. IN MM.
0°	4.6	14°	12.0	22°	19.8	30°	31.8
5	6.5	15	12.8	23	21.0	31	33.7
8	8.0	16	13.6	24	22.4	32	35.6
9	8.6	17	14.5	25	23.7	33	37.7
10	9.2	18	15.5	26	25.2	34	39.9
11	9.8	19	16.5	27	26.7	100	760.0
12	10.5	20	17.5	28	28.3		
13	11.2	21	18.6	29	30.0		

III. Electromotive Series of the Metals

The ionic form of each metal (in normal concentration) is discharged by every metal preceding it in this series.

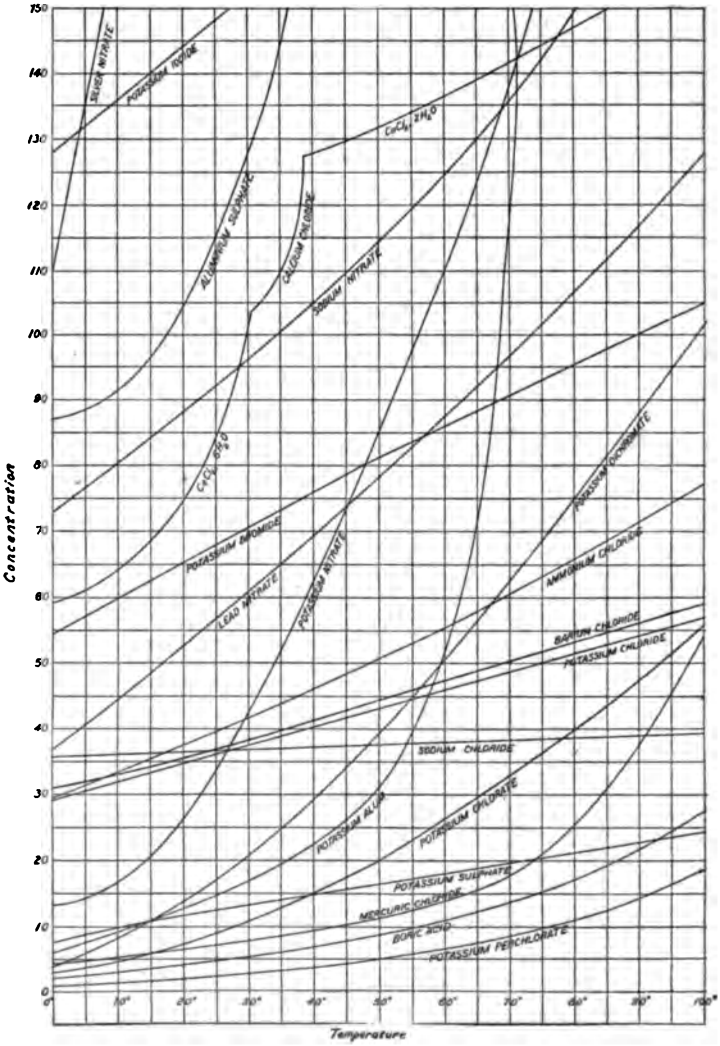
Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Cadmium
Iron ($Fe^{\cdot\cdot}$)
Cobalt
Nickel
Tin ($Sn^{\cdot\cdot}$)
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury ($Hg^{\cdot\cdot}$)
Silver
Palladium
Platinum
Gold

IV. Solubilities of Bases and Salts in Water at 18°

	K	Na	Li	Ag	Ca	Sr	Ba	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	$0.0_{3}16$ $0.0_{4}10$	73.19 5.4	51.09 3.0	37.24 1.7	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	$0.0_{4}1$ $0.0_{6}6$	143.3 5.2	96.52 3.4	103.6 2.9	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	$0.0_{6}35$ $0.0_{7}1$	200.0 4.8	169.2 3.9	201.4 3.8	148.2 4.1	419.0 6.9	0.08 $0.0_{2}2$
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	0.0016 $0.0_{3}2$	0.012 0.001	0.16 $0.0_{2}92$	0.0076 $0.0_{2}14$	0.005 $0.0_{3}5$	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	121.8 5.2	66.27 2.7	8.74 0.33	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	179.3 5.3	174.9 4.6	35.42 1.1	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	85.17 2.3	30.0 0.9	0.8 0.02	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 $0.0_{3}14$	0.25 0.007	0.25 $0.0_{2}57$	0.05 0.001	6.87 0.26	0.83 0.02	0.0019 $0.0_{4}3$
OH	142.9 18.0	116.4 21.0	12.04 5.0	0.01 0.001	0.17 0.02	0.77 0.063	3.7 0.22	0.001 $0.0_{3}2$	$0.0_{3}5$ $0.0_{4}5$	0.01 $0.0_{3}4$
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	0.20 0.015	0.011 $0.0_{3}6$	$0.0_{3}23$ $0.0_{4}10$	35.43 2.8	53.12 3.1	0.0041 $0.0_{3}13$
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0026 $0.0_{3}19$	0.4 0.03	0.12 0.006	$0.0_{3}38$ $0.0_{4}15$	73.0 4.3	— —	$0.0_{4}2$ $0.0_{6}5$
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 $0.0_{3}12$	$0.0_{3}56$ $0.0_{4}43$	0.0046 $0.0_{3}27$	0.0086 $0.0_{3}38$	0.03 0.0027	$0.0_{3}64$ $0.0_{4}47$	$0.0_{4}15$ $0.0_{5}5$
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 $0.0_{3}1$	0.0013 $0.0_{3}13$	0.0011 $0.0_{4}7$	0.0023 $0.0_{3}11$	0.1 0.01	0.001 $0.0_{4}8$	$0.0_{3}1$ $0.0_{4}3$

In each square is given (as **upper number**) the solubility in grams of anhydrous salt or base in 100 cc. of water, and (as **lower number**) the number of gram-molecular weights contained in 1 liter of the saturated solution, *i.e.* the molar solubility.

V


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Concentration
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
Temperature
SILVER NITRATE
POTASSIUM IODIDE
$CaCl_2 \cdot 2H_2O$
ALUMINIUM SULPHATE
CALCIUM CHLORIDE
SODIUM NITRATE
$CaCl_2 \cdot 6H_2O$
POTASSIUM BROMIDE
LEAD NITRATE
POTASSIUM NITRATE
POTASSIUM DICHROMATE
AMMONIUM CHLORIDE
BARIUM CHLORIDE
POTASSIUM CHLORIDE
SODIUM CHLORIDE
POTASSIUM ALUM
POTASSIUM CHLORATE
POTASSIUM SULPHATE
MERCURIC CHLORIDE
BORIC ACID
POTASSIUM PERCHLORATE

VI. Degree of Ionization of Ionogens

The figures given below represent the fractional parts of the ionogens which exist in ionic form in a deci-normal aqueous solution at 18°. Figures for other concentrations are given wherever those for deci-normal concentrations are lacking or for special purposes.

BASES

KOH	0.90	$Ca(OH)_2(N/64)$	0.90
$NaOH$	0.90	$Sr(OH)_2(N/64)$	0.93
NH_4OH	0.014	$Ba(OH)_2(N/64)$	0.91
$Ba(OH)_2$	0.76	H_2O	0.0_61

ACIDS

HNO_3	0.92	$HClO_3(N/2)$	0.88
HNO_3 (10 N)	0.17	$H.H_2PO_4(N/2)$	0.18
HNO_3 (conc.) (16 N)	0.09	$H.HC_2O_4$	0.50
HCl	0.91	$H.HC_4H_4O_6$	0.08
HCl (10 N)	0.17	$H.C_2H_3O_2$	0.011
HCl (conc.) (13N)	0.13	$H.C_2H_3O_2$ (N)	0.004
H_2SO_4	0.58	$H.HCO_3$	0.0_217
H_2SO_4 (10 N)	0.18	$H.HS$	0.0_37
H_2SO_4 (conc.) (36N)	0.01	$H.H_2BO_3$	0.0_31
HBr	0.92	HCN	0.0_31
HI	0.90	H_2O	0.0_61

SALTS

KCl	0.86	$AgNO_3$	0.81
KBr	0.863	$NaCl$	0.84
KI	0.87	$NaNO_3$	0.83
$KClO_3$	0.83	Na_2SO_4	0.70
KNO_3	0.83	Na_2CO_3	0.70
K_2SO_4	0.72	$Na_2.HPO_4$	0.73
K_2CO_3	0.71	$NaC_2H_3O_2$	0.78
$KMnO_4(N/32)$	0.92	$CaSO_4(N/100)$	0.64
$K_2Cr_2O_7(N/32)$	0.94	$BaCl_2$	0.75
NH_4Cl	0.85	$ZnCl_2$	0.73
$CuSO_4$	0.38	$ZnSO_4$	0.41

VII. Apparatus

1. Laboratory Equipment:

Balances
Barometer (with thermometer)
Blast-lamps (and attachments)
Burners, fish-tail
Cork press
Drying oven (or radiator)
Jars for refuse
Lens (or microscope)
Magnet
Pneumatic troughs
Paper, smooth (in roll)
Scales
Spectroscope
Thread, 1 spool

2. Supply Room:

These articles to be obtained on temporary order from the supply room. They must be returned immediately after use.

Burettes, plain(50 cc.)
Condensers, with rubber tubing, clamp and holder
Distilling flasks (125 cc.)
Dropping funnels (60 cc.) (stem 6 mm.)
Electrolytic cells
Iron crucibles
Lead dishes
Thermometers
Rubber stoppers, 1-hole, No. 6
Sand baths
U-tubes with side arms (100 mm. and 150 mm.)
Weights, Set, 10 mgm. to 50 g.

3. Students' Outfit. Cards with these lists accompany each outfit. These are to be checked by the student, signed, and returned to the supply room.

a. Non-returnable

1 Clay triangle
1 Cork borer, (5 mm.) with rod
12 Corks, assorted, small
1 Crucible, porcelain, No. 0 (with cover)
1 File, round
1 File, triangular
Filter paper, pkg. 10 cm.
Gas tubing, 60 cm.
Glass tubing, (6 mm.) 150 cm.
Glass tubing, (18 mm.) 30 cm.
Litmus paper, both colors
1 Pinch clamp
1 Platinum wire (7 cm.)
2 Rubber stoppers, 1-hole, No. 1
1 Rubber stopper, 2-hole, No. 6
Rubber tubing, (5 mm.) 30 cm.
Sponge
Test-tube brush, small
Test-tube holder
Wire gauze, 12 × 12 cm.
Matches, one box
Muslin, one yard

Reagents:

Hydrochloric acid (conc.) (13 N)
Hydrochloric acid (dilute) (5 N)
Nitric acid (conc.) (16 N)
Nitric acid (dilute) (5 N)
Sulphuric acid (conc.) (36 N)
Sulphuric acid (dilute) (5 N)
Silver nitrate (¼ N)
Sodium carbonate (3 N)
Sodium hydroxide (3 N)
Ammonium hydroxide (dilute) (5 N)

b. Returnable

5 Beakers, nest, Nos. 1, 2, 3, 4, 5
1 Boat, porcelain, 8 cm.
1 Bottle, special, 1 liter
4 Bottles, wide-mouthed, 250 cc.
1 Bunsen burner
1 Burette clamp
1 Crucible tongs
1 Cylinder, 100 cc., graduated
1 Deflagrating spoon
1 Evaporating dish, No. 0
1 Evaporating dish, No. 1
1 Evaporating dish, No. 3
1 Flask, 125 cc.
1 Flask, 250 cc.
1 Flask, 500 cc.
2 Funnels (5 cm.), short stem
1 Funnel support, 2-hole
4 Glass squares (7 × 7 cm.)
2 Glass stirring rods
1 Mortar (10 cm.) and pestle
10 Reagent bottles, 125 cc.
1 Ring stand, small
3 Rings, iron, 3 sizes
1 Spatula, glass
12 Test-tubes (13 cm.)
12 Test-tubes (15 cm.)
1 Test-tube (20 cm.)
2 Test-tubes, hard glass (15 cm.)
1 Test-tube rack
1 Thistle safety tube (stem 6 mm.)
12 Tincture bottles, 60 cc. for unknowns
1 Tube, hard glass (22 × 250 mm.)
1 U-tube, with side arm (100 mm.)
1 Watch glass (50 mm.)
1 Watch glass (75 mm.)
1 Watch glass (100 mm.)

VIII. List of Chemicals

Solids are placed upon one side-shelf and solutions (or liquids) upon another. When a substance is called for in one experiment only the number designating this experiment is given in heavy type. In a few instances specially prepared solutions are required; these are marked [Special] and should be removed to a special shelf if convenient. The normality of a solution is given in the majority of cases. The weight of a substance in 1 liter of its solution is sometimes given in parentheses when this is desirable

Solids

1. Acid, oxalic, commercial
2. Albumin, bird
3. Aluminium, gran.
4. Aluminium oxide (**17**)
5. Aluminium sulphate, hydrated
6. Ammonium chloride
7. Ammonium nitrate (**94**)
8. Ammonium phosphate (**128**)
9. Ammonium sulphate
10. Antimony, pulv.
11. Antimony trichloride
12. Arsenic, gran.
13. Arsenic trioxide, pulv.
14. Asbestos, short fibre (**185**)
15. Barium chloride
16. Barium oxide
17. Barium peroxide, anhyd.
18. Bismuth, gran.
19. Bisque plate, small pieces
20. Bleaching powder
21. Calcium, gran. (**11** *a*)
22. Calcium carbide (**110**)
23. Calcium carbonate, pulv.
24. Calcium carbonate (marble), com'l, gran.
25. Calcium chloride, gran.
26. Calcium fluoride, pulv.
27. Calcium oxide (quicklime), com'l
28. Calcium phosphide (**98**)
29. Calcium sulphate, pulv.
30. Calcium sulphate (gypsum), cryst. (**27**)
31. Calico, colored
32. Charcoal, animal, pulv.
33. Charcoal, wood, pulv.
34. Chromium potassium sulphate (chrome-alum)
35. Cloth, cotton (and cotton)
36. Cloth, woolen
37. Congo red paper
38. Copper, disks
39. Copper, finely powdered (**7** *b*)
40. Cupric bromide (**60**)
41. Cupric chloride
42. Cupric oxide, pulv.
43. Cupric sulphate, hydrated
44. Ferric oxide
45. Ferric sulphate
46. Ferrous ammonium sulphate
47. Ferrous sulphide, gran.
48. Gelatine
49. Iodine
50. Iron, pulv. (fine filings)
51. Iron pyrites (**78**)
52. Labels, paper
53. Lead, pulv.
54. Lead dioxide
55. Lead monoxide
56. Lead nitrate
57. Lead oxide, red (minium)
58. Magnesite, gran.
59. Magnesium, ribbon
60. Magnesium, powder
61. Manganese dioxide, pulv. com'l
62. Mercury (with dropper)
63. Paraffine
64. Phosphorus, red
65. Phosphorus pentachloride (**102**)
66. Phosphorus pentoxide (**99**)
67. Potassium bromide
68. Potassium carbonate
69. Potassium chlorate
70. Potassium chloride (**125**)
71. Potassium dichromate
72. Potassium hydrogen tartrate
73. Potassium hydroxide
74. Potassium iodide
75. Potassium nitrate
76. Potassium perchlorate
77. Potassium permanganate
78. Potassium sulphate
79. Silica, (sand) pulv.
80. Soda lime (**109** *a*)
81. Sodium acetate, fused
82. Sodium ammonium phosphate (microcosmic salt)
83. Sodium carbonate, anhydrous
84. Sodium carbonate, hydrated
85. Sodium chloride
86. Sodium hydrogen carbonate
87. Sodium hydroxide
88. Sodium nitrate
89. Sodium nitrite
90. Sodium hyposulphite ("hydrosulphite")
91. Sodium peroxide
92. Sodium phosphate
93. Sodium sulphate, hydrated
94. Sodium sulphide
95. Sodium sulphite
96. Sodium tetraborate (borax), pulv.
97. Starch
98. Strontium sulphate (**140** *e*)
99. Sugar
100. Sulphur, flowers
101. Sulphur, roll
102. Talc, pulv. (**118**)
103. Tin, foil (**23** *c*)
104. Tin, gran.
105. Turmeric paper (**120** *b*)
106. Vaseline
107. Wood splints
108. Wood splints (charred at end)
109. Yeast (**112**)
110. Zinc, pulv. (dust)
111. Zinc, gran.
112. Zinc, gran., com'l.

Liquids and Solutions

113. Acid, acetic, glacial [Special] (**59**)
114. Acid, acetic 5 N
115. Acid, boric (sat.)
116. Acid, hydriodic 5 N (**49**)
117. Acid, hydrochloric, Normal [Special] (**124** *b*)
118. Acid, oxalic 2 N
119. Acid, picric (20 g. + 100 cc. alcohol)
120. Acid, phosphoric 46 N (sp. gr. 1.73)
121. Acid, tartaric N
122. Alcohol
123. Alizarin (50 g. of 20 % paste) (**167** *f*)
124. Aluminium sulphate
125. Ammonium carbonate 2 N (78.5 g. + 300 cc. NH_4OH)
126. Ammonium chloride 4 N
127. Ammonium molybdate + HNO_3 (70 g. + 180 cc. HNO_3)
128. Ammonium oxalate N
129. Ammonium sulphide, yellow ($NH_4HS + S$)
130. Ammonium thiocyanate N
131. Amyl alcohol (**114** *b*)
132. Barium chloride N
133. Barium hydroxide (baryta-water) $\frac{1}{2}$ N
134: Bismuth nitrate N (161g. + 80 cc. HNO_3)
135. Bromine
136. Bromine-water (saturated)
137. Cadmium sulphate N
138. Calcium chloride 2 N
139. Calcium hydroxide (lime-water) .04 N (sat.)
140. Carbon disulphide
141. Chlorine-water (sat.)
142. Chloroform
143. Cobalt chloride N
144. Cochineal (**167** *e*)
145. Congo red (**167** *c*)
146. Cotton seed oil
147. Cupric sulphate N
148. Ether
149. Ethyl acetate (**115** *a*)
150. Ferric chloride N
151. Glucose syrup (**112**)
152. Glycerol
153. Hydrogen peroxide, 3 %
154. Indigo suspension (5 g. 20 % paste)
155. Lead nitrate N
156. Litmus, neutral solution
157. Magnesium chloride N (**155**)
158. Magnesium sulphate N
159. Manganous chloride N
160. Mercuric chloride $\frac{1}{2}$ N
161. Mercurous nitrate, $\frac{1}{2}$ N (70 g. + 4 cc. HNO_3 + Hg)
162. Methyl orange (**132**)
163. Nickel sulphate N
164. Phenolphthalein (1 g. + 500 cc. alcohol)
165. Phosphorus trichloride (**102**)
166. Potassium arsenate 2 N (KH_2AsO_4)
167. Potassium arsenite ($KAsO_2$ + H_3AsO_3
168. Potassium bromate $\frac{1}{2}$ N
169. Potassium bromide N
170. Potassium chlorate $\frac{1}{2}$ N (sat.)
171. Potassium chloride 4 N (sat.)
172. Potassium chromate N
173. Potassium cyanide N
174. Potassium dichromate $\frac{1}{2}$ N
175. Potassium ferricyanide $\frac{1}{2}$ N
176. Potassium ferrocyanide $\frac{1}{2}$ N
177. Potassium hydroxide 15 N (840 g.) [Special] (**83**)
178. Potassium iodide $\frac{1}{2}$ N
179. Potassium permanganate $\frac{1}{2}$ N
180. Pyrogallol (278 g.) [Special] (**83**)
181. Silver sulphate $\frac{1}{25}$ N (sat.)
182. Sodium acetate N
183. Sodium chlorate 6.5 N (sat.) (**133**)
184. Sodium chloride 5.5 N (sat.)
185. Sodium hydrogen sulphate (sat.)
186. Sodium hydroxide, Normal [Special] (**63** *a* and **77**)
187. Sodium phosphate N
188. Sodium silicate (sat.) (**117**)
189. Sodium thiosulphate N
190. Stannous chloride N (112.5 g. + 500 cc. HCl + Sn)
191. Stannic chloride
192. Starch emulsion
193. Strontium chloride N
194. Toluene
195. Toluene + dry HCl
196. Zinc acetate $\frac{1}{2}$ N
197. Zinc chloride $\frac{1}{2}$ N
198. Zinc sulphate $\frac{1}{2}$ N

Printed in the United States of America.

The page references for any desired Text-Book on General Chemistry are here to be inserted by the student at the suggestion of the Instructor. See *Note* 6.

R. Text		R. Text		R. Text		R. Text	
1		21		41		61	
2		22		42		62	
3		23		43		63	
4		24		44		64	
5		25		45		65	
6		26		46		66	
7		27		47		67	
8		28		48		68	
9		29		49		69	
10		30		50		70	
11		31		51		71	
12		32		52		72	
13		33		53		73	
14		34		54		74	
15		35		55		75	
16		36		56		76	
17		37		57		77	
18		38		58		78	
19		39		59		79	
20		40		60		80	