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A COURSE IN
General Chemistry



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A COURSE IN
General Chemistry

SEMI-MICRO ALTERNATE FORM

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Preface to the Semi-Micro Edition

The replacement of time-consuming and often sloppy filtrations by centrifugation has definite advantages. The procedures are faster and the amounts and character of the precipitates more readily observed. The expense of the centrifuges and additional equipment may be recovered in a few years by the savings in the quantities of chemicals consumed.

In addition to the introduction of the semi-micro techniques, there are in this edition several modifications in the instructional methods. A greater use of pictorial presentation of laboratory techniques has been employed. In analytical procedures, the variations of solubilities with hydrogen ion concentration which form the basis for the procedures are presented graphically. An amplification of acid-salt buffer solutions and the relation to the acid ionization constant has been made in Assignment 24. In general the emphasis upon the principles of qualitative analysis has been increased with the belief that a student who has completed these Assignments can use not one but any system of qualitative analysis.

The authors wish to express their appreciation for the assistance of Miss Marie Morholt, the illustrator of this edition.

WENDELL M. LATIMER
RICHARD E. POWELL

BERKELEY, CALIFORNIA
January, 1950

Preface to the Third Edition

The present edition embodies the results of over twenty-five years of experimentation, at the University of California, on the problem of teaching the principles of general inorganic chemistry through the medium of a series of logically connected laboratory experiments. The general plan of instruction, presented in the introductory chapter, is not changed, but the text has been completely revised.

An important new feature is the inclusion of many optional problems, mainly on the quantitative treatment of equilibria. While the qualitative understanding of reversible reactions and equilibrium states has proved a satisfactory and sufficient goal for the majority of the students in a first year course, the quantitative problems should furnish a desirable stimulus to many of the better students.

The experiments have been reorganized to present in the first term a more complete survey of various types of equilibria. This change was made for the benefit of the students who take no further work in inorganic chemistry. This has required the preparation of new assignments on equilibria involving hydroxides of metals and ammonia complex ions; and the earlier introduction of the assignments on oxidation-reduction couples and electric cells.

The assignments of the second term which deal with the systematic study of the reactions of positive ions have been revised. This has been done in part to give better correlation with the treatment of oxidation-reduction reactions in terms of standard potentials, as given in the *Reference Book of Inorganic Chemistry* by Latimer and Hildebrand, and in part to provide additional drill on those properties of these ions which are of importance in qualitative analysis.

Some clarification of the assignments on systematic

analysis also has been made. We are satisfied that the results attained with the previous editions fully justify the unconventional approach to the problem of systematic analysis. The number of occasions upon which a chemist uses a complete system of qualitative analysis is so limited that the usefulness of teaching a complete system may well be questioned. The authors prefer to develop the fundamental principles of systematic separations by starting with the study of the properties of a few ions, and of the methods which may be employed to separate them. When these principles are mastered additional ions are then included in the scheme. We believe that this is the best type of training to equip students to solve the analytical problems which they are likely to encounter.

WILLIAM C. BRAY

WENDELL M. LATIMER

BERKELEY, CALIFORNIA

December, 1939

Preface to the First Edition

The course presented in this text is that given at the University of California during 1921-23. Its development was begun in 1912 by a group of instructors under the leadership of G. N. Lewis. Since then many changes have been made in the material of the course and in the order and method of presentation, and it is expected that further changes will be made in the future.

Beginning in 1915 there were privately printed each year outlines of the lectures, by Hildebrand, and of the laboratory work, by Bray and Rosenstein, which have been used to some extent outside of the University of California. In 1918 the lecture outlines were superseded by Hildebrand's *Principles of Chemistry*, Macmillan, which has since been used as the chief reference book in the course. In 1921 the fourth complete revision of the laboratory manual was undertaken by the undersigned. Each of the Assignments in the present book has thus been subjected to an actual test in the laboratory of from two to seven years' duration.

An outline of the course is given in the introductory chapter. This is intended primarily for the instructor; it contains a weekly schedule of the lectures and laboratory work, and a discussion of a number of topics in which the method of presentation differs more or less from that usually adopted in an elementary course. In this discussion and throughout the text all unnecessary duplication of the material in Hildebrand's book has been avoided.

In the development of this text a great deal has been contributed by the instructors in the course. We wish especially to acknowledge our indebtedness to Professors G. N.

Lewis, J. H. Hildebrand, Edward Booth and E. D. Eastman and to Doctors Ludwig Rosenstein and W. L. Argo.

WILLIAM C. BRAY

WENDELL M. LATIMER

BERKELEY, CALIFORNIA

July, 1923

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A COURSE IN
General Chemistry

Outline of the Course

This course in General Chemistry has been developed with the conviction that it is the duty of a university to train its students to meet new problems, and that it is more important to give the student a scientific training than it is to sort out for him those facts which may have a special bearing on the particular line of work that he is intending to follow. To quote from an article by Hildebrand:¹ "We have been inspired by the opportunity offered by a fundamental course to present science in such a way as, first, to win for scientific careers the keen-minded students who are repelled by the drudgery and memory work of the old-fashioned course in descriptive chemistry; and second, to encourage the average student to adopt the scientific attitude towards his everyday problems. . . . Our aim in giving this course is not simply to teach chemistry, but through it to teach science. Whether the student proceeds to advanced work in chemistry or enters one of the numerous fields for which it is prerequisite, or even takes no further scientific studies, it is important for him to have scientific training. . . . We have been convinced that, in order to attain these ends, the laboratory work must be the central feature of the course, and that it must involve the solution of problems rather than the mere performance of illustrative experiments. . . . The lecture work is organized to supplement closely the laboratory work and to contribute an element of stimulus and inspiration."

The material has been selected and arranged with the idea

¹ Hildebrand, "The Early Training of Scientists," *Science* 55, 355 (1922).

of so interlocking the theoretical and experimental parts that each supports the other in the final structure, for only when a student can use a principle to solve a given experimental problem are we sure that the principle is more than a mere set of words or the experimental facts more than isolated observations. Moreover it is thus possible for the student to acquire the habit of connecting experimental facts with each other and with theories to such an extent that the assimilation of new material becomes comparatively easy.

In the laboratory the effort is made constantly to throw the student upon his own responsibility especially in observing accurately and in drawing conclusions from his experiments. He is often called upon to predict results of untried experiments. Numerous questions and problems are introduced to draw attention to essential points which the inexperienced or the careless student might pass over. The problem of "keeping the gifted student busy at his level of achievement" ¹ may be partly solved by allowing him to work slightly ahead of the rest of the class, for he welcomes the opportunity of overcoming the difficulties by his own efforts even though this involves more work than if he had waited for the class discussion.

The success of the course will depend upon its organization as a unit and the efficient co-operation of a group of competent instructors. It is essential to have weekly meetings of the instructors, at which there is a frank discussion of all questions which may arise, including the content of the course and methods of presentation. It has been our experience that an able graduate student is competent to take charge of a laboratory section. The chief factor in the success of a laboratory instructor, aside from his knowledge of chemistry, is his ability to understand the difficulties of the individual student. The establishing of this close relation between students and instructor is facilitated by plac-

¹ Seashore, "The Gifted Student and Research," *Science* 56, 641 (1922).

ing the instructor in charge of both the laboratory and quiz work of a small group of students, not to exceed twenty-five in number. The division of the laboratory into small rooms, each large enough for only one section, is recommended. The assignment of students to sections on the basis of their ability is desirable, whenever possible, since the division into homogeneous groups not only simplifies the work of each instructor but is advantageous for the students in the various groups.

The weekly schedule on page 4 is presented as an example of satisfactory correlation between lectures and laboratory work, and to show the time required in the laboratory for each Assignment. It is assumed that the course extends through two sixteen-week terms; that each week two hours are available for lectures, and two three-hour periods for laboratory and quiz work; and that an average student may be expected to devote seven hours a week to the study of the material presented in the lectures and laboratory Assignments. Whenever it seems desirable, a lecture may be replaced by a definite reading assignment. After allowance is made for class discussion and short examinations there remain at least four hours per week for laboratory work.

The references to the *Principles of Chemistry*, Fifth Edition, by Hildebrand and to the *Reference Book of Inorganic Chemistry* by Latimer and Hildebrand are given as H and LH respectively, followed by the Roman numeral which indicates the chapter.

If there is difficulty in completing this schedule in the first term, all or parts of Assignments 21, 25, and 27 may be given as outside exercises. In this event the experiments of Assignments 25 and 27 should be performed and discussed in the lecture periods.

The sequence with which ideas and problems are introduced is such that high school chemistry is not necessarily a prerequisite; indeed a thorough training in elementary physics is more to be desired than a scanty knowledge of

WEEKLY SCHEDULE

LECTURE AND READING TOPICS

LABORATORY
ASSIGNMENTS*First Term*

1. Kinds of matter. Atoms and molecules. Weight relations in chemical reactions. H I and II.	1
2. The gas laws and kinetic theory, H III.	2
3. Volume of gases. Molecular weights. H IV.	3
4. Atomic structure, H V. Chemistry of hydrogen, LH I.	4
5. Group O, LH II. Titration of acids and bases, H VI.	6
6. Ionic theory, H VIII. Chemistry of oxygen, LH III.	7
7. Chemical nomenclature, H X. Speed of chemical reaction, H XI.	21 and 22
8. Chemical equilibrium, H XII.	23
9. Group 1, LH IV. Hydrolysis, H XIII (in part).	24
10. Group 2, LH V.	25
11. Equilibria of carbonic acid and its ions, H XXI.	27
12. Group 3, B and Al, LH VI. Amphoteric hydroxides, H XIII (in part).	28
13. Complex ions, H XIII.	29
14. Oxidation and reduction, H XV.	30
15. Review of term's work as related to atomic, ionic, and kinetic theories.	31

Second Term

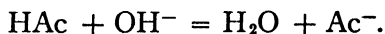
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elementary chemistry. That a student should enter the university without either high school chemistry or physics usually indicates a natural antipathy to physical sciences and such students are not likely to do well in this course. Students who have not had elementary chemistry will require some additional attention from the laboratory instructor during the first six weeks.

During the first weeks of the term the serious difficulty will be encountered that a large proportion of the students appear unable to work simple problems in chemical arithmetic. This difficulty is due mainly to the established habit of using rules and type problems as substitutes for thought, and to a failure to understand and remember the exact meaning of defined terms. Thus some students will even calculate that a given weight of iron can be produced from a smaller weight of iron ore and report the result without recognizing the fallacy, and many will fail to recognize the difference between a 2 molal solution of sulfuric acid and 2 moles of this substance. These students can usually overcome their difficulties if they are brought to a realization that it is necessary to think while making calculations. Since the use of proportion without thought is so general we advise that the solutions of such problems be written out as simple exercises in logic, or that fractions be used in such a way that the correctness of each step may be checked (see Hildebrand, Chapter III).

Before presenting the subject of equilibrium in ionic reactions we have thought it necessary to develop the concept of ions as substances: thus chloride ion is to be thought of as a substance with a definite set of properties common to solutions of all chlorides, and not merely as a negatively charged chlorine atom. With this as a starting point it is hoped that a student may be led to realize what has happened in a reaction involving ions by considering the approximate quantities of the various substances present in the original solutions and in the final solution, and to sum-

marize the result in the form of an equation (or equations). The writing of equations thus is merely the interpretation of experimental results. To stress this point, the writing of the equation for the net reaction in a given experiment is required (see Assignments 21 and 22). For example, when solutions of acetic acid and sodium hydroxide are mixed in any proportion the net reaction is



This is a statement of an experimental fact, while the possible ionic mechanism



which is often unduly emphasized, is merely an hypothesis, since there is no proof that un-ionized acetic acid cannot react directly with hydroxide ion.

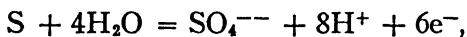
An understanding of ionic equilibria includes also a knowledge of the approximate concentrations of all the substances present at a given equilibrium state. In the example just cited this knowledge may be attained either by the experimental study of the properties of an acetate solution or by a consideration of the relative ionization of acetic acid and water (Assignment 25). Throughout the course there is emphasized the possibility of predicting experimental results from a knowledge of the equilibria involved, such as relative solubility, ionization, and volatility.

The effect of change of concentration in displacing an equilibrium has been treated from a qualitative rather than a quantitative standpoint. For the average student the quantitative Mass Law is merely a mathematical formula, and its use operates against the attainment of a clear molecular picture of what may be expected to happen. However, for the bright student, the quantitative treatment of equilibrium problems is often very stimulating and many "starred" problems are introduced for his benefit.

We have treated strong electrolytes as completely ionized.

Our original justification for this (in 1912) was based on grounds of simplicity and the belief that there was a fundamental difference in the nature of highly polar substances and weak electrolytes. The subsequent success of the Debye Hückel theory of activity coefficients has substantiated our belief. However, the transition, in many cases, from the electrostatic type of attraction, which exists in dilute solutions, to electron pair bond formation in concentrated solutions, should certainly be pointed out.

We have (in the 1940 edition) restricted the meaning of the term valence to the number of electron pair bonds which an element forms in a given compound. This of course corresponds to the general use of the term in organic chemistry, and also to the term "coordination number" in inorganic chemistry. We have used the term oxidation state or oxidation number for that classification of the compounds of an element which is so important from the standpoint of oxidation and reduction. For simple ions this is the positive or negative charge on the ion. In ions, such as sulfate, in which electrons are shared between atoms, the oxidation numbers do not correspond to the actual charges on the sulfur and oxygen atoms, but to the arbitrary charge which one calculates upon the assumption that the electrons of the bond belong entirely to the oxygen. Possibly a simpler way of defining the oxidation number is in terms of the number of electrons which are involved in the "half-reaction" which relates the free element to the element in a given compound. Thus for sulfur in sulfuric acid,



and we say that the oxidation state of sulfur in sulfuric acid is +6.

In the arrangement of oxidation-reduction couples in a table according to their strengths, emphasis is placed upon planning and carrying out such reactions as are necessary in order to fix the position of each couple studied. The

student should understand the use of the table in determining which reactions have a tendency to take place practically to completion and which may be expected to proceed only until a measurable equilibrium is reached. The displacement of an equilibrium due to changes in the concentration of the substances involved (including H^+ or OH^-) and the possible resulting alteration in the arrangement of the couples in the table, should present no serious difficulty.

The construction of simple electrical cells is an interesting as well as instructive exercise, and the direct measurement of oxidation-reduction potentials by this means serves to add reality to these quantities which are of such great importance in the interpretation of inorganic chemistry.

The experimental fact that certain reactions are slow requires special attention. Thus the exact position of the couple hydrogen-hydrogen ion in the table can be determined only when a catalyst is used, such as platinum; if the catalyst is not used, experiments at room temperature with reducing agents and oxidizing agents would place this couple in two positions, $H_2 \leftarrow H^+$ as a weaker oxidizing agent and $H_2 \rightarrow H^+$ as a weaker reducing agent, on opposite sides of the equilibrium position $H_2(\text{on Pt}) - H^+$. Conversely when the equilibrium position of a couple in the table has been determined by some method other than direct experiments at room temperature, it will frequently be found that reactions which have a tendency to take place do not proceed at an appreciable rate.

In the introduction to qualitative analysis, which constitutes a large part of the laboratory work of the second term, the emphasis is placed on the devising and testing of methods of separation for a few elements and the gradual building up of a scheme of analysis as additional elements are investigated, rather than on the study and use of a finished scheme of analysis. The latter method was tried without modification for two years, and was only gradually replaced by the present method as this was developed and

demonstrated to be a more satisfactory method for the correlation of experimental facts and principles. The more able students can do the assigned work unaided, but the rest of the class will require assistance from the instructor. If more time is available, and it is desired to use it in qualitative analysis, a standard text-book such as that of A. A. Noyes and E. H. Swift should be used for the additional work.

Note to Students

GENERAL SUGGESTIONS

1. Decide what is the real purpose of each Assignment.—Before beginning the experimental work of an Assignment and preferably before coming to the laboratory, read carefully the first paragraphs, review earlier related topics, and note the connection between the lectures and laboratory work. (Cf. the weekly schedule on page 4.) It is important to form the habit of looking up any term not fully understood, e. g., by means of the indexes of the text-books used in the course. Some specific references to these books are inserted in the text, and new terms are printed in heavy type.

2. Master each idea before proceeding to the next one. Form the habit of consulting the instructor whenever you are not certain of the correctness of your answers to questions and of your conclusions from the experiments. The frequent short written examinations will be of great assistance to you in deciding whether or not you have really understood the work.

3. An average student who has understood the earlier work can complete an Assignment in the regular laboratory time allotted to it. Students who cannot finish in the stated time, announced by the instructor, must consider themselves behind the class, and should plan immediately to do extra work at home and in the laboratory.

4. Your success depends upon your own efforts. If you are in serious difficulty, then there is something wrong with

your methods. The instructor can assist you in finding out what is wrong, but he cannot do your work for you. No effort on his part can make up for lack of initiative on your part, failure to assume the responsibility of mastering each idea, or inability to improve your method of doing the work.

SPECIAL DIRECTIONS

5. A laboratory note book about $6\frac{1}{2}$ inches wide, opening at the side, and not loose-leaved, is recommended. This book and the laboratory manual will be needed at each meeting of the laboratory section, including the first one.

6. The recording of experiments, observations, and conclusions at once in the note book is an essential part of the laboratory work. Entries made from memory or from memoranda on scraps of paper are not records of the experimental work. The value of the original record is improved: by dating each day's notes; by numbering the pages of the note book; by never erasing an entry or tearing out a page; by leaving space for additions and corrections; by adopting a plan of distinguishing between the record of the experiments actually performed and the other entries such as answers to questions, solutions of problems, etc.; by making all calculations neatly at the bottom or side of the page; and by writing entries in such a way that they will be easily understood when the work is reviewed. The descriptions of the experiments performed should be very brief when detailed directions are given in the manual, but must be complete when, as in the later work, experiments are devised by the student. Much time may be saved by making arithmetical calculations with a slide rule. An inexpensive one is adequate in this course.

7. The laboratory desk must be kept neat and dry. An old towel should be used for cleaning the desk top and another towel should be kept clean for use on apparatus. When cleaning apparatus use tap water and a brush to remove all visible dirt and rinse finally with a little distilled

water. Before leaving the laboratory the apparatus should be locked up in the desk. The contamination of laboratory reagents can be avoided by keeping each stopper clean and replacing it at once in the proper bottle, and by never pouring anything back into a reagent bottle.

8. At the first meeting of each laboratory section the instructor will distribute desk keys with lists of apparatus. Check the apparatus in the locker, sign the list, and return it to the instructor. Begin work on Assignment 1.

SAFETY MEASURES

1. Certain hazards are always present in the operations of a chemistry laboratory, but with normal good judgment the chance of an accident in this course is extremely small.

2. The most frequent accidents are burns from concentrated acids and alkalis. Acid or alkali in the eye may be particularly serious, and must be treated immediately by washing the eye with plenty of water for at least five minutes. A doctor should be consulted promptly. It is easier to prevent eye accidents than to treat them: Never get your face over a boiling solution, for it may superheat and "bump." Never pour a little water into concentrated sulfuric acid, for the heat evolved may cause violent sputtering; pour the acid into the water instead.

3. Accidents occasionally happen when students are inserting glass tubing into stoppers. Lubricate the tubing and the hole in the stopper, and hold them in such a way that your hand will not be cut badly if the glass should break.

4. A number of volatile substances will be encountered which are toxic: Fumes containing chlorine, bromine, nitrogen dioxide, or hydrogen sulfide must not be breathed in high concentrations. Experiments which give rise to these gases must be performed in a hood or out of doors.

5. Unauthorized experiments may have unknown hazards and are strictly forbidden.

OBSERVE THESE PRECAUTIONS!

BOILING SOLUTIONS

DANGEROUS



A solution boiled over a direct flame may super-heat and bump.

H_2SO_4 or NaOH in the eye may produce degeneration of the eye followed by death.

SAFE

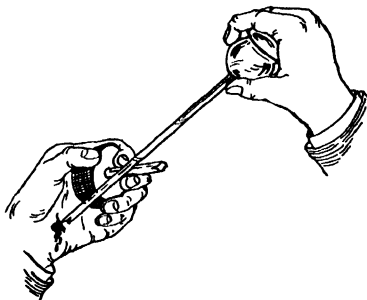
Keep your face away from boiling liquids:



or better yet, heat test tubes in a beaker of boiling water

INSERTING GLASS TUBING INTO STOPPERS

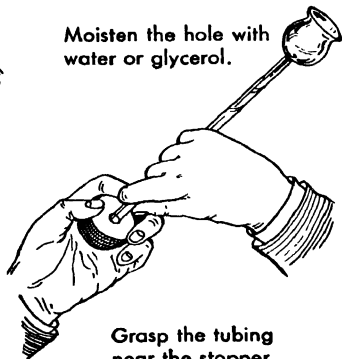
DANGEROUS



The jagged ends of broken glass tubing may cut your hand badly.

SAFE

Moisten the hole with water or glycerol.



Grasp the tubing near the stopper.

LIST OF APPARATUS

1. Regular equipment of each locker. Additional articles may be obtained at the office by filling out an "order slip" and signing your name and locker number. Whenever any article is returned to office sign a "return slip." At the end of the term the locker must contain the same amount of apparatus, no more and no less; the locker must be clean; the apparatus must be clean and dry, and in good condition; glass stoppers must fit, and be protected by the insertion of a piece of paper.

- | | |
|---|---|
| 1 Key. | 1 Pipet, 1 cc. |
| 5 Beakers, 100 cc., 150 cc., 250 cc.,
400 cc., 600 cc. | 1 Watch-glass. |
| 5 Reagent Bottles. | 2 Casseroles. |
| 4 Sample Bottles, 50 cc. | 1 Crucible, with cover. |
| 1 Graduated Cylinder, 25 cc. | 1 Evaporating Dish. |
| 2 Florence flasks, 250 cc., 500 cc. | 1 Crucible Tongs. |
| 3 Erlenmeyer flasks, two 250 cc.,
one 50 cc. | 1 Bunsen Burner, with rubber
tubing. |
| 1 Wash-bottle, equipped with
glass Tubing and rubber stop-
per. | 1 Wire Gauze. |
| 2 Funnels. | 1 Triangle. |
| 2 Blue Glasses. | 1 Test-tube Brush. |
| 2 Glass Rods, 3 × 180 mm. | 1 Centrifuge cone brush. |
| 30 cm. Glass Tubing. | 1 Test-tube Holder. |
| 8 Test-tubes, six 18 × 150 mm.,
two 10 × 75 mm. | 1 Test-tube Rack. |
| 6 Centrifuge tubes, conical, 15 cc. | 1 Package Filter Paper. |
| | 2 Towels. |
| | 1 Box of Matches. |
| | Litmus Paper in a bottle. |

2. The following additional articles may be obtained at the office:

- (a) *By signing the regular order slips.* Small short-stemmed funnels; corks; rubber stoppers.
- (b) *By signing "temporary order slips."* Special apparatus for Assignments 2 and 5; burets, with clamps and pinch-cocks; graduated cylinders, 10 cc. and 250 cc.; thermometers. These articles should be returned when possible during the same laboratory period.

Section I

Weight Relations in Chemical Reactions

Assignment 1

The Synthesis of a Sulfide of Copper and the Determination of Its Formula

Special Material:¹ Sample of copper wire approximately 1 gram in weight, powdered sulfur.

1. In Assignment 1 we shall study quantitatively a chemical reaction in which two **elements**,² a **metal** and a **non-metal** unite to form a new **substance**. The experiment consists in heating a weighed quantity of copper with excess of sulfur and determining the weight of the product. As the result of a large number of such experiments the ratio of these weights has been found to be constant, from which it follows that the copper and sulfur have combined to form a definite **compound**. The problem is to interpret this result in terms of atoms, that is, by the use of the **atomic weights** to calculate the relative number of atoms of copper and sulfur in the compound. **Questions.** If 3.04 g. of a certain metal, when burned in oxygen, yield 5.04 g. of a pure compound of the metal and oxygen, what weight of oxygen will combine with 1.00 g. of this metal? What additional information is necessary before the relative number of atoms of the two elements in the compound can be calculated?

2. **Experiment.** Support a clean porcelain crucible, with a cover, on a triangle and heat with the colorless flame of a

¹ Under this heading is listed only that material, required in the Assignment, which is not regularly placed in the lockers or on the reagent shelves.

² See Note to Students, Paragraph 1.

bunsen burner to low redness. Let the crucible cool about 10 minutes, and weigh it, with the cover, to 10 milligrams.

Note. Do not make any weighings until you have read Appendix IA and the instructor has discussed the use of the balance.

3. While the crucible is cooling obtain from the shelf a clean piece of copper wire, weighing about 1 g., and weigh it to 10 mg. **Note.** See Paragraph 7 for the form to be used in recording the data.

4. Place the copper in the weighed crucible and add enough powdered sulfur to cover the copper. Place the cover on the crucible and heat gently (with a small flame) until the sulfur ceases to burn at the edges of the cover, but do not remove the cover while the crucible is hot. Then heat more strongly until the bottom of the crucible just becomes dull red. Again allow to cool about 10 minutes and weigh.

5. Carefully remove the cover and note the appearance of the contents of the crucible, but do not touch the substance. If there is any free sulfur on the cover or the wall of the crucible, replace the cover, heat the crucible and cover, and weigh again. Check the correctness of your result by adding a small quantity of sulfur and repeating the experiment; continue until two consecutive results agree within 10 mg. At the end of the experiment remove the substance formed, break it, and describe its properties. Clean the crucible with hot nitric acid in a porcelain dish, wash with distilled water, dry by heating, and check the original weight.

6. **Questions.** What conclusions can you draw from each of the following observations: (a) the properties of the product are different from those of either copper or sulfur; (b) the product appears to be homogeneous and its weight is greater than that of the copper used? What additional evidence is necessary to prove that the product is a pure substance and not a **solid solution**?

7. Calculations. Arrange your results in tabular form in your note book, as follows; and make the calculations necessary to complete the table:

	FIRST WEIGHING	SECOND WEIGHING	VALUE CHOSEN
(a) Weight of crucible.....			
(b) Weight of copper.....		_____	
(c) Weight of crucible and product..			
(d) Weight of product.....	_____	_____	
(e) Difference between (d) and (b)...	_____	_____	
(f)	_____	_____	

Calculate what the increase in weight (e) would have been if one **gram atom** (H, II; LH, glossary)¹ of copper had been used, and enter in the table as line (f); **show this result** to your instructor at once. How does this number compare with the atomic weight of sulfur? How many gram atoms of sulfur have combined with one gram atom of copper? What, then, is the simplest **formula** of the substance formed? What is the corresponding **molecular weight**? Write the equation for the reaction, and write out in words what this equation means, in terms of (a) atoms and molecules, (b) gram atoms and **moles**, (c) grams, and (d) pounds.

8. Problems. (1) In order to determine the effect of a small error in weighing, repeat your calculations, Paragraph 7, using a weight of copper 10 mg. greater than your experimental value, but the same weights as before of crucible and crucible plus product. What difference is thus produced in the weight of sulfur which combines with one gram atom of copper? How does this difference compare with the difference between your experimental result and the theoretical one based on the atomic weight of sulfur, 32.06?

(2) A sulfide of iron contains 53.8 per cent iron. What is the formula? (In solving this problem consider one gram atom of iron and one gram atom of sulfur as the fundamental units for iron and sulfur. Calculate first the weight of

¹ Hildebrand, *Principles of Chemistry*, Chapter II; Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*. See Note to Students, Paragraph 1.

sulfur and then the number of gram atoms of sulfur combined with one gram atom of iron.)

(3) The formulas of hydrogen sulfide and of ferrous sulfide are H_2S and FeS , respectively. What are their molecular weights? What weight of sulfur is contained in one mole of hydrogen sulfide? In one mole of ferrous sulfide? What weight of hydrogen sulfide could be made from one mole of ferrous sulfide?

(4) *How many atoms are in 1 gram atom? Calculate the weight of (a) 1 atom of hydrogen, (b) 1 atom of oxygen.

(5) *If 1 cc. of sea water contained 9×10^{11} atoms of gold, what would be the weight of gold in grams?

(6) *The density of sodium chloride, NaCl , is 2.16 g. per cc. The arrangement of the atoms is cubic with alternate sodium and chlorine atoms. Calculate the distance between the centers of the sodium and chlorine atoms.

Ans. 2.8×10^{-8} cm.

(7) *If the element X is made up of two isotopes with the atomic weights 90.010 and 92.025, what is the average atomic weight if the element consists of 10.0 per cent of the first and 90.0 per cent of the second?

* Problems marked with an asterisk are not an essential part of the course and may be omitted at the discretion of the instructor. However they are recommended for students who plan to take advanced work in chemistry.

Assignment 2

The Relation between the Mass and Volume of Gases. The Determination of the Volume of a Mole of Oxygen

Special Material: Hard-glass test-tube, rubber tube, rubber stopper, clamp, potassium chlorate mixed with about 1 per cent of manganese dioxide. A 250 cc. graduated cylinder (to be supplied by the instructor).

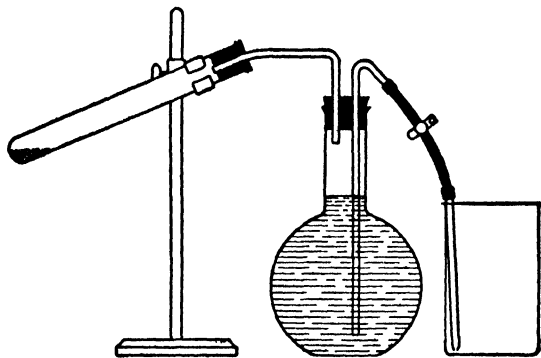
1. It is often necessary to know the volume of a given mass of a substance, or conversely the mass of a given volume. While in the case of a solid or liquid the relation between the mass and the volume must be determined for the particular substance, the problem is simplified when we are dealing with a gas, since a mole of every gas occupies nearly the same volume under similar conditions. In this Assignment we shall determine, under definite conditions of temperature and pressure, the volume of a known weight of oxygen and calculate the volume of one mole at **standard conditions**. **Questions.** What information is needed before you can calculate the weight of 10 cc. of mercury? A given solution of sodium chloride in water contains 25.0 per cent sodium chloride and the **density** of the solution is 1.19 g. per cc.; what volume of solution in cc., and in liters, contains 100 g. of sodium chloride?

2. When solid potassium chlorate is strongly heated it decomposes with the evolution of oxygen, and the loss in weight gives the weight of oxygen evolved. The volume of the oxygen is determined by measuring the volume of water displaced by an equal volume of oxygen. When pure potas-

sium chlorate is used it must be heated in a hard-glass (difficultly fusible) test-tube. The potassium chlorate decomposes more readily and at a lower temperature when a small quantity of manganese dioxide is present. The hard-glass test-tube may then be replaced by a heavy-walled test-tube of ordinary easily fusible glass; but care must be taken not to heat the latter tube to a higher temperature than is necessary for the reaction. The manganese dioxide is a **catalyst** in this reaction, and all of it may be recovered after the potassium chlorate has been decomposed into potassium chloride and oxygen.

3. Two students working together obtain from the office the "special apparatus for Assignment 2"; the order slip should be signed by one student. The apparatus should be returned as soon as the experiment is finished. Each student must keep a complete record of the experiment in his note book.

4. **Experiment.** Set up the apparatus according to the accompanying diagram. Since the apparatus must be gas



tight, glass tubing and stoppers must be carefully fitted. If your tubes and stoppers do not fit, exchange them at the office. Do not use the glass tubing of your wash-bottle as the constriction in the tip will produce too large a pressure in the flask. Directions for bending glass tubing are given in Appendix IB.

5. Place in the heavy-walled test-tube about 5 g. of potassium chlorate mixed with about 0.05 g. of manganese dioxide; estimate the amount by comparison with a sample in the laboratory. Wipe off any powder that is on the outside of the tube or on the inside near its mouth. Assemble the apparatus as before.

6. Before starting the experiment it is necessary to dry the potassium chlorate and manganese dioxide. To do this heat the tube gently with a moving gas flame, leaving the pinch-cock open on the rubber tube outlet. Moisture will appear on the walls of the test-tube; this must be driven out by gradually warming the tube to within about one inch of the stopper, and at the same time heating the mixture until gas evolution begins and some water passes over into the beaker. Care must be taken not to scorch the rubber stopper. The drying will usually be sufficiently complete when 50 to 100 cc. of water have passed into the beaker. Allow the apparatus to cool; close the pinch-cock near the outer end of the rubber tube, which should remain filled with water. Disconnect the chlorate tube (which should now show no signs of moisture), and weigh it with the dry material inside to 10 mg.

7. Immediately replace the tube in its proper position, open the pinch-cock while the end of the delivery tube is under the water, raise the beaker until the surfaces of the water inside and outside the flask are at the same level, close the pinch-cock again, place a dry beaker under the delivery tube, and open the pinch-cock. If the water continues to siphon into the beaker your apparatus is not gas tight and must be rebuilt. Again heat the tube gradually until from 250 to 300 cc. of water have been forced over into the beaker. (**Caution.** Take care that the hot potassium chlorate does not come in contact with the rubber stopper.) Allow the tube to cool, equalize the level of the water in the beaker and the flask, and then close the pinch-cock on the siphon tube. By means of a 250 cc. graduated cylinder

measure the amount of water which the oxygen has forced out of the flask. Finally weigh carefully the hard-glass tube containing the partially decomposed chlorate. **Question.** Why is it necessary to cool the test-tube and to have the water in the beaker and flask at the same level before closing the pinch-cock?

8. Repeat the **experiment**, Paragraph 7. The three weighings and two volume measurements give two independent sets of experimental data. Compare the results of your two experiments by preparing a table which will show for each experiment: the weight of oxygen, the corresponding volume of water displaced, the data referred to in 10 to 11 below, and the results of the calculations in 12.

9. Clean the test-tube by placing water in it and shaking. The manganese dioxide is almost insoluble in water, while both potassium chlorate and potassium chloride dissolve readily. Suggest a method of recovering the manganese dioxide and obtaining a mixture of dry potassium chloride and potassium chlorate practically free from manganese dioxide.

10. To make the calculations it will be necessary to know the barometric pressure at the time you perform each experiment, and the temperature of the water in the flask. The temperature of the water may be assumed to be that of the room, and the barometric pressure will be posted on the blackboard. Enter these data in your note book before leaving the laboratory. Below is given a table of the vapor pressure of water at different temperatures:

VAPOR PRESSURE OF WATER

TEMP. °C.	VAPOR PRESSURE	TEMP. °C.	VAPOR PRESSURE
0	0.5 cm. mercury	26	2.5 cm. mercury
14	1.2 " "	28	2.8 " "
16	1.3 " "	30	3.2 " "
18	1.5 " "	32	3.5 " "
20	1.7 " "	34	4.0 " "
22	2.0 " "	99	73.3 " "
24	2.2 " "	100	76.0 " "

11. Questions. Assuming that the level of the water in the beaker and the flask was the same when the pinch-cock was closed, what was the total pressure of the gas in the flask? What was the **partial pressure** (H III) of the water-vapor? Of the oxygen? If the gas collected in your experiment were dried without changing the volume what would be the pressure in the flask?

12. Calculations. From each of your two sets of experimental data, by means of the Gas Laws (H III), calculate the volume of 1 mole (32 g.) of pure oxygen at 1 atmosphere pressure and 0°C . Compare your results with the value given in your reference book (H IV). Your results should not differ from this value by more than 5 per cent (check your calculations). **Show your tabulated results** to your instructor, and repeat the experiment if necessary.

13. Questions. What is the formula of the oxygen molecule? What value is usually accepted as a close approximation for the volume of 1 mole of gas under standard conditions? Use this value to calculate (a) the weight of a liter of hydrogen chloride gas, HCl , under standard conditions; (b) the molecular weight of a gas whose density at standard conditions is known to be 0.001977 g. per cc.

14. Write an equation to represent the decomposition of potassium chlorate, KClO_3 , into potassium chloride, KCl , and oxygen; and write out what this equation means in terms of (a) molecules, (b) moles, and (c) grams of the substances involved.

15. Problems. (1) One g. of potassium chlorate is completely decomposed into potassium chloride and oxygen. Calculate (a) the weight of oxygen that could be obtained, (b) the volume of the oxygen (in liters and in cc.) at standard conditions, and (c) the volume of the oxygen at 27°C . and 750 mm. mercury pressure.

(2) A one gram sample of an unknown mixture of potassium chlorate and chloride is found to yield 121 cc. of oxy-

gen measured under standard conditions. What is the per cent of KClO_3 in the mixture?

(3) Two volumes of a certain gas react with 1 volume of oxygen to form 2 volumes of another gas. Give the reasoning by which, from this result, you can conclude that the molecule of oxygen contains an even number of atoms.

(4) The formulas of carbon monoxide and carbon dioxide are CO and CO_2 , respectively. Write the equation for the combustion of carbon monoxide to carbon dioxide, and interpret it in terms of (a) moles, (b) liters, and (c) grams.

(5) Forty liters of nitrogen were collected over water at 25°C . and 765 mm. pressure. Calculate the volume of the dry gas at standard conditions.

(6) What would happen if a flask containing water initially at 25°C . were attached to a pump which maintained a pressure of 12 mm. of mercury? Cf. Table of Vapor Pressure of Water.

(7) To determine the value of 1 atmosphere pressure in grams per sq. cm. calculate the weight in grams of a column of mercury 76.0 cm. high and 1 sq. cm. in cross section. The density of mercury at 0°C . is 13.60 g. per cc. Calculate also the weight in pounds of a column of the same height and a cross section of 1 sq. in. 1 in. = 2.54 cm. 1 lb. = 453.5 g.

(8) *How many He atoms are in 1 cc. at 20°C . and 1 atm. pressure? The radius of the He atom is 0.8×10^{-8} cm. What fraction of the volume is occupied by the He atoms at 20°C . and 1 atm.?

(9) *The average velocity of a H_2 molecule at 20°C . is 1.9×10^5 cm. per sec. At one atmosphere the average path between collisions is 1.7×10^{-5} cm. How many collisions will a H_2 molecule make per second?

Assignment 3

The Determination of the Molecular Weight of a Liquid from Its Vapor Density

Special Material: A cork stopper to fit a 250 cc. flask. A 250 cc. graduated cylinder. Sample of liquid (to be supplied by the instructor; a number of non-inflammable halogen-paraffins may be used).

1. The general relation between the mass and volume of gases can be employed to determine the molecular weight of a substance which exists in the liquid state under room conditions, provided it is possible to vaporize the liquid and determine the density of its vapor at some definite temperature and pressure. In this Assignment the molecular weight of an unknown liquid will be determined by this method. The liquids employed boil in the range 65 to 80° C., and a bath of boiling water may therefore be used to maintain the vapor at a constant temperature. **Question.** What is the molal volume of a perfect gas at 100° C. and 753 mm. pressure?

2. The procedure consists in heating some of the liquid in a carefully weighed flask in a bath of boiling water. About a fourfold excess of liquid is taken; the excess vapor is expelled through a small outlet and carries with it the air originally in the flask. The flask is then removed from the bath and cooled, whereby the vapor is condensed and air again re-enters. The gain in weight of the flask gives the weight of vapor in the definite volume of the flask at the barometric pressure and the boiling point of water. From these data the molecular weight, i. e., the weight of the

molal volume under the experimental conditions, may be calculated.

3. Experiment. Fit a 250 cc. flask with a cork stopper which is as free from imperfections as possible. Drill the stopper and insert in it a 4 to 5 cm. length of glass tubing which is drawn down to about 0.5 mm. bore at the upper end. The lower end of the tube should extend slightly below the bottom of the stopper. Weigh the flask and stopper to 5 mg. (see Paragraph 5). Secure from your instructor a sample of an unknown liquid and pour about 3 cc. of it into the flask. Place the flask in a 600 cc. beaker and fasten it down by running a wire around the beaker and two wires across the top of the stopper. Fill the beaker with water to within an inch of the rim and loosen the wires slightly if the flask still touches the bottom of the beaker. Wrap a towel about the neck of the flask and the tip of the glass tube which extend slightly above the beaker, so that this portion of the apparatus will be heated to the temperature of the steam. Heat the water to boiling and continue the heating about 5 minutes after the disappearance of the drops of liquid which at first condense in the tube. Remove the flask, cool, and weigh it. Record the weight of the condensed liquid. Determine carefully the volume of the flask including the glass tube, and record also the barometric reading.

4. Calculate the molal gas volume for the conditions of the experiment. (Assume that the temperature was $100^{\circ}\text{C}.$) What fraction of the molal volume is the volume of the flask? What then is the molecular weight of the liquid? **Show your calculations** to your instructor, who will give you the formula of the compound if your result is satisfactory.

5. Note. Occasionally condensation of water in the pores of an imperfect cork stopper causes the result to be too high. A correction for this error may be applied if the stopper with its tube is weighed before and after the experiment.

6. **Problems.** (1) The density of benzene, C_6H_6 , is 0.82 g. per cc. at its boiling point, $80^\circ C$. Calculate the increase in volume when one mole of the liquid is vaporized at the boiling point.

(2) To determine the temperature of the boiling water corresponding to the barometric pressure in your experiment, use the vapor pressures at $99^\circ C$. and $100^\circ C$. given in the Table in Assignment 2, and make a linear interpolation between these temperatures. Calculate the error in the molecular weight that was introduced by assuming the temperature to be $100^\circ C$.

(3) The volume of a glass flask is 300 cc. at $20^\circ C$. What would it be at $100^\circ C$. if the average coefficient of cubical expansion of the glass is 1.4×10^{-5} per degree C. between these temperatures?

(4) *If the liquid used in the determination has a vapor pressure of 60 mm. at room temperature, what error (in the weight of the substance in a 250 cc. flask) is introduced by the assumption that the vapor pressure is zero?

Assignment 4

The Reaction between Certain Metals and Hydrochloric Acid. The Further Use of the Molal Volume of Gases

Special Material: Sample of metal (to be supplied by the instructor), short-stemmed funnel, thistle tube.

1. Certain metals, aluminum, zinc, magnesium, etc., react with a solution of an acid, with evolution of hydrogen gas and formation of a salt in solution. In this Assignment we shall dissolve a definite weight of a metal in excess of hydrochloric acid, measure under definite conditions of temperature and pressure the volume of the hydrogen liberated, and calculate the weight of the metal that would form one gram atom of hydrogen. From this result and the atomic weight of the metal we can then determine: the number of atoms of hydrogen formed when one atom of the metal reacts with the acid, the number of molecules of acid (HCl) which react with one atom of metal, and the formula of the chloride of the metal formed. **Questions.** What experimental facts and reasoning have led to the conclusion that the formula of the hydrogen molecule is H_2 ? If the charge on the chlorine atom in a chloride is -1 what is the charge on the sodium and calcium, respectively, in the compounds NaCl and $CaCl_2$?

2. The instructor will supply to each student a sample of a metal as an "unknown." **Experiment.** Take a portion of the metal weighing between 0.4 and 0.5 g. Clean it, if necessary. Weigh to 5 mg.

3. Obtain a small short-stemmed funnel at the office, and select a beaker of such size that the funnel when placed in it can be completely covered with water. Place the weighed metal in the beaker, place the inverted funnel over it, and pour freshly distilled water (or tap water boiled to remove air) into the beaker until the funnel is completely covered. **Note.** If the weighed metal is wrapped in a small piece of copper gauze, the chance of the liberated hydrogen escaping under the edge of the funnel is greatly lessened.

4. Pour distilled water into a half-liter flask until the water completely fills the flask. Moisten a piece of filter paper slightly larger than the mouth of the flask, cover the mouth of the flask with the paper, taking care that no bubble remains below the paper. Invert the flask (over an empty vessel) and lower it into the beaker in such a manner that the stem of the funnel enters the neck of the flask. If a bubble of air enters the flask repeat this operation. The apparatus now consists of a beaker containing a funnel inverted over the metal, and a flask filled with water and inverted over the funnel. Place this apparatus in a large beaker or other vessel, to prevent the water from overflowing on the desk during the remainder of the experiment.

5. Insert a thistle tube or long-stemmed funnel into the water so that the lower end touches the bottom of the beaker at the rim of the inverted funnel, and through it pour 25 cc. of concentrated hydrochloric acid. If the liquid is not stirred the concentrated acid, which is 1.19 times as dense as water, will remain for some time as a layer at the bottom of the beaker, and the metal will be dissolved rapidly. If all the water in the inverted flask is displaced by the hydrogen you have used too much metal or too small a flask and must begin the experiment over again.

6. When the metal has all dissolved (except a few dark-colored flakes of impurities of negligible weight), place the apparatus in a large basin of tap water and carefully remove the beaker and funnel without allowing any air to

enter the inverted flask. Keep the flask in the water for several minutes in order that it may be at the same temperature as the water. Then raise or lower the flask until the level inside and outside the flask is the same. (What is now the pressure of the gas inside the flask?) While the flask is in this position, cover the mouth of the flask with the palm of the hand, remove the flask from the water, and invert it. While the gas is escaping, collect some in a test-tube, and test to prove that it is hydrogen.

7. Determine the volume of the gas which was contained in the flask by measuring the volume of water now required to fill the flask completely. Record in your note book the barometric pressure (written on the blackboard) and the temperature of the water in which the flask was immersed.

8. You now have the weight of metal taken, and the volume, at a definite temperature and pressure, of a corresponding amount of hydrogen saturated with water-vapor. What is the partial pressure of the water-vapor at the temperature of the experiment? What was the partial pressure of the hydrogen in the flask?

9. **Calculate** from these data:

The volume at standard conditions that the hydrogen would occupy if it were dry.

The weight of the hydrogen. (Use the molecular weight 2.016 and the volume of 1 mole of gas, Assignment 2.)

The weight of metal that would have liberated 1 gram atom of hydrogen. **Report** this value to your instructor, who will tell you the name of the metal if your result is correct to within about 5 per cent.

By means of the atomic weight of the metal calculate the number of atoms of hydrogen formed when 1 atom of the metal dissolves in acid.

10. **Questions.** How many molecules of HCl react with 1 atom of the metal? Assuming that the hydrogen of the acid is replaced by the metal, what is the formula of the chloride formed? Write the equation for the reaction. **In-**

terpret it in terms of grams of metal and liters of hydrogen at standard conditions.

11. Problems. (1) From the density of hydrogen at standard conditions, 0.00008987 g. per cc., calculate the actual volume of 1 mole of hydrogen. What percentage error did you make in the calculations in Paragraph 9 by assuming the value 22.40 liters?

(2) If sulfuric acid, H_2SO_4 , had been used in the above experiment instead of hydrochloric acid, the same result would have been obtained and the final solution would have contained a sulfate of the metal. Write the equation for the reaction.

(3) The student will have noted that in the first four Assignments we have assumed a knowledge of atomic weights. The arbitrary choice of the unit $\text{O} = 16.00$ should present no difficulty, but it is often not clear why a particular value is chosen for the atomic weight of an element rather than some fraction or multiple of this value, e. g., in the case of chlorine why 35.46 is chosen instead of say 17.73 or 70.92. To illustrate how this choice is made on the basis of the experimentally obtainable quantities, molecular weight and percentage composition, the following data may be used. (The molecular weights given in the second column of the table are the accurate values, and not approximate values such as would be obtained directly from the weight of 22.40 liters of gas under standard conditions.)

SUBSTANCE	MOLECULAR WEIGHT	PER CENT CHLORINE	NO. GRAMS CHLORINE IN 1 MOLE
Chlorine.....	70.92	100	
Hydrogen chloride.....	36.47	97.2	
Chlorine oxide (1).....	86.92	81.6	
Chlorine oxide (2).....	67.46	52.6	
Phosphorus chloride.....	137.36	77.4	
Carbon chloride.....	153.85	92.2	

Calculate the values required for the fourth column of the table. What value would you choose for the atomic weight

of chlorine? No compound of chlorine has ever been made which contains in 1 mole less than 35.46 grams of chlorine. How many atoms of chlorine are contained in a molecule of each of the six substances listed in the table? Write the formula for chlorine gas.

(4) For the substances listed in Problem (3) calculate the number of grams of each element other than chlorine in one mole. The atomic weight of each of these elements has been determined by a procedure similar to that illustrated for chlorine. The values are $H = 1.008$, $P = 30.98$, $C = 12.01$. Using these values and the value for oxygen, calculate for each substance the number of gram atoms in a mole and write its formula.

(5) *On the basis of the following data discuss the deviations of O_2 and CO_2 from the perfect gas laws in terms of forces of attraction between the molecules. (The temperature is $50^\circ C.$)

	O_2		CO_2	
P (atm.)	1	100	1	100
V (liters)	1	0.0097	1	0.0042

(6) *What slight changes in temperature would you expect when a gas in which the attractive force between the molecules exceeds the repulsive force is allowed to expand from a high pressure into a vacuum?

Assignment 5

The Analysis of Copper Oxide

Note. No new principles are introduced in this Assignment, and it may therefore be omitted. However, the problems in Paragraph 10 may be assigned as an outside exercise.

Special Material: Hard-glass test-tube fitted with a two-holed rubber stopper, two-holed rubber stopper (to fit half-liter flask), thistle tube, clamp, calcium chloride drying tube fitted with rubber stoppers and glass and rubber tubes and closed with short glass rods, 10 g. of zinc, sample of either cuprous or cupric oxide.

1. In this Assignment, as an example of chemical analysis, we shall determine the composition of an oxide of copper. The analysis will be made by heating a weighed portion of the oxide in a current of hydrogen and weighing the metallic copper which remains. The oxygen of the oxide unites with the hydrogen to form steam. As in Assignment 1, we shall determine the formula of the compound by assuming the atomic weights of copper and oxygen. It is to be noted, however, that the results could be used to determine the relative atomic weights of copper and oxygen if the formula of the compound were known. Our experimental data, of course, will not be sufficiently accurate to make worth while the calculation of the atomic weight of copper.

2. **Experiment.** Two students may work together; one should sign the order slip for "special apparatus for Assign-

ment 5." The apparatus should be returned as soon as the experiment is finished.

3. Set up a "hydrogen generator" by fitting your half-liter flask with a thistle tube extending through the rubber stopper nearly to the bottom of the flask, and an outlet tube bent at right angles (see note on glass manipulation). Place in the flask about 10 g. of zinc and cover it with about 100 cc. of water. To the outlet tube attach a "drying tube" (containing solid calcium chloride, which has the property of absorbing moisture). Make sure that the apparatus is air-tight and wrap the flask in a towel.

4. Set up the remainder of the apparatus according to the directions of the instructor. Dry the thick-walled glass test-tube that is to contain the copper oxide by heating it gently. When it is cool weigh it carefully, together with any portion of the apparatus that may come in contact with the copper oxide. Place in the tube about 1 g. of copper oxide; wipe off any particles that are not in the portion of the tube that is to be heated. Weigh again carefully to obtain the weight of copper oxide used. Attach the apparatus to the hydrogen generator, pour about 40 cc. of concentrated hydrochloric acid down the thistle tube, and allow the hydrogen to pass through the apparatus until it has swept out the air. (**Caution.** Do not place a flame near the outlet nor heat the oxide while the apparatus contains a mixture of oxygen and hydrogen. A dangerous explosion might result.) Collect the gas in small test-tubes by displacement of water and ignite it. Explain how this test may be used to determine when the hydrogen is no longer mixed with oxygen.

5. When pure hydrogen is passing over the copper oxide, begin to heat the oxide very gently with a small flame and continue to heat cautiously until all the oxide changes color. If moisture collects in the farther end of the tube, drive it out by heating the tube carefully. **Question.** Where does this moisture come from?

6. Allow the tube to cool in the current of hydrogen, and weigh it. If you have time, check this result at once by repeating the heating in the current of hydrogen and then weighing; if not, set the tube aside in order that you may do so if the results of the following calculations are unsatisfactory.

7. **Calculate** the number of (a) grams, (b) gram atoms, of copper that are combined with 1 gram atom of oxygen. What, then, is the formula of this oxide of copper? Repeat the experiment if your results are inconclusive.

8. Write the equation for the reduction of copper oxide by hydrogen, and interpret in terms of (a) atoms and molecules, (b) gram atoms and moles, and (c) grams.

9. **Calculate** the per cents of copper and of oxygen in this oxide of copper (a) from your experimental results, (b) from the formula and the atomic weights of copper and oxygen.

10. **Problems.** (1) The formulas of cuprous oxide and cupric oxide are Cu_2O and CuO , respectively. Write equations for the reactions between the heated oxides and hydrogen to form copper and steam. What weight of copper would be obtained from one gram of each oxide? What is the percentage composition of each oxide?

(2) What weight of water could be obtained from 1 g. of cupric oxide? What volume would this amount of water occupy at 1 atmosphere pressure and (a) 4°C ., (b) 273°C .? What volume of hydrogen at 273°C . and 1 atmosphere pressure is required to form this amount of water?

(3) What are the formulas of cuprous sulfide, cupric sulfide, and hydrogen sulfide? Cuprous and cupric sulfides are also reduced to copper when they are heated in a current of hydrogen; hydrogen sulfide is formed. Write equations for the reactions.

(4) What is the **oxidation number** of copper in cuprous and cupric oxides? Assume oxygen to have the same oxidation number as in water.

Assignment 6

The Reaction between an Acid and a Base in Solution. Concentration in Terms of Moles per Liter. Titration of Solutions of Acids and Bases

Special Material: Iron (or platinum) wire, labels. Burets and clamps. Standardized 0.250 M H_2SO_4 .

1. In this Assignment we shall study the reaction between sodium hydroxide and hydrochloric acid in solution. In the preceding Assignments the amount of a substance was determined by weighing or by measuring the volume of the pure substance. It is often more convenient to determine such a quantity by measuring the volume of a solution which contains a known amount of the substance in a unit volume of the solution. **Definition.** The amount of the substance in a unit volume of solution is called the **concentration**. **Question.** If the concentration of a salt solution is known to be 10 g. per liter, what volume would you measure out in order to have 0.5 g. of salt?

2. We shall first examine separately the properties of the three solutions, the base, acid, and salt. **Experiment.** Prepare dilute solutions of sodium hydroxide, $NaOH$, and of hydrochloric acid, HCl , by diluting 5 cc. of the laboratory solution of each with 50 cc. of distilled water, and also a dilute solution of $NaCl$ by dissolving, in 50 cc. of distilled water, about two grams of the salt (estimated by comparison with a sample prepared by the instructor).

To portions of the three solutions add a few drops of phenolphthalein solution. Test also with litmus paper.

Taste each solution by dipping a glass rod into the liquid and touching it to the tongue. (**Caution.** Do not taste any substance in the laboratory unless directed to do so.)

Test a drop of each solution in a colorless gas flame by means of an iron (or platinum) wire. A yellow flame proves the presence of sodium.

Evaporate to dryness in a casserole 1 cc. of HCl solution, and of NaCl solution. In each case examine if there is a residue. **Question.** What conclusion can you draw in regard to the volatility of water and hydrogen chloride as compared to sodium chloride? What results would you predict if a solution containing both NaCl and HCl were evaporated? Pure sodium hydroxide is a stable non-volatile substance which would be left as a solid when a solution containing it is evaporated to dryness. (**Caution.** Do not evaporate alkaline solutions to dryness. Glass and porcelain are slowly attacked by hot concentrated alkali and a porcelain dish is spoiled if an alkali residue is heated strongly in it.)

Summarize in a table the properties of the three solutions examined above.

3. Neutralization. Experiment. Measure out about 2 cc. of your laboratory NaOH solution. Pour the solution into a small casserole. Now add portions of your HCl solution, stirring after each addition, until the solution is acid to litmus paper. Place the dish containing the solution on your wire gauze and heat until the solution begins to boil. Reduce the size of the flame and allow the solution to boil gently. As it approaches dryness, sputtering may occur, and the dish may be covered loosely with the watch-glass or held above the flame and moved carefully back and forth. Finally heat more strongly until no further trace of water-vapor is expelled. Allow the dish and residue to cool.

4. Dissolve a portion of the residue in a small amount of

water and test as in Paragraph 2. State what evidence you have that a reaction has taken place between the acid and base, and that the solid residue obtained is sodium chloride. Write the (non-ionic) equation for the **neutralization** reaction between NaOH and HCl and interpret it in terms of (a) molecules, (b) moles, (c) grams of the substances involved. **Note.** The interpretation in terms of ions will be presented in Assignment 21.

5. The reaction just considered is typical of the reaction between any acid and any base. In every case H of the acid unites with OH of the base to form water. Write the equations for the reactions between the following bases and acids, and interpret each equation in terms of moles of the substances involved:

Sodium hydroxide and nitric acid, HNO_3 .

Sodium hydroxide and sulfuric acid (to form two moles of water from one mole of H_2SO_4).

Barium hydroxide, $\text{Ba}(\text{OH})_2$, and hydrochloric acid.

Barium hydroxide and sulfuric acid.

6. Since the mole is a convenient unit of weight to use in studying chemical reactions, concentration is often expressed in terms of the number of moles of substances in a liter of solution. **Definition.** A solution which contains in one liter one mole of dissolved substance is called a **molal** solution; one which contains in one liter one-tenth mole of dissolved substance is called a tenth molal solution, etc. Molal hydrochloric acid is designated thus: 1 *M* HCl; tenth molal sulfuric acid would be written 0.1 *M* H_2SO_4 , etc.

7. In the above paragraphs we learned that an acid and a base in solution will neutralize each other. We shall now see how this reaction can be used in determining the concentration of one of these solutions when that of the other is known. The operation is called a **titration**. It is evident that a pure solution of a salt may be prepared by mixing the corresponding acid and base in exactly the right proportion; this **end-point** in the titration is determined by

means of a suitable indicator. The relative concentrations of the two solutions can be calculated when the relative volumes of the two solutions used in the titration are known. **Questions.** How many moles of NaOH are required to neutralize exactly 0.01 mole of (a) HCl, (b) H_2SO_4 ? How many cc. of 0.50 *M* NaOH solution will exactly neutralize 0.01 mole of (a) HCl, (b) H_2SO_4 ?

8. **Experiment.** Take 40 cc. of your laboratory NaOH solution, place it in a clean half-liter flask, and dilute with 440 cc. of distilled water. Shake the flask in order that the solution shall be uniform throughout. Cork the flask and label it "NaOH solution for Assignments 6 and 7." **Question.** What approximately is the ratio of the initial volume of the sodium hydroxide solution to the final volume? What is the concentration of NaOH (assuming the laboratory solution to be 6 *M*, which is only approximately correct)?

9. **Experiment.** Prepare 250 cc. of approximately 0.5 *M* HCl from your laboratory 6 *M* solution, place it in a flask, and shake it. Cork the flask and label it "HCl solution for Assignments 6 and 7." Clean a small flask and label it "known H_2SO_4 solution," rinse the flask with distilled water, and set it aside to drain in order to have it ready for use later in this Assignment.

10. Since in the titration of an acid by a base the solution at the desired end-point is that of the corresponding salt, the nature of the end-point with any indicator may be determined by adding a few drops of the indicator to a solution of the salt, noting the color, and then observing the effect produced by adding a drop of acid and a drop of base to separate portions of the solution. **Experiment.** Dissolve about 2 g. of NaCl in 200 cc. of water. To each of two 50 cc. portions add two drops of phenolphthalein, stir the solution, and record the color. To one portion add a drop of your NaOH solution (approximately 0.5 *M*) and to the other a drop of your approximately 0.5 *M* HCl. **Note.** Small drops are conveniently added from a glass dropper

(see Appendix IB). Finally determine the nature of the end-point when about 2 g. of sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is used instead of NaCl .

11. The volumes of the solutions used in a titration are measured by means of burets. Read directions in Appendix IC. Two burets will be placed on your desk before the beginning of the Assignment. At the end of the period rinse them with distilled water and leave them on your desk.

12. Rinse one buret with a little of your approximately 0.5 molal HCl solution, and fill the buret with this solution. Rinse and fill the other buret with the 0.5 molal NaOH solution. Record the readings of the burets side by side in your note book; run about 15 cc. of the acid solution into a clean Erlenmeyer flask standing on white paper. Add two drops of phenolphthalein, and about 20 cc. of distilled water. Then run in the sodium hydroxide solution from the other buret, a little at a time, and towards the end, very carefully, a drop or two at a time, swirling the flask constantly, until the faintest perceptible permanent pink color is obtained. Wash down the inside of the flask by means of a jet of water from the wash-bottle. If the color of the solution is deeper than a faint pink, too much of the basic solution has been added; decolorize the solution by adding a little of the acid and determine the end-point more accurately. Record the final readings of each buret under the initial readings, and calculate the actual volumes of each solution used in titration. Calculate the volume of sodium hydroxide necessary to neutralize one cubic centimeter of the hydrochloric acid; this is the **volume ratio**.

13. Repeat this **experiment**, using about 20 cc. of the acid solution, and make the same calculations. Do not fill up the buret each time unless there is not enough solution in it for the titration. **Questions.** If the error in measuring out a volume of solution by means of a buret is 0.03 cc. what is the percentage error if 1 cc. of solution is measured? If

20 cc. of solution are measured? Why is it important not to use less than 10 cc. in any titration?

14. Compare the volume ratios calculated from two titrations. If the result differs from the average by more than 1 per cent, perform additional titrations until you are satisfied that you have determined the volume ratio with an accuracy better than 1 per cent. **Questions.** (a) From an examination of the equation for the neutralization of sodium hydroxide by hydrochloric acid state the ratio of the number of moles of base to the number of moles of acid when exact neutrality is reached.

(b) From your average volume ratio state which solution, acid or base, is the more concentrated, and what is the ratio of the concentrations.

15. Take your clean, dry, labelled flask, Paragraph 9, to the office to obtain a sulfuric acid solution of known concentration.

16. Empty the HCl out of the buret, rinse it with about 5 cc. of the sulfuric acid solution of known concentration, and fill it with the sulfuric acid solution. Determine the volume ratio as before from three (or more) titrations. From the volume ratio and the reaction between sodium hydroxide and sulfuric acid calculate the concentration of the sodium hydroxide solution in moles per liter. Calculate also the concentration of your hydrochloric acid solution.

17. Make a list of the sources of error. (Many of them have been mentioned in the above directions.)

18. Save the remainder of the NaOH and HCl solutions, whose concentrations you have determined, in corked flasks for use in Assignment 7.

19. **Problems.** (1) How many cc. of 0.10 *M* Ba(OH)₂ will be required to neutralize 40 cc. of 0.50 *M* HCl?

(2) What is the molality of a sulfuric acid solution, 40 cc. of which neutralizes 30 cc. of 0.20 *M* NaOH?

(3) What is the concentration of H₂O in moles per liter in pure water?

Assignment 7

Volumetric Analysis: The Determination of the Equivalent Weight of an Unknown Acid

Special Material: Samples of "unknown" solid acids.

Reference. Hildebrand, Chapter VI.

1. In Assignment 7 there will be introduced another unit of quantity, **the equivalent**. This unit and the corresponding unit of concentration, **equivalents per liter**, are frequently more convenient than the units, mole, and moles per liter. The mole and equivalent are identical for HCl, HNO₃, NaOH, NaCl, etc., but a mole of H₂SO₄, Ba(OH)₂ or Na₂SO₄, etc., contains two equivalents. **A solution which contains one equivalent in a liter is called a normal solution and is designated 1 N.** The convenience of this unit of concentration depends upon the fact that when one equivalent of any acid reacts with one equivalent of any base the resulting solution contains one equivalent of the corresponding salt. **Question.** What is the normal concentration of a molal solution of H₂SO₄, NaOH, and Na₂SO₄ respectively? How many equivalents of acid can be neutralized by 10 cc. of 0.1 N NaOH? Calculate the normal concentrations of your solutions of NaOH, HCl and H₂SO₄ used in Assignment 6.

2. Weighed portions of an unknown solid acid will be titrated with your NaOH solution. By means of the concentration of the NaOH solution (determined in Assignment 6) the number of grams in one equivalent of the acid will be calculated. The correctness of this result depends,

of course, on the accuracy of your work in Assignment 6. It is to be noted that if you had started with a solid acid of known equivalent weight, you could have used the results obtained in this Assignment to determine the concentration of the sodium hydroxide solution.

3. **Experiment.** Obtain from the office a sample tube containing approximately 2 g. of a crystalline acid of unknown composition. Clean two 250 cc. flasks and label them No. 1 and No. 2. Weigh the sample bottle with its cork and contents. Remove the cork, taking care that none of the solid which may be sticking to it drops off, and shake half the sample into flask No. 1. Replace the cork and weigh again. Shake the remainder of the sample into flask No. 2, and weigh the empty sample bottle and cork. All weighings should be made to 5 mg.

4. Pour about 50 cc. of distilled water into each flask, and shake the mixtures. To each add two drops of phenolphthalein and titrate to the appearance of the first pink color with the sodium hydroxide solution prepared in Assignment 6. If you should pass the end-point in a titration add from a second buret an acid solution of known concentration until the pink color is discharged, and again titrate to the end-point with the sodium hydroxide.

5. For each sample calculate the number of cubic centimeters of NaOH solution needed to neutralize 1 g. of the acid. If the results differ by more than 2 per cent repeat the experiment.

6. From your two (or more) measurements obtain an average value of the number of cubic centimeters of sodium hydroxide solution per gram of acid. From this average value and the concentration of the NaOH solution calculate the number of moles of NaOH needed to neutralize 1 g. of the acid.

7. **Questions.** How many equivalents are in one gram of the acid? How many grams are in one equivalent of the acid?

Report this value to your instructor at once. If your result is unsatisfactory check your calculations in Assignments 6 and 7 and repeat as much of the work as is necessary.

8. Problems. (1) Among the acids suitable for this Assignment are: oxalic, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; citric, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$; tartaric, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and potassium acid sulfate, KHSO_4 . Write the equations for the reaction between NaOH and (a) oxalic acid (to form $\text{Na}_2\text{C}_2\text{O}_4$), and (b) KHSO_4 ; and calculate the equivalent weight of the acid in each of these reactions.

(2) What is the normal concentration of a sulfuric acid solution, 25 cc. of which neutralizes 20 cc. of 0.20 *N* NaOH ?

(3) Chemically pure ("C. P.") sulfuric acid, nitric acid, hydrochloric acid, and ammonia, as supplied by the manufacturers, are concentrated aqueous solutions of these substances. The concentration of each solution is guaranteed not to be less than a certain minimum value, and this is tested by measuring the density (or the specific gravity). The following table contains the density and the percentage composition by weight of the concentrated laboratory reagents.

	DENSITY G. PER CC.	PER CENT BY WEIGHT	CONCENTRATION EQUIVALENTS PER LITER
H_2SO_4	1.84	95.6% H_2SO_4	
HNO_3	1.42	69.8% HNO_3	
HCl	1.19	37.2% HCl	
NH_4OH	0.90	57.5% NH_4OH	

For each solution calculate the normal concentration and record the results in the fourth column of the table.

Caution! The concentrated acids, especially sulfuric and nitric, produce dangerous burns and should not be used carelessly. When you are directed to use one of these acids carefully pour just enough of it for your experiment into a dry beaker.

(4) What will be the normality of a solution made by.

diluting 10.0 cc. of the concentrated sulfuric acid (1.84 density) to a volume of 400 cc.?

(5) Excess silver nitrate was added to 25.0 cc. of a solution of hydrochloric acid and the chloride was precipitated as AgCl. The weight of AgCl was found to be 0.356 g. Calculate the normality of the HCl.

Section II

Ionic Theory Rapid Reversible Reactions and Equilibrium

Assignment 21

Aqueous Solutions of Strong Electrolytes. Ionic Reactions

Reference. Hildebrand, Chapter VIII.

1. This Assignment, which contains no experimental work, is introduced in order that the student may become familiar with the fundamental ideas underlying the Ionic Theory before proceeding to use these ideas in later Assignments.

2. The use of the terms acids and bases in designating two distinct groups of substances implies that the members of each group have a set of properties in common. The properties characteristic of all acid solutions, which were observed in Assignment 6, are ascribed to a substance called hydrogen ion, represented by the symbol H^+ ; and those of basic solutions to the substance hydroxide ion, written OH^- . In addition to the properties of the hydrogen ion, each acid in solution has a group of properties different from those of any other acid but common to solutions of all salts of that acid. Thus hydrochloric acid has a set of properties which is characteristic of solutions of all chlorides and is ascribed to a substance called chloride ion, Cl^- . Likewise, a solution of sodium hydroxide has a group of properties which is characteristic of solutions of all sodium salts and which is attributed to the sodium ion, Na^+ . **Questions.** What is the evidence from freezing point data that there are approximately 2 moles of substance present when one

mole of hydrogen chloride is dissolved in water? How does the electrical conductivity of hydrochloric acid solution support the idea that the molecule of hydrogen chloride in solution is broken up into hydrogen ion and chloride ion? How does a chloride ion differ from an atom of chlorine, and a hydrogen ion differ from an atom of hydrogen? List briefly differences in properties of the substances hydrogen ion and hydrogen gas.

3. Many substances in dilute aqueous solution may be considered as **completely ionized**. These substances are called **strong electrolytes** and include:

Practically all salts.

A few acids as HCl and HNO_3 (and H_2SO_4 , below about $0.001\ M$)¹

A few bases as NaOH , KOH , and $\text{Ba}(\text{OH})_2$.

The student should memorize this list and should form the habit of thinking of a solution of a strong electrolyte in terms of the ions present and not merely in terms of the specific solid, liquid, or gas used in making the solution. It is important to realize, however, that each strong electrolyte in the solid or gaseous state is a single pure substance with its own specific properties. Hydrogen chloride gas and solid sodium chloride will therefore be represented by the formulas HCl and NaCl , and the aqueous solutions by $\text{H}^+ + \text{Cl}^-$ and $\text{Na}^+ + \text{Cl}^-$. **Questions.** What are the principal substances present in each of the following solutions; what is the quantity of each solution in moles, and what is its concentration in moles per liter?

(1) A solution which contains 0.1 mole of HNO_3 in 2 liters. (Answer. H^+ and NO_3^- ; 0.1 mole of each at $0.05\ M$ concentration.)

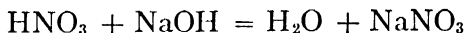
¹ H_2SO_4 is completely ionized into H^+ and HSO_4^- , but the ionization of HSO_4^- into H^+ and SO_4^{--} is far from complete in a 0.1 molal solution of H_2SO_4 or KHSO_4 . However, for the sake of simplicity, these electrolytes are often assumed to be completely ionized.

(2) A solution which contains 0.1 mole of NaOH in 1 liter.

(3) A solution which is made by mixing (1) and (2). (Note that there is a chemical reaction and that the volume is increased to 3 liters.)

(4) A solution which contains 0.1 mole of Na_2SO_4 and 0.1 mole of NaCl in 500 cc.

4. **Ionic reactions.** Having realized what substances are present in solutions of strong electrolytes we are now in a position to interpret reactions involving such solutions. We shall first consider what is the ionic reaction when a strong acid neutralizes a strong base, and shall take as an example the reaction between nitric acid and sodium hydroxide solutions. The equation



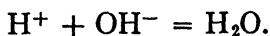
is a statement of the reaction that takes place whenever HNO_3 and NaOH solutions are mixed, and we have seen that it may be interpreted in terms of molecules, and of moles, equivalents, grams, or any other weight units. It records no experimental detail, such as volumes or concentrations of solutions, or the use of either reagent in excess; and additional notes are necessary when such a record is desired.

This equation can be interpreted according to the ionic theory (a) by adding a note that HNO_3 , NaOH, and NaNO_3 are strong electrolytes and that H_2O is a **weak electrolyte**, or (b) by rewriting the equation to give the same information:



It is evident that the Na^+ and NO_3^- shown to be in the final solution were present in the two initial solutions, and that these substances have undergone no change during the reaction. It is incorrect to say that "sodium ion and nitrate ion have combined." Since H^+ and OH^- are the substances

used up and H_2O the substance formed, we may write for the net reaction:



5. The statement that a substance is a weak electrolyte is equivalent to saying that the ions of that substance cannot exist in the presence of each other except at low concentrations, and it is obvious that any reaction which involves the formation of a weak electrolyte from its ions may be expected to take place. Accordingly, we shall be able to predict a number of reactions in aqueous solutions when we have classified the substances involved as strong or weak electrolytes.

6. Another reaction, which involves the ions of a strong electrolyte, is the precipitation of a **slightly soluble salt**. Again the statement that a salt, such as silver chloride, AgCl , is slightly soluble is equivalent to saying that its ions cannot exist together in solution except at the low concentrations corresponding to the solubility of the salt. **Write** the non-ionic equation for the reaction that takes place when dilute solutions containing equivalent amounts of NaCl and AgNO_3 are mixed. What substances are present at relatively high concentrations in each of the initial solutions and in the final solution? Write the equation for the net reaction. Consider next the case in which silver nitrate solution in excess is added to a sodium chloride solution, answer the same question, and write the equation. It should be obvious that the reaction is the same in both cases, and that, therefore, the two equations should be identical.

7. Problems. (1) Does anything happen in the following experiments? A dilute solution of sodium chloride is mixed with a dilute solution of (a) potassium nitrate, (b) nitric acid.

(2) Write the equation for the net reaction in each of the following: (a) A solution of $\text{Ba}(\text{OH})_2$ is neutralized by dilute nitric acid. (b) A precipitate of barium sulfate, BaSO_4 , is

formed by mixing solutions of barium chloride and sodium sulfate. (c) A sodium sulfate solution is evaporated to dryness. (d) Hydrogen chloride gas is dissolved in water.

(3) Barium hydroxide is a strong base, and the solubility of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is $0.22\text{ }M$ at 20° . What is the concentration of each of the ions present in the saturated solution?

(4) If the freezing point of water is lowered approximately 1.86° per mole of substance in solution in 1000 g. of water, what is the freezing point of a 0.1 molal solution of (a) a non-electrolyte, (b) HNO_3 , (c) $\text{Ba}(\text{NO}_3)_2$?

(5) *What is the electron structure of: (a) sodium atom, (b) sodium ion, (c) chlorine atom, (d) chlorine molecule, (e) chloride ion, (f) hydrogen atom, (g) hydrogen molecule, (h) hydrogen ion?

(6) *The electron structures of F^- and Na^+ are the same but the radii are 1.36 and $0.95 \times 10^{-8}\text{ cm.}$ respectively. Explain why Na^+ is the smaller.

(7) *The radius of sodium atom is $1.8 \times 10^{-8}\text{ cm.}$ and that of the sodium nucleus $4 \times 10^{-13}\text{ cm.}$ If the radius of the atom were one mile, what would be the radius of the nucleus if the same ratio were maintained?

Assignment 22

Strong and Weak Acids. The Use of Indicators to Measure Hydrogen Ion Concentration

1. Indicators can be used to measure the concentration of hydrogen ion, or of hydroxide ion, in a solution. The color change for each indicator occurs in a definite range of concentrations of hydrogen ion (or hydroxide ion), which is characteristic of the indicator. In the present Assignment, by using solutions of known concentration of the **strong acids** listed in Assignment 21, we shall develop a method of determining approximately the concentration of hydrogen ion in any acid solution. This indicator method will then be used to measure the concentration of hydrogen ion in solutions of a typical **weak acid**. Two reactions involving this acid will be studied.

2. **Experiment.** Prepare 60 cc. of 1 *N* HCl by adding distilled water to the proper volume of the 6 *N* laboratory reagent and shaking the mixture. From this solution, or from your known HCl solution, Assignment 6, prepare between 50 and 100 cc. of 0.10 *N* HCl, and from this solution prepare 50 to 100 cc. of 0.01 *N* HCl; also prepare a 0.001 *N* HCl solution. On account of the error in measuring volumes by means of a graduated cylinder, and the probable variation of the concentration of the laboratory solution from 6 *N*, the concentrations of these solutions are known only approximately.

3. Pour into marked test-tubes 10 cc. of each HCl solution (1 N , 0.1 N , 0.01 N , 0.001 N) and pour 10 cc. of water into a fifth test-tube. Add to each solution from a glass tube a single drop of methyl violet solution. Hold the tubes in a vertical position over a piece of filter paper, look down through the surface, record the color of each solution, and note the smallest concentration of hydrochloric acid which shows with this indicator a color different from that of water. If the indicator solution is so dilute that one drop does not produce a distinct color add 1 or 2 more drops, but record the number of drops, and use the same number in all the tubes. State how the indicator, methyl violet, may be used to determine the approximate concentration of a hydrochloric acid solution. (The color in the more concentrated solution will fade on standing. It may be restored by adding another drop of the indicator.) **Note.** Set aside the remainder of the 0.01 N and 0.001 N HCl for use later in this Assignment, Paragraphs 5 and 8.

4. **Experiment.** Repeat the experiment with nitric acid, using the same concentrations as before (1 N , 0.1 N , 0.01 N , 0.001 N). Compare the colors obtained with the different acids. **Questions.** Are the colors characteristic for each acid? If not, what substance determines the color? If hydrochloric acid is completely ionized what conclusion can you draw with respect to the ionization of nitric acid?

5. If you have performed the above experiments correctly and understood them you will realize that the indicator methyl violet can be used to determine, approximately, concentrations of hydrogen ion between 1 N and 0.001 N . However, while the concentration of H^+ in the dilute solution, 0.001 N (which is often written $10^{-3} N$), is small compared with the normal solution, it is 10,000 times as great as in pure water. We shall now make use of the indicator methyl orange to examine solutions in which the concentration of H^+ is between $10^{-3} N$ and that of pure water, $10^{-7} N$. **Experiment.** By a 10-fold dilution of your

10^{-3} *N* HCl solution, prepare 50 or 100 cc. 10^{-4} *N* HCl; and from this prepare a 10^{-5} *N* solution. Test 10 cc. portions of these three solutions and of water with 1 drop of methyl orange. Would you expect the results to be the same if you had used nitric or sulfuric acid? **Note.** Save the 10^{-4} *N* solution for later use, Paragraph 8.

6. Summarize your results with the two indicators in a table which shows the colors obtained at various concentrations of H^+ . **Show your table** to the instructor.

7. The weak acid which we shall now proceed to study is acetic acid, $HC_2H_3O_2$. It is a white, crystalline, rather volatile solid which melts near room temperature and is very soluble in water. The formula of its sodium salt, sodium acetate, is $NaC_2H_3O_2$. We shall abbreviate these formulas to HAc and NaAc, respectively. **Questions.** How many moles of acetic acid are contained in 1 liter of 6 *N* acid? How many moles of sodium acetate could be prepared from this quantity of acetic acid?

8. **Experiment.** From the laboratory 6 *N* HAc prepare solutions which are approximately 1 *N*, 0.1 *N*, and 0.01 *N*. We wish to determine by means of indicators the approximate concentration of H^+ in each of these solutions. Place a 10 cc. portion of each of the solutions in a labelled test-tube, place 10 cc. distilled water in another test-tube, and test each solution with methyl violet as in Paragraph 3. For comparison, repeat the test with HCl solutions of suitable concentrations. (**Note.** In color comparisons it is not safe to trust the memory, or even written descriptions.) Estimate approximately the concentration of hydrogen ion in the 1 *N* and 0.1 *N* solutions. Repeat the **experiment**, but use methyl orange instead of methyl violet, and estimate the concentration of H^+ ion in the 0.1 *N* and 0.01 *N* solutions.

9. The acetic acid in the solution must be present either in the form of ions, H^+ and Ac^- , or in the un-ionized form, HAc. From your estimate of the concentration of H^+ in

the 0.1 normal solution, calculate the fraction of the acetic acid which is ionized, and the fraction which is un-ionized. The fraction of the acid which is in the form of ions is called the **degree of ionization**. State also the concentrations of acetate ion, Ac^- , and of the un-ionized acid, HAc , in the 0.1 normal acetic acid solution.

10. **Calculations.** The concentration of the ions in acetic acid solutions has been determined by other methods more accurately than is possible by these color experiments. The concentrations of hydrogen ion in these solutions at room temperature are given in the following table:

CONCENTRATION ACID	CONCENTRATION OF H^+	CONCENTRATION OF Ac^-	CONCENTRATION OF UN-IONIZED HAc	DEGREE OF IONIZATION
1 <i>N</i>	0.0040 <i>N</i>			
0.5 <i>N</i>	0.0029 <i>N</i>			
0.1 <i>N</i>	0.0013 <i>N</i>			
0.01 <i>N</i>	0.0004 <i>N</i>			

Fill in the remaining columns of the table in your note book and **show your table** to the instructor at once.

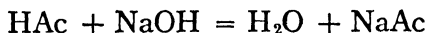
11. Memorize the fact that acetic acid and water are weak electrolytes. **Questions.** Refer to Assignment 21, Paragraph 5, and state what you would expect to happen if a solution containing Ac^- at high concentrations were mixed with a solution containing H^+ at high concentration. What solutions would you mix to try this experiment, and how could you prove with an indicator that a reaction had taken place?

12. **The reaction between sodium acetate and hydrochloric acid solutions. Experiment.** Prepare some approximately half normal hydrochloric acid. Measure out two 15 cc. portions in test-tubes, and add two or three drops of methyl violet to each. Measure 10 cc. of 1 *N* sodium acetate and add the solution, a few drops at a time, to one of the 0.5 *N* hydrochloric acid solutions. After each addition shake the mixture, record the color, and note the volume of

the sodium acetate solution added. Write the equation for the reaction that has taken place between H^+ and Ac^- .

Questions. If solutions containing 0.15 mole of HCl and 0.05 mole of $NaAc$ are mixed what are the principal substances present in the resulting solution? What would be the concentrations of HAc and H^+ if the final volume were (a) 1 liter, (b) 500 cc.?

13. The neutralization of sodium hydroxide solution by acetic acid. The concentration of H^+ in an acetic acid solution is small in comparison with the total concentration of acid in the solution, but the student must not jump to the conclusion that the results on neutralization found in Assignment 6 would have been materially different if acetic acid had been used throughout instead of hydrochloric acid. In the following experiment we shall study qualitatively the reaction between $NaOH$ solution and acetic acid; cf. the corresponding experiment in Assignment 6, Paragraph 3. **Experiment.** To 10 cc. of 6 *N* $NaOH$ in a porcelain dish add about 8 cc. of 6 *N* HAc . (Does the mixture become warm?) Add 1 drop of phenolphthalein and continue to add acetic acid slowly until the solution becomes colorless; test again with the indicator (since the phenolphthalein color fades in a concentrated $NaOH$ solution) and finally add about 2 cc. of acid in excess. Evaporate the solution until crystals of salt begin to separate. (**Caution.** Do not evaporate the solution to dryness, since the $NaAc$ may decompose.) Allow the mixture to cool, collect some of the moist salt, $NaAc \cdot 3H_2O$, and dry it between filter papers. Prove that the salt contains sodium by the flame test, and acetate by warming with 6 *N* sulfuric acid and noting the odor of acetic acid. **Question.** What evidence is furnished by this experiment that the neutralization reaction



takes place when solutions of HAc and $NaOH$ are mixed? The concentration of an acetic acid solution can be de-

terminated by titration with a known sodium hydroxide solution if an indicator is used which shows when the final solution has the composition of pure sodium acetate solution (cf. Assignment 6, Paragraph 10). Phenolphthalein is suitable in this case (and the student may perform the titration if time permits).

14. We shall now examine the above reaction in the same way as we have already done in Assignment 21, Paragraph 4, in the case of the reaction between a strong acid and a strong base. **Questions.** Which of the four terms in the above equation represent strong and which weak electrolytes? What substance is present at high concentration in an acetic acid solution which is not present at high concentration in a sodium acetate solution? What substance is present in a sodium hydroxide solution which is not present at high concentration in a sodium acetate solution? What substance is present at high concentration in a sodium acetate solution which is not present at high concentration in either of the initial solutions? Summarize your answers to these questions by writing the equation for the **net reaction**; show it to your instructor. The study of this reaction will be continued in Assignment 25.

15. **Problems.** (1) If the same volume of NaOH solution is required to titrate 20.0 cc. of acetic acid and 16.0 cc. of 0.50 N H_2SO_4 , what is the concentration of the acetic acid?

(2) Outline experiments to distinguish between

- (a) 1.0 N HNO_3 and 0.10 N HNO_3 .
- (b) A solution of nitric acid and one of acetic acid which give the same bluish color with methyl violet.

Assignment 23

Rapid Reversible Reactions and Equilibrium

Special Material: 4 *N* sodium acetate solution free from chloride.

Reference. Hildebrand, Chapter XII.

1. While certain reactions proceed to completion, as the transformation of metallic copper into cuprous sulfide studied in Assignment 1, many reactions do not. For example, when solutions containing equivalent amounts of a strong acid and sodium acetate are mixed the resulting solution still contains about 1 per cent of the reacting substances H^+ and Ac^- , i. e., the reaction $H^+ + Ac^- = HAc$, although it takes place very rapidly, stops when about 99 per cent of the possible amount of HAc has been formed. In the final solution, the concentrations of the three substances involved in the reaction are the same as in the corresponding acetic acid solution. Similarly, if we had started with pure acetic acid, which is un-ionized in the solid, liquid, or gaseous state, and dissolved it in water, the reaction $HAc = H^+ + Ac^-$ would have taken place rapidly, but only until about 1 per cent of the acetic acid had been ionized.

Question. From your results in Assignment 22, Paragraph 10, what would be the concentrations of H^+ , Ac^- , and HAc in a solution made (a) by dissolving 1 mole of HAc to give a liter of solution, and (b) by dissolving 1 mole of HCl and 1 mole of $NaAc$ to give a liter of solution?

2. The reaction just considered is an example of a rapid, **reversible reaction**, and the three substances involved in this reaction are **in equilibrium** with each other in the final

solution. In general whenever it has been shown experimentally that a reaction can be made to take place in both directions, i. e., is reversible, then it may be concluded that under suitable experimental conditions a state of equilibrium can be realized in which all the substances involved in the reaction are present together. For each set of experimental conditions there is a definite state of equilibrium; and when the experimental conditions are altered, e. g., by changing the concentration of one or more of the substances involved or by changing the temperature, the reaction takes place in one direction or the other until equilibrium is again established. The problem is to learn to predict what will happen in any given case when the experimental conditions are altered.

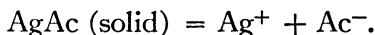
3. The effect of changing the concentration of one of the substances involved in an equilibrium. Experiment. Place two 10 cc. portions of 1 *N* acetic acid in two test-tubes, a 10 cc. portion of 0.1 *N* acetic acid in a third test-tube, and a 10 cc. portion of water in a fourth test-tube. To each solution add the same number of drops of methyl orange solution. To one of the normal solutions add a small amount of solid sodium acetate (or of 4 *N* solution); compare the colors of the four solutions. **Questions.** What conclusion can you draw with regard to the change in the concentration of hydrogen ion on the addition of sodium acetate? What reaction must have taken place? When equilibrium has again been established after the addition of the sodium acetate, is the concentration of each of the substances H^+ , Ac^- , and HAc greater or less than its concentration in the original acetic acid solution? State briefly how this experiment illustrates the general statement: **the effect of changing the concentration of one of the substances involved in an equilibrium is to cause that reaction to take place which tends to counteract the change.** The condition for equilibrium in any dilute solution at a definite temperature is given by the expression,

$$\frac{(C_{H^+})(C_{Ac^-})}{C_{HAc}} = K$$

where C_{H^+} , C_{Ac^-} , and C_{HAc} are the equilibrium concentrations (moles per l.) of H^+ , Ac^- , and HAc , and K is a constant which is called the **ionization constant** of acetic acid.

4. Calculate the value of the ionization constant for acetic acid, as defined in the preceding paragraph, from the concentrations of HAc , H^+ , and Ac^- which you have tabulated in Paragraph 10, Assignment 22. Compare the values you obtained for the four different concentrations of the acid. How could you calculate the concentration of H^+ in 0.001 M HAc ?

5. As another example of the effect of change of concentration upon equilibrium we shall study the equilibrium between solid silver acetate and its ions. The solubility of silver acetate is 0.06 mole per liter at room temperature; while it is much more soluble than a "slightly" soluble salt, as silver chloride, it is much less soluble than such salts as silver nitrate, sodium nitrate, or sodium acetate. The reversible reaction is:



Since the concentration of the $AgAc$ solid is constant the condition for equilibrium at a given temperature is:

$$(C_{Ag^+})(C_{Ac^-}) = K$$

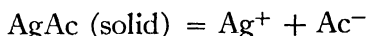
where K is a constant which is known as the **solubility product** of silver acetate. **Experiment.** Prepare some solid silver acetate by adding to 25 cc. of 4 N $NaAc$ solution (free from chloride) ¹ about 20 cc. of 0.1 N $AgNO_3$ solution, and shaking the mixture several times. Collect the solid on a filter paper (see Appendix IE), and dry it by pressing between dry filter papers. Prepare a saturated solution by

¹ If chloride is present it may be removed from the $NaAc$ solution by adding some $AgNO_3$ solution, shaking the mixture, and filtering off the precipitated $AgCl$. The resulting solution contains some $NaNO_3$ and should be used only in this Assignment.

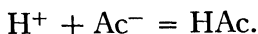
shaking the solid with 10 cc. of water at intervals for about 10 minutes. (The saturated solution can be prepared somewhat more conveniently by warming the mixture to 40 or 50°, but it must be cooled to room temperature before continuing the experiment.) Allow the solid to settle. Pour half of the clear saturated solution into another test-tube and set it aside for later use, Paragraph 7. To the remaining mixture of solid and saturated solution add 6 *N* HNO₃ drop by drop, shaking the mixture after each drop is added. When the silver acetate has dissolved, heat the solution nearly to boiling and note the odor.

Note. Place all silver residues, including any solutions which contain an appreciable amount of silver, in the jar marked "Silver Waste."

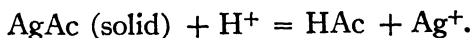
6. The disappearance of solid silver acetate on the addition of a strong acid may be considered to be due to a shifting of the equilibrium



as a result of the establishment of the second equilibrium



When a drop of nitric acid is added the H⁺ converts some Ac⁻ to HAc; in order to again build up the concentration of Ac⁻, and thus restore equilibrium, some solid AgAc goes into solution. When more HNO₃ is added the same processes are repeated, until finally all the silver acetate is dissolved. From this discussion of the "mechanism" of the reaction it is evident that the result of the experiment could have been predicted from the fact that acetic acid is a weak acid. The principal substances that have disappeared are solid AgAc and H⁺, and those that have formed are Ag⁺ and HAc; and we may, therefore, write for the "net reaction" the equation:



The same equation is obtained by adding together the two equations considered in discussing the mechanism of the reaction. It is important, however, to realize that in such a case as this no single equation can represent all that has happened in the reaction. Thus, the concentration of Ac^- , although small throughout the experiment, is much smaller in the final solution than in the initial AgAc solution; this small decrease is due to the reaction $\text{H}^+ + \text{Ac}^- = \text{HAc}$, but is not taken into consideration in the equation which we have written for the net reaction.

7. Predict what will happen when sodium acetate is added to a saturated solution of silver acetate. **Experiment.** Test your answer by adding a small amount of chloride free 4 *N* NaAc to the clear saturated solution of silver acetate which you have just prepared. **Questions.** How does this experiment illustrate the general statement in Paragraph 3? Re-word that statement to make it apply specifically to the change of solubility of a salt when the concentration of one of the ions of the salt is changed. What will happen when solid silver nitrate is added to a saturated solution of silver acetate?

8. **Problems.** (1) For each of the following reactions:

- (a) H_2O (liquid) = H_2O (gas)
- (b) H_2O (solid) = H_2O (liquid)
- (c) NH_3 (in solution) = NH_3 (gas)
- (d) $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$ (solid) (**Note.** The solubility of AgCl is 1.0×10^{-5} moles per liter)

outline an experiment to show that the reaction can take place as written and a second experiment to show that the reverse reaction can also take place.

(2) In each case in Problem (1) point out the conditions under which equilibrium can be realized. A satisfactory answer in (a) is the following: whenever water and water-vapor are present together in a closed vessel equilibrium is quickly established, and remains unchanged as long as the

temperature remains constant; when the closed vessel contains only water and water-vapor, the pressure at equilibrium is 1 atmosphere when the temperature is 100° ; cf. Assignment 2, Paragraph 10, for the pressure of water-vapor at room temperature.

(3) Give an example of a reaction which can be shown to be reversible at high temperature, but which proceeds so slowly at room temperature that equilibrium will not be realized in several months. Note that all the substances involved in this reaction can exist together at room temperature but that such a fact does not constitute a proof that equilibrium has been established.

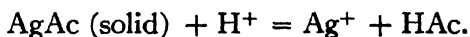
(4) From your table in Assignment 22, Paragraph 10, state what fraction of the acetic acid is ionized in the 0.1 *N* and 0.01 *N* solutions. What reaction takes place when 1 liter of 0.1 *N* solution is diluted to 10 liters of 0.01 *N* solution?

(5) State how the experimental result in Problem (4) could have been predicted from **kinetic** considerations, on the assumption that the two opposing reactions, $\text{HAc} = \text{H}^+ + \text{Ac}^-$ and $\text{H}^+ + \text{Ac}^- = \text{HAc}$, are actually taking place at equilibrium.

(6) When one of the substances involved in an equilibrium is a solid, what is the effect of adding more of this solid to an equilibrium mixture? Does the solubility of a salt at room temperature depend on the amount of the salt in contact with the saturated solution? Give another example of a reversible reaction involving a solid substance.

(7) *If the solubility product of silver acetate at a given temperature is 3.6×10^{-3} , what would be the concentration of Ac^- in equilibrium with solid AgAc when the concentration of Ag^+ is 0.1 *M*?

(8) *From the ionization constant of HAc and the solubility product of AgAc , calculate the constant for the equilibrium



(9) *If the concentrations of HAc and H^+ are 1 M and 10^{-3} M , respectively, in a solution in equilibrium with AgAc, what is the concentration of Ag^+ ?

(10) *The solubility of XI_2 at a given temperature is 2×10^{-6} M . Calculate the solubility product.

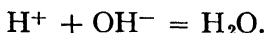
(11) *If the K for the ionization of HSO_4^- is 1.2×10^{-2} , what value would you calculate for the concentration of H^+ in a 0.1 M solution of $KHSO_4$?

Assignment 24

The Equilibrium between Hydrogen Ion, Hydroxide Ion, and Water. Use of Indicators, Continued. Weak Bases

Special Material: Standardized solutions, 1 *N* and 0.001 *N* HCl, 1 *N* and 0.001 *N* NaOH. Solutions of "unknown" H^+ concentration; the student will supply three clean sample bottles labelled A, B, and C.

1. We have seen that the neutralization reaction between strong acids and strong bases in aqueous solution is simply



The reaction, however, does not proceed quite to completion but stops when the concentrations of the hydrogen ion and hydroxide ion are each 10^{-7} moles per liter. The reaction is rapid and reversible and 10^{-7} *M* is merely the equilibrium concentration of the ions for the special case in which their concentrations are equal, as in pure water. The general relation at the equilibrium is

$$C_{H^+} \times C_{OH^-} = 1.0 \times 10^{-14} \text{ (at } 25^\circ \text{ C.)}.$$

This is the equilibrium constant for the ionization of water, $H_2O = H^+ + OH^-$. It is therefore possible to calculate the concentration of one of these ions in an aqueous solution when the concentration of the other is known. **Question.** What is the concentration of H^+ (a) in 1 *N* NaOH, (b) in 0.005 *N* NaOH?

2. In Assignment 22 it was found possible to measure the

concentration of hydrogen ion by means of indicators. It is desired now to extend the use of indicators to much lower concentrations of H^+ , i. e., to strongly alkaline solutions. While any weak acid differing in color from its salt may be used as an indicator, the following are especially useful, and cover the range between $1\ N\ H^+$ and $10^{-14}\ N\ H^+$.

INDICATOR	USEFUL H^+ RANGE, NORMALITY
Methyl violet.....	$1-10^{-3}$
Methyl orange.....	$10^{-3}-10^{-5}$
Bromphenol blue.....	$10^{-3}-10^{-5}$
Bromcresol green.....	$10^{-4}-10^{-6}$
Bromthymol blue.....	$10^{-6}-5 \times 10^{-8}$
Cresol red.....	$10^{-7}-10^{-9}$
Phenolphthalein.....	$10^{-8}-10^{-10}$
Alizarin yellow R.....	$10^{-10}-10^{-12}$
Indigocarmine.....	$10^{-11}-10^{-14}$

3. The concentration of H^+ in equilibrium with a mixture of an acid HX and its ion X^- is determined by the ionization constant, K , of the acid:

$$C_{H^+} = K \frac{C_{HX}}{C_{X^-}}$$

If the ratio C_{HX}/C_{X^-} is one, the molar concentration of H^+ is equal to the value of K . Moreover, to a solution in which this ratio is one, moderate quantities of acid or base may be added without greatly changing the H^+ concentration. Thus for a solution containing $1\ M\ HAc$ and $1\ M\ Ac^-$, the addition of enough OH^- to make the solution $0.9\ M\ HAc$ and $1.1\ M\ Ac^-$ only changes the concentration of H^+ from K to $0.9\ K/1.1$ or $0.82\ K$, i. e., from 1.8×10^{-5} to 1.47×10^{-5} . Such a solution is known as a **buffer solution**. Buffer solutions are commonly used when it is wished to maintain the H^+ concentration at a fixed value. In the following experiments a number of buffer solutions will be employed as standards of known H^+ concentration.

4. Prepare a table to summarize your results with the

various indicators as follows. To the left of the page list in a vertical column the indicators named in Paragraph 2. List across the top of the table every ten-fold concentration of H^+ between 1 N and 10^{-14} N . Enter in this table the colors obtained with the indicators in Assignment 22 and in the following experiments.

5. Experiment. Two students may carry out this experiment together. Heat 200 cc. of distilled water in a pyrex flask to boiling, and then cool it. (**Note.** Ordinary distilled water contains sufficient carbon dioxide to give a H^+ concentration of 10^{-5} or 10^{-6} N . This may be removed by boiling, but prolonged boiling should be avoided because enough glass will dissolve to give a distinctly alkaline reaction.) Prepare a set of solutions, covering the concentration range from 1 N to 10^{-4} N H^+ by diluting the standardized (1 N and 0.001 N) HCl solutions with boiled distilled water. Prepare solutions covering the range from 10^{-10} N to 10^{-14} N H^+ by diluting the standardized $NaOH$ solutions with boiled distilled water. Make each ten-fold dilution by measuring a definite volume (say 5 cc.) of a known solution in your graduated cylinder and adding water to the required volume. To ensure mixing, pour the solution into a clean flask, wash out the graduated cylinder with the solution, and stir the mixture in the flask. Store the solutions in labelled flasks or test-tubes, which first have been rinsed with a few cc. of the solutions. Solutions covering the concentration range from 10^{-5} N to 10^{-9} N cannot be prepared satisfactorily by diluting more concentrated solutions of acid or base. As standard solutions in this concentration range, use the buffer solutions which are provided.

For each indicator determine its colors in the H^+ range given in Paragraph 2. In each experiment with an indicator use 5 cc. of solution and 2 drops of indicator. Show your table to the instructor.

6. Analyses 24-A and B. Determine the concentration of H^+ in each of the solutions. Make your first test with

bromthymol blue. **Show** the written report of your experimental results and conclusions to your instructor.

7. Ammonium hydroxide as an example of a weak base.

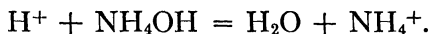
In the next experiment we shall determine the concentration of OH^- in solutions of the weak base, ammonium hydroxide, NH_4OH . The laboratory reagent, cf. Assignment 7, Problem (3), is prepared by dissolving ammonia gas, NH_3 , in water until the solution is nearly saturated with NH_3 at room temperature. Write the equation for the formation of ammonium hydroxide from ammonia and water.

8. Experiment. From the laboratory 6 *N* NH_4OH solution prepare solutions which are approximately *N*, 0.1 *N*, 0.01 *N*, and 0.001 *N*. By experiments with the indicators suitable for high OH^- concentrations (write out the details of these experiments in your note book) estimate the concentration of OH^- in at least two of these solutions. In each case give also the concentration of NH_4^+ and of unionized NH_4OH , and calculate the degree of ionization. **Note.** The degree of ionization of NH_4OH is almost the same as that of acetic acid.

9. The reaction between ammonium chloride and sodium hydroxide solutions. Predict what will happen when a solution of ammonium chloride is added to a solution of sodium hydroxide; cf. Assignment 22, Paragraphs 11 and 12. Plan an experiment to demonstrate this result and try the **experiment**. Write the equation for the net reaction.

10. The neutralization of sulfuric acid by ammonium hydroxide. Experiment. To 10 cc. of 6 *N* H_2SO_4 in a flask add 6 *N* NH_4OH from a graduate until the solution, after shaking, has a distinct odor of NH_3 . Evaporate in a porcelain dish until a considerable quantity of salt has separated, cool the mixture, collect some of the salt, and dry it between filter papers. Prove that the salt contains (a) sulfate, by dissolving some of it in water and adding barium chloride (to precipitate BaSO_4), and (b) the ammonium radical, by warming with sodium hydroxide solution and noting the

odor of NH_3 . Give the experimental evidence and reasoning in favor of the conclusions that, when solutions of a strong acid and ammonium hydroxide solutions are mixed, the net reaction is:



This study will be continued in Assignment 25.

11. Analysis 24-C. Determination of the ionization constant of a weak acid. From the discussion in Paragraph 3, it is evident that the ionization constant of a weak acid can be determined by measuring the H^+ concentration of a solution containing equal amounts of the acid and its ion. **Experiment.** Dissolve about 1 gram of Unknown 24-C in about 100 cc. of distilled water. (These amounts need not be measured precisely.) Titrate the resulting solution with 1.00 *N* NaOH to the phenolphthalein end-point, note exactly the volume of NaOH used in the titration, and add exactly one-half that volume of 1.00 *N* HCl. With the aid of suitable indicators, determine the concentration of H^+ in the solution you have prepared. Report the ionization constant of your weak acid.

12. Problems. (1) How many (a) moles, (b) equivalents of ammonium sulfate are in 100 cc. of 6 *N* NH_4OH ?

(2) Solutions containing 0.02 mole of NH_4Cl and 0.10 mole of NaOH are mixed. Calculate the quantities of the principal substances present, and their concentrations when the final volume of the solution is 200 cc.

(3) Outline two experimental methods of distinguishing between: 1.0 *N* NaOH and 0.1 *N* NaOH.

(4) Estimate the concentration of an ammonium hydroxide solution which gives an orange color with the indicator, alizarine yellow R.

(5) *The ionization constant of NH_4OH is 1.81×10^{-5} . Calculate the concentration of OH^- in (a) 0.01 *M* NH_4OH , (b) a solution containing 1 mole of NH_4OH and 1 mole of NH_4Cl in a liter.

Assignment 25

The Reversibility of Neutralization Reactions. Hydrolysis

1. In earlier Assignments we have studied various examples of neutralization reactions and have shown that the net reactions which take place are represented by the following equations:

- (a) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ when a strong acid reacts with a strong base.
- (b) $\text{HA} + \text{OH}^- = \text{H}_2\text{O} + \text{A}^-$ when a weak acid reacts with a strong base.
- (c) $\text{H}^+ + \text{BOH} = \text{H}_2\text{O} + \text{B}^+$ when a strong acid reacts with a weak base.

In the present Assignment we shall find that these reactions are reversible and we shall study the equilibrium that is established in each case. When the Assignment is finished the student should be able, from a knowledge of the relative strengths of various acids, and of various bases, to predict the approximate concentrations of the various substances at equilibrium in any given neutralization reaction.

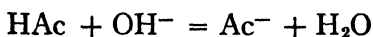
2. We wish to examine experimentally the properties of the solution that is obtained when equivalent amounts of a given acid and base react. To do this we shall take advantage of the fact that a solution of a pure salt is identical with the solution prepared by mixing exactly equivalent amounts of the corresponding acid and base. In other words we shall make use of the reaction which is the reverse

of neutralization in establishing the equilibrium state that we desire to study. The experimental work will consist in determining by means of indicators the approximate concentration of H^+ or OH^- in solutions of various salts. **Note.** In the following experiments it is important that all test-tubes should be clean, and that freshly boiled distilled water be used.

3. **Experiment.** Test 5 cc. portions of 1 *N* NaCl solution and distilled water by adding to each the same number of drops of bromthymol blue. **Questions.** What conclusions can you draw with regard to the relative concentrations of H^+ or OH^- in sodium chloride solution and in water? Write again the equation for the net reaction in the neutralization of NaOH by HCl solutions, and state whether the Na^+ and Cl^- are involved in the reaction. What are the concentrations of Na^+ , Cl^- , H^+ , and OH^- in the solution made (a) by dissolving 1 mole of NaCl in water to give a liter of solution, and (b) by dissolving exactly 1 mole of HCl and 1 mole of NaOH to give a liter of solution?

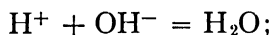
4. **Experiment.** Estimate approximately the concentration of OH^- in the 1 *N* NaAc solution using one or more of the indicators studied in Assignment 24. **Questions.** Is the concentration of OH^- in 1 *N* NaAc solution greater or less than in pure water? From the fact that the solution must be identical with that obtained by mixing exactly equivalent amounts of acetic acid and sodium hydroxide, what conclusions can you draw with regard to the completeness of the neutralization reaction between HAc and OH^- ? To account for the formation of OH^- when NaAc is dissolved in water, what reaction must take place? What are the approximate concentrations of Na^+ , Ac^- , HAc, and OH^- in the 1 *N* NaAc solution?

5. It will be observed that the net reaction which accounts for the neutralization of HAc by NaOH,

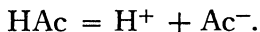


or the reverse of this reaction considered in the preceding paragraph, involves the disappearance of one weak electrolyte and the formation of another. Both the OH^- and the Ac^- are competing for the H^+ . From the fact that water is a far weaker electrolyte than acetic acid, it could have been predicted that when equilibrium is reached the OH^- will have taken nearly all the H^+ away from the Ac^- ; i. e., the concentration of the HAc and OH^- will be very small and that of the Ac^- very large. **Question.** From your table of the concentrations of H^+ in acetic acid solutions, Assignment 22, what is the ratio of the concentration of H^+ in normal acetic acid to that in pure water?

6. As indicated in the preceding paragraph, this neutralization reaction may be considered to have a mechanism parallel to that of the dissolving of silver acetate in a solution of a strong acid, Assignment 23. When an acetic acid solution is neutralized by NaOH solution, the OH^- may unite with H^+ which is present at small concentration in the acetic acid solution:



then, in order to restore equilibrium again, the HAc dissociates,



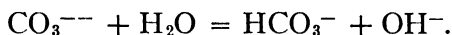
These two reactions continue to take place simultaneously until equilibrium is established. The sum of the two gives the equation which we wrote for the net reaction. **Note.** Strictly speaking the net reaction accounts for only about 99 per cent of the neutralization, the remaining 1 per cent being the reaction $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$.

7. Discuss in a similar way the mechanism of the reaction between Ac^- and H_2O which takes place when sodium acetate is dissolved in water. This, of course, involves the reverse of the two reactions written in Paragraph 6. Write the equation for the net reaction in this case.

8. The reaction which is the reverse of neutralization is called **hydrolysis**. In the reaction which we have just considered a small amount of the acetate ion is said to be **hydrolyzed**. **Question**. Why would you expect the Ac^- to be hydrolyzed slightly when the Cl^- is not hydrolyzed at all?

9. The dissociation of HCO_3^- , bicarbonate ion, into H^+ and carbonate ion, CO_3^{--} , is far less than the dissociation of acetic acid. **Questions**. What reaction would you expect to take place between CO_3^{--} and H_2O when Na_2CO_3 is dissolved in water? Which would you expect to be the more basic, a solution of Na_2CO_3 or a solution of NaAc of the same concentration? Test your answer by the following experiment.

10. **Experiment**. Estimate the approximate concentration of OH^- in a 0.5 *M* Na_2CO_3 solution by testing 5 cc. portions with suitable indicators. The net reaction for the hydrolysis of CO_3^{--} is



Questions. What would be the concentration of OH^- if the CO_3^{--} were completely hydrolyzed? What fraction of the CO_3^{--} is actually hydrolyzed? What are the approximate concentrations in moles per liter of Na^+ , CO_3^{--} , HCO_3^- , and OH^- in a solution prepared by dissolving 0.5 mole of NaHCO_3 and 0.5 mole of NaOH to give 1 liter of solution?

11. **Experiment**. Estimate the concentration of H^+ in 1 *N* NH_4Cl . **Questions**. How do you account for the fact that a solution of NH_4Cl is slightly acid while that of NaAc is slightly basic? Write the net reaction for the hydrolysis of the NH_4^+ , and the two reactions which may be used to explain the mechanism of the reaction. What is the concentration of each of the principal substances present in a solution made by dissolving 1 mole of HCl and 1 mole of NH_4OH to form a liter of solution?

12. Summarize your results for the sodium acetate, so-

dium carbonate, and ammonium chloride solutions and show them to your instructor.

13. Problems. (1) From the results of the experiments in this Assignment and your table of indicators select one or more indicators which might be used to determine the end-point (i. e., to determine when equivalent amounts of acid and base are present) in each of the following titrations:

- (a) NaOH solution with HCl or HNO_3 solution.
- (b) HAc solution with NaOH solution.
- (c) NaHCO_3 solution with NaOH solution.
- (d) NH_4OH solution with HCl solution.

(2) An ammonium acetate solution gives the same colors with indicators as does water: What hydrolysis reactions must occur when solid NH_4Ac is dissolved in water? State what substances are present in the solution.

(3) Point out the relation between the strength of acids and the hydrolysis of their negative ions; also that between the strength of bases and the hydrolysis of their positive ions.

(4) *The ionization constant of acetic acid is 1.8×10^{-5} . From this value and the ionization constant of water, calculate the hydrolysis constant of Ac^- . Calculate the concentration of OH^- in 1 *M* NaAc.

(5) *The ionization constant of hydrocyanic acid is 2×10^{-9} . Repeat the calculations of Problem (4) for CN^- and 1 *M* NaCN.

(6) *The ionization constants for HAc and NH_4OH are very closely the same 1.8×10^{-5} . Calculate the constant for the hydrolysis of NH_4Ac , i. e., $\text{NH}_4^+ + \text{Ac}^-$.

(7) *Calculate the concentration of H^+ in 1 *M* (a) NH_4Cl , (b) $\text{N}_2\text{H}_5\text{Cl}$. The ionization constant for the weak base hydrazine, $\text{N}_2\text{H}_5\text{OH}$, is 1.2×10^{-8} .

Assignment 26

A Quantitative Study of the Solubility Product. The Solubility of Potassium Perchlorate in Water and Potassium Chloride Solution

Special Material: Three 125 cc. flasks, 3 small evaporating dishes with watch-glasses, 25 cc. pipette, powdered potassium perchlorate.

1. In Assignment 23 we studied qualitatively the change in the solubility of silver acetate that occurs when the concentration of one of the ions in a saturated solution of the salt is altered. We shall now take up the quantitative treatment of the solubility of another uni-univalent salt as an illustration of the **solubility product law**, that the product of the concentrations of the ions in a saturated solution is constant.

2. The procedure will consist in the determination of the solubility of potassium perchlorate in pure water and in 0.05 *M* and 0.1 *M* KCl.

3. **Experiment.** Place in three flasks of about 125 cc. capacity, 50 cc. each of water, 0.05 *M* KCl, and 0.1 *M* KCl. Label the flasks. Obtain about 15 g. of powdered potassium perchlorate and place one-third of this in each flask. Heat the solutions to the boiling point, place them in a pan of water, and shake at intervals while cooling. About half an hour will suffice to establish temperature equilibrium between the three flasks and the water of the bath.

4. While the flasks are cooling obtain three small porce-

lain evaporating dishes and watch-glass covers. Number with ink, heat and accurately weigh each dish with its cover. When the solutions in the flasks have cooled, record the temperature of the water bath, pipette out 25 cc. of each solution (free from solid), and place the sample in one of the three dishes. Before pipetting each solution wash the pipette with the solution to be used by drawing a little of the solution into the pipette and rinsing with this. Now place the loosely covered evaporating dishes on a sand bath and heat sufficiently to boil the liquid slowly. After the solutions have evaporated raise the temperature slightly to drive off the last traces of moisture. Cool and weigh.

5. Subtract the calculated weights of potassium chloride in the various solutions to obtain the solubility of potassium perchlorate in grams per 25 cc. Calculate the solubility in moles per liter for each of the three solutions. From your value for the solubility in pure water, calculate the solubility product, i. e.,

$$C_{K^+} \times C_{ClO_4^-} = K,$$

assuming complete dissociation of the salt. Using this value for the constant, calculate the solubility of the potassium perchlorate in the 0.05 *M* and 0.1 *M* KCl. Compare the calculated results with your experimental values.

6. In these calculations it has been assumed that the actual **activities** of the ions are equal to their concentrations. For a discussion of the error involved in this assumption see LH, Appendix IV. In the case of potassium perchlorate the actual activity in the saturated solution at 25° C. is 70 per cent of the concentration.

7. **Problems.** (1) Write the solubility product expression for $Ba(OH)_2$, and calculate the constant from its solubility in water [cf. Assignment 21, Problem (3)].

(2) What weight of $Ba(OH)_2$ would be lost if a quantity of this substance were washed with 100 cc. of 1.0 *N* NaOH?

Assignment 27

Carbonate Ion, Bicarbonate Ion, and Carbonic Acid

Special Material: Two-holed rubber stoppers to fit a half-liter flask and a small flask, two pieces of rubber tubing, thistle tube. Hard-glass test-tube with a one-holed rubber stopper.

1. This Assignment, in which we shall study the chemistry of carbonic acid and its ions, is introduced, not only because this subject is an extremely important one, but also because it serves to illustrate how a large number of facts can be correlated when the equilibria involved in a few simple, reversible reactions are understood. Carbonic acid, H_2CO_3 , is a **weak, dibasic acid**; and, like other weak acids which contain more than one acidic hydrogen in the molecule, it ionizes in steps, to form (1) bicarbonate ion, HCO_3^- , and (2) carbonate ion, CO_3^{--} , thus:

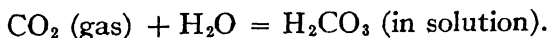


In order to understand what happens in the various reactions considered, it is necessary to know the relative concentrations, in the initial and final solutions, of the substances involved in these two rapid reversible reactions. Our problem, then, is to determine how the concentrations of H^+ (or OH^-), H_2CO_3 , HCO_3^- , and CO_3^{--} at equilibrium in a solution vary as the experimental conditions are changed.

2. **Preparation and properties of carbon dioxide. Experiment.** Make a carbon dioxide generator by fitting your half-liter flask with the thistle tube (passing through the stopper nearly to the bottom of the flask), and an outlet tube bent at right angles. Make a wash-bottle for washing the CO_2 gas by equipping a small flask with an entry tube extending nearly to the bottom of the flask, and a delivery tube. Fill the small flask about half full of water. Place in the generator a few lumps (about 5 grams) of limestone, cover with water, and add hydrochloric acid, a little at a time, through the thistle tube.

3. Note the color and the odor of the gas. Calculate from the molecular weights the relative densities of carbon dioxide and oxygen, and of carbon dioxide and nitrogen, at the same temperature and pressure. **Question.** Is carbon dioxide denser or lighter than air? **Experiment.** Collect some carbon dioxide in a test-tube by displacement of air; and determine if it is inflammable, and if it supports combustion.

4. Suggest an experiment to prove that carbon dioxide is moderately soluble in water at room temperature. Try the **experiment**. When CO_2 dissolves in water the reaction is



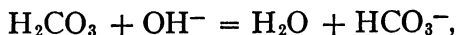
What evidence have you that the reverse reaction can take place? Under what conditions is there an equilibrium? **Note.** At room temperature a solution in equilibrium with CO_2 gas at 1 atmosphere pressure contains about 0.04 moles H_2CO_3 in 1 liter. **Question.** How is this equilibrium altered by an increase of temperature?

5. We shall now consider what the principal substances are in a saturated carbonic acid solution. **Experiment.** Prepare a small quantity of nearly saturated solution of CO_2 and test it with the indicators, which are suitable for the range 10^{-2} — 10^{-5} N hydrogen ion; for comparison repeat indicator tests with water and with an acid solution of

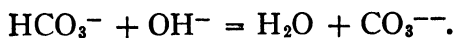
known H^+ concentration. What conclusion can you draw with regard to the concentration of H^+ in the saturated CO_2 solution? **Note.** The concentration of H^+ in this solution has been determined by other methods to be about $0.0001\ N$ ($10^{-4}\ N$). From this value for the concentration of H^+ , calculate the concentration of OH^- in the same solution (cf. Assignment 24).

6. **Experiment.** Test the action of carbonic acid on Ca^{++} by passing CO_2 gas into a dilute solution of $CaCl_2$. Since calcium carbonate is slightly soluble (the solubility product, $C_{Ca^{++}}C_{CO_3^{--}} = 4.8 \times 10^{-9}$), what conclusion can you now draw with regard to the concentration of CO_3^{--} in carbonic acid solution? The concentration of CO_3^{--} in the $0.04\ M$ H_2CO_3 solution has been found by other methods to be of the same order of magnitude as that of OH^- . **Questions.** Making use of the fact that the only ions in this solution are produced by the ionization of H_2CO_3 (and H_2O), what conclusion can you draw with regard to the extent to which each of the reactions (1) and (2), Paragraph 1, has taken place in a solution of carbonic acid? What is the approximate concentration of HCO_3^- in the $0.04\ M$ H_2CO_3 solution? List the substances present in this solution (*a*) at moderate concentration, (*b*) at small concentration (two substances), and (*c*) at extremely small concentration (two substances).

7. **The neutralization of carbonic acid.** When $NaOH$ solution is added gradually to a carbonic acid solution the neutralization of H_2CO_3 takes place in steps corresponding to the two steps in the dissociation of H_2CO_3 . The net reaction for the first step in the neutralization is



and the solution made from equal molal quantities of H_2CO_3 and $NaOH$ is a sodium bicarbonate solution. The second step in the neutralization of H_2CO_3 is



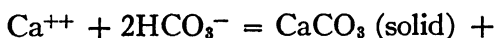
This is the reaction for the neutralization of HCO_3^- by a strong base, and was considered in Assignment 25.

8. Substances present in a solution of sodium carbonate. Experiment. To 5 cc. of N (0.5 M) Na_2CO_3 add a somewhat greater volume of N CaCl_2 . The precipitation of the carbonate is practically complete (see solubility product, Paragraph 6). Write the equation for the net reaction. On the basis of this experiment predict the result of passing a small amount of CO_2 into a solution of Ca(OH)_2 . This reaction may be used as a **test for carbon dioxide**. Since BaCO_3 is also slightly soluble, Ba(OH)_2 solution may be used in place of Ca(OH)_2 .

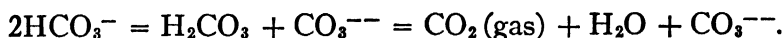
Review your notes, Assignment 25, on the relative concentrations of CO_3^{--} , HCO_3^- , and OH^- in a 0.5 M Na_2CO_3 solution; and calculate the concentration of H^+ in this solution. The concentration of H_2CO_3 in this solution is also extremely small, but of course is greater than the concentration of H^+ . **Questions.** How would you prepare 1 mole of solid Na_2CO_3 from 1 mole of NaHCO_3 , and also from 1 mole of H_2CO_3 ? What quantity of NaOH would be required in each case? List the substances which are present in a solution of Na_2CO_3 , (a) at moderate (or high) concentration, (b) at relatively small concentration (two substances), and (c) at extremely small concentration (two substances).

9. Substances present in a solution of sodium bicarbonate. Since HCO_3^- is a weak acid, the principal substances in a solution of NaHCO_3 are Na^+ and HCO_3^- . Noting that the substance HCO_3^- is intermediate in composition between H_2CO_3 and CO_3^{--} , and considering the equilibria involved, would you expect the concentration of CO_3^{--} in a solution of NaHCO_3 to be greater or less than in a solution of (a) H_2CO_3 , (b) Na_2CO_3 ? The following experiment, on the precipitation of CaCO_3 by NaHCO_3 solution at room temperature, furnishes evidence with regard to the concentration of CO_3^{--} in this solution, but it should be remembered that more CaCO_3 is precipitated than corresponds to

the actual concentration of the CO_3^{--} since on account of the displacement of equilibrium some more CO_3^{--} forms as the CaCO_3 is precipitated. **Experiment.** To 10 cc. of M NaHCO_3 in a flask add about 50 cc. of water, and 10 cc. of N CaCl_2 ; shake the mixture. Filter and note the amount of the CaCO_3 precipitate. Heat the filtrate to boiling, and test the gas evolved by passing it into a clear solution of Ca(OH)_2 or Ba(OH)_2 (cf. Paragraph 8). Compare the amount of the precipitate now obtained with that formed in the cold solution. Complete the following equation:



and suggest an explanation for the shifting of the equilibrium when the mixture is heated to boiling. The reaction that takes place when a solution of NaHCO_3 is heated to boiling is



Questions. How will the concentrations of H_2CO_3 and CO_3^{--} in a NaHCO_3 solution be changed (1) when the solution is boiled, and (2) when CaCl_2 solution is added at room temperature? What conclusions can you draw with regard to the relative concentrations of HCO_3^- and either H_2CO_3 or CO_3^{--} in a freshly prepared, cold solution of NaHCO_3 ?

10. **Experiment.** Test a freshly prepared, approximately molal solution of NaHCO_3 with suitable indicators in order to estimate approximately the concentration of OH^- and H^+ in the solution. Repeat the experiment with a solution which has been heated to boiling, or which has been allowed to stand in the laboratory for several days. From your results in Paragraphs 9 and 10 state which substances are present in a pure NaHCO_3 solution, (a) at moderate (or high) concentration, (b) at relatively small concentration (two substances), and (c) at still smaller concentration (two substances).

11. Summarize in tabular form the lists referred to in the

last sentence of each of the three Paragraphs, 6, 10, and 8, arranging the columns in the order H_2CO_3 , NaHCO_3 , and Na_2CO_3 . Note the regular change in the concentration of each substance, e. g., H_2CO_3 , when the three solutions are considered in this order. **Show the table** to your instructor.

Question. What is the equation for the net reaction when 0.1 equivalent of strong acid is added to a solution containing (a) 0.1 mole of Na_2CO_3 , and (b) 0.05 mole of Na_2CO_3 ?

12. The decomposition of solid sodium bicarbonate. Experiment. Place about 1 g. of NaHCO_3 in a hard-glass test-tube and lead the delivery tube into a solution of $\text{Ba}(\text{OH})_2$, or of CaCl_2 and NH_4OH . Heat the tube until no more gas is given off, remove the delivery tube from the solution, and allow the hard-glass tube to cool. What is the evidence that CO_2 was formed? That water was formed? What must the residue be if H_2O and CO_2 are formed in equimolal quantities? (This experiment may be performed quantitatively by weighing the hard-glass tube (1) empty, (2) with NaHCO_3 , and (3) with the residue.)

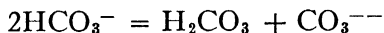
Experiment. Continued. Clean the delivery tube and lead it into a fresh solution of $\text{Ba}(\text{OH})_2$. Pour water carefully into the hard-glass tube until it is half full, but do not stir the mixture. Add 4 cc. of 6 *N* HCl , and at once insert the stopper. What is the gas evolved? Warm the mixture slowly by placing the hard-glass tube in a beaker of water and heating the latter. **Questions.** If the gas volumes had been measured, what would have been the ratio of the volumes in the two parts of the experiment? If all the CO_2 evolved had been converted into BaCO_3 , what would have been the relative amounts obtained in the two parts of the experiment?

13. Reaction between an acid and the negative ion of a weaker acid. Give examples of the action of a strong acid on a solution of the salt of a weak acid. **Experiment.** Determine the action of dilute acetic acid on NaHCO_3 . Which is the stronger acid, HAc or H_2CO_3 ? Taking into

consideration the fact that HCO_3^- , the negative ion of H_2CO_3 , is also a weak acid (whose ions are H^+ and CO_3^{--}), and the additional fact that H_2CO_3 is a stronger acid than HCO_3^- predict what will happen when H_2CO_3 is introduced into a solution of a carbonate.

14. **Experiment.** Test your answer to the last question by placing a small amount of freshly precipitated CaCO_3 in about 100 cc. of water and saturating the mixture with CO_2 . Filter off any CaCO_3 that remains and heat the filtrate to boiling.

15. Summarize all the evidence presented in this Assignment that the reaction



is reversible, noting especially the experimental conditions under which the reaction will proceed almost completely, (a) as written, and (b) in the reverse direction. **Question.** Suggest an explanation of the fact that the OH^- concentration in a pure bicarbonate solution is much less than would be predicted from the weakness of H_2CO_3 and the resulting hydrolysis. **Note.** This may be answered by writing the equation for the hydrolysis of HCO_3^- and considering how this equilibrium is affected by the neutralization reaction between one of the products and HCO_3^- . What is the net reaction?

16. **Problems.** (1) Predict what, if anything, would happen if the following substances were mixed at high concentrations at room temperature.

- | | |
|--|---|
| (a) H_2CO_3 and Ca^{++} | (f) HCO_3^- and H^+ |
| (b) H_2CO_3 and OH^- | (g) HCO_3^- and OH^- |
| (c) H_2CO_3 and CO_3^{--} | (h) HCO_3^- and CO_3^{--} |
| (d) H_2CO_3 and HCO_3^- | (i) CO_3^{--} and OH^- |
| (e) H_2CO_3 and H^+ | (j) Ca^{++} and HCO_3^- |

In case a reaction takes place, state whether it would proceed nearly to completion or would reach an equilibrium in

which the two reacting substances are present at moderate concentrations.

(2) What weight of Na_2CO_3 can be obtained from 8.4 g. of NaHCO_3 , (a) by heating, and (b) by treating the bicarbonate with NaOH solution? What is the least volume of N NaOH that can be used in (b)?

(3) What volume of CO_2 at standard conditions can be obtained from 8.4 g. of NaHCO_3 , (a) by heating, and (b) by treating the bicarbonate with HCl solution? What is the least volume of N HCl that can be used in (b)?

(4) When a current of CO_2 is passed into a solution of Ca(OH)_2 a precipitate is observed to form, and then dissolve. If the final solution is now heated to boiling, a precipitate again appears. State what has happened in this experiment, and write an equation for the net reaction in each of the stages.

(5) *The ionization constants for carbonic acid are $K_1 = 4.3 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. Calculate (a) C_{H^+} in 0.04 M H_2CO_3 , (b) $\text{C}_{\text{CO}_3^{--}}$ in 0.04 M H_2CO_3 , (c) C_{OH^-} in 1 M Na_2CO_3 .

Assignment 28

Oxides and Hydroxides of Metals, Solubility in Water, Hydrogen Ion, and Ammonium Ion. Amphoteric Hydroxides

1. The oxides of Group I and of the heavier elements of Group II react readily with water to form hydroxides which are soluble strong bases; i. e., their solutions contain hydroxide ion and the ions of the metals. The oxides of the non-metallic elements are soluble in water, with but few exceptions, to form acid solutions. This difference in behavior depends mainly upon the size and charge of the positive kernel or ion (cf. LH III).

The oxides of the remaining metals, in general, do not react with water; but compounds (hydrous oxides, hydrated oxides, or hydroxides) are usually formed when solutions of the positive ions are made alkaline. In a few cases the precipitate is the anhydrous oxide. When the precipitates consist of particles of the oxides with an indefinite amount of absorbed water they are called **hydrous oxides**, e. g., $\text{SnO}_2 \cdot x\text{H}_2\text{O}$. If there is a definite number of water molecules combined with the oxide, the name **hydrated oxide** is applied, e. g., $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. However, the hydrated oxides may absorb an indefinite amount of water to form gelatinous precipitates or hydrous hydrated oxides. In some cases the precipitate has a definite hydroxide structure, especially with ions having a +2 charge, e. g., $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ and these may be correctly called **hydroxides**.

If, as is often the case, additional absorbed water is present they may be referred to as hydrous hydroxides. The character of a hydrous precipitate varies with the method of preparation and changes upon ageing and drying. For the sake of simplicity, we shall often write the hydroxide formula without implying that this is correct.

2. The solubilities of the precipitated hydroxides or oxides vary greatly. In the more soluble class are: $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, Ag_2O , $\text{Mn}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, and $\text{Zn}(\text{OH})_2$. Members of this group dissolve readily in H^+ and their solubility is greatly increased in NH_4^+ solutions. Examples of less soluble hydroxides are: $\text{Cu}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ or AlOOH , and $\text{Fe}(\text{OH})_3$ (probably better written $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$). These compounds are soluble in excess of $0.1 M \text{H}^+$, and it is sometimes necessary to add some acid to solutions of the salts to prevent precipitation by hydrolysis. Manganese dioxide, MnO_2 , is an example of a class of oxides not appreciably soluble in $1 M \text{H}^+$. An equivalent statement is that Mn^{+4} is almost completely hydrolyzed in water.

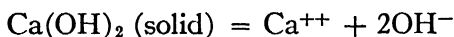
3. Many oxides or hydroxides exhibit both acidic and basic properties and are called **amphoteric**. In some cases, as for example zinc hydroxide, the two properties are about equal and the hydrated oxide dissolves readily in both acid and base. Often, however, one property predominates; for example, cupric hydroxide is very soluble in dilute acid and only slightly soluble even in $6 M \text{OH}^-$. Ferric hydroxide behaves similarly, while As_2O_3 is an amphoteric oxide which is more acidic than basic.

4. A number of examples of equilibria involving various types of hydroxides will be studied in this Assignment.

5. **Precipitation of hydroxides by OH^- . Experiment.** To 1 cc. of the laboratory solutions of each of the following, $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , and $\text{Fe}(\text{NO}_3)_3$, add 10 cc. of water and 5 cc. of $1 N \text{NaOH}$ (prepared by diluting the $6 N \text{NaOH}$). Record the color and character of the precipitates. The formulas of the solids are $\text{Cu}(\text{OH})_2$, Ag_2O , and $\text{Fe}(\text{OH})_3$.

(or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$). When the precipitates have settled decant the solutions and determine if the solids are soluble in hydrogen ion by adding 1 *N* HNO_3 . Write net reactions for both the precipitation and the solution in acid. Repeat the **experiment** with Cu^{++} but this time heat the solution almost to boiling before the addition of the NaOH . The precipitate is CuO . **Note.** The same results would be obtained by the addition of small amounts of NH_4OH to the solutions of the metal ions; however, with excess of NH_4OH the $\text{Cu}(\text{OH})_2$ and Ag_2O dissolve with the formation of complex ammonia ions (cf. Assignment 29).

6. **Calcium hydroxide.** If solid calcium hydroxide is shaken with water until a saturated solution is obtained an equilibrium between solid $\text{Ca}(\text{OH})_2$ and the ions Ca^{++} and OH^- is established. The equation for the reaction that has taken place is



The solubility of $\text{Ca}(\text{OH})_2$ at room temperature is 0.02 moles per liter. **Questions.** What is the concentration of calcium ion, of hydroxide ion, (1) in moles per liter, and (2) in equivalents per liter? Is the reaction just considered reversible? What solutions would you mix in order to prepare solid $\text{Ca}(\text{OH})_2$? Try the **experiment**.

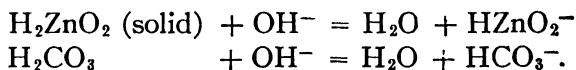
7. Which contains the larger concentration of OH^- , a saturated solution of $\text{Ca}(\text{OH})_2$ or 1 *N* NH_4OH (see Assignment 24)? State what you think will happen when a dilute solution of calcium chloride is made alkaline by adding a few drops of ammonium hydroxide. Try the **experiment**. Explain the result if your prediction was incorrect. **Note.** If the laboratory solution of ammonium hydroxide is contaminated with carbonate some CaCO_3 will precipitate.

8. State what would happen if a solution of calcium hydroxide were treated with (1) hydrochloric acid, (2) ammonium chloride. Predict what would happen if solid

$\text{Ca}(\text{OH})_2$ were also present in each case. **Experiment.** Test your answers by experiments.

9. **Magnesium hydroxide. Experiment.** Prepare three solutions containing Mg^{++} by mixing 1 cc. of 0.1 M $\text{Mg}(\text{NO}_3)_2$ and 10 cc. of water. Add to (1) 1 M NaOH , to (2) 1 M NH_4OH , and to (3) an equal mixture of 1 M NH_4OH and 1 M NH_4Cl . **Question.** From the results of these experiments what can you say regarding the relative concentrations of OH^- in (a) a saturated solution of $\text{Mg}(\text{OH})_2$, (b) 1 M NH_4OH , and (c) a solution made by mixing equal volumes of 1 M NH_4OH and 1 M NH_4Cl ? Predict what you would observe if solid $\text{Mg}(\text{OH})_2$ were treated with 1 M NH_4Cl solution. Write the equation for the net reaction. From the experiments on $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, what can you say regarding the relative solubilities of these two hydroxides?

10. **Zinc hydroxide. Experiment.** Prepare some $\text{Zn}(\text{OH})_2$ by treating a solution containing Zn^{++} with a very small amount of NaOH . Collect the $\text{Zn}(\text{OH})_2$ on a filter, treat a portion with a strong acid, and another portion with NaOH or KOH solution. Save the latter solution for use in Paragraph 11. **Question.** What evidence is furnished by this experiment that zinc hydroxide is an amphoteric substance? **Note.** The reaction between zinc hydroxide and excess OH^- is analogous to the first stage in the neutralization of carbonic acid:



The negative ion, HZnO_2^- , is usually called **zincate ion**, though strictly speaking this name should be reserved for the ion ZnO_2^{--} . The latter substance probably forms to some extent when the concentration of OH^- is very large. Solid NaHZnO_2 has not been prepared, but Na_2ZnO_2 can be made by fusing zinc oxide with NaOH .

11. Predict what will happen when a solution of a strong

acid is added slowly to sodium zincate solution. Test your answer.

12. Aluminum hydroxide. Experiment. To dilute solutions of $\text{Al}(\text{NO}_3)_3$ add very slowly (1) an excess of 1 *M* NH_4OH , (2) an excess of 1 *M* NaOH . The precipitate is hydrous AlOOH . Note its flocculent character. With excess NaOH , aluminate ion, AlO_2^- , is formed. **Question.** What can you say regarding the concentration of OH^- required to dissolve aluminum hydroxide? Predict the effect of adding solid ammonium nitrate to your solution of sodium aluminate. Verify your prediction by an **experiment**. Write equations for all net reactions.

13. Copper hydroxide. Experiment. Add some 6 *M* NaOH to a small volume of $\text{Cu}(\text{NO}_3)_2$ solution. The deep blue color is due to the formation of cuprate ion. Sodium cuprate, unlike the aluminate and zincate, is not very soluble. Ferric hydroxide is also somewhat acidic and dissolves appreciably in high concentration of OH^- .

14. Problems. (1) How could you prepare $\text{Cu}(\text{OH})_2$ from CuO ?

(2) What can you state regarding the relative acidity of solutions of $\text{Mg}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$.

(3) Both stannic and stannous hydroxides are amphoteric but the former is the stronger acid. Which would be more hydrolyzed, a solution of stannate or stannite?

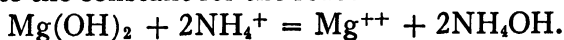
(4) Starting with ZnSO_4 , how could you prepare a solution containing sodium zincate which is free from sulfate?

(5) If solid $(\text{NH}_4)_2\text{SO}_4$ were heated with $\text{Ca}(\text{OH})_2$ solution would you be able to observe the odor of ammonia?

(6) Write the equation for the hydrolysis of Mn^{++} (cf. Paragraph 2).

(7) *A saturated solution of $\text{Mg}(\text{OH})_2$ is 1×10^{-4} *M*. Calculate the solubility product.

(8) *The dissociation constant of NH_4OH is 1.8×10^{-5} . Calculate the constant for the reaction



(9) *Calculate the concentration of Mg^{++} in equilibrium with the solid hydroxide in a solution containing 1 M NH_4^+ and 1 M NH_4OH .

(10) * XOH is very slightly soluble in water, but an acid solution in equilibrium with the solid contains 1 M X^+ when H^+ is 1 M . Calculate the solubility product of XOH .

Assignment 29

Ammonia Complex Ions

Reference. Hildebrand, Chapter XIII.

1. Copper, silver, and the neighboring elements in the periodic system form complex ions with ammonia. The formulas of the silver and cupric ammonia complexes are $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_4^{++}$. The "free pair" of electrons on the ammonia is shared with the positive ions to form a very stable bond. **Questions.** What are the elements which have atomic numbers one lower and one higher than copper and silver? Indicate from the electron structures of NH_3 and NH_4^+ why a complex may be formed by the ammonia molecule but not by the ammonium ion. Since the behavior of ammonium hydroxide as a reagent is of special importance, a few examples of equilibria involving the ammonia complex ions will be studied.

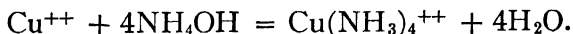
2. **Experiment.** Dilute 1 cc. of N CuSO_4 with 10 cc. of water and add two or three drops of $1 N$ NH_4OH , made by diluting the $6 N$ laboratory reagent. The precipitate is $\text{Cu}(\text{OH})_2$, or basic copper sulfate. **Note.** The concentration of Cu^{++} in a saturated solution of $\text{Cu}(\text{OH})_2$ is about $10^{-7} M$.

3. Continue to add the NH_4OH solution until, after shaking, the solution is clear. Observe the volume of NH_4OH used. What is the evidence that a new substance is formed? Compare the result with the experiment in Assignment 28, Paragraph 5, where 5 cc. of $1 N$ NaOH were

added. State the reasoning by which you may conclude that the substance obtained in the experiment with NH_4OH solution is not formed by a reaction between OH^- and $\text{Cu}(\text{OH})_2$ similar to that between OH^- and $\text{Zn}(\text{OH})_2$. Try an **experiment** with CuSO_4 solution and NH_4Cl in order to determine if Cu^{++} reacts with NH_4^+ in the same way as with NH_3 or NH_4OH .

4. The new substance formed when $\text{Cu}(\text{OH})_2$ dissolves in NH_4OH solution is $\text{Cu}(\text{NH}_3)_4^{++}$. The final solution contains NH_4OH , and OH^- must be present; it may therefore be concluded that the concentration of Cu^{++} is extremely small, since, otherwise, $\text{Cu}(\text{OH})_2$ would precipitate. **Questions.** Which solution has the greater concentration of Cu^{++} , a saturated solution of $\text{Cu}(\text{OH})_2$ or a solution of the complex ion containing NH_4OH ? How is the equilibrium between $\text{Cu}(\text{OH})_2$ and its saturated solution affected when NH_4OH is added?

5. The equation for the net reaction when a solution of a copper salt is treated with excess NH_4OH is



A simple method of demonstrating that the reverse reaction will take place is to remove the NH_4OH . Suggest two methods of doing this and try your methods.

6. **Experiments.** To a dilute solution of ZnSO_4 add NH_4OH solution drop by drop, shaking the mixture after each addition of NH_4OH , until the precipitate of zinc hydroxide which first forms is dissolved. The solubility of the hydroxide in excess of the reagent is due to the formation of the complex ion $\text{Zn}(\text{NH}_3)_4^{++}$. It may be shown by suitable experiments that the concentration of hydroxide ion in ammonium hydroxide is not sufficient to form zincate (compare the action of NaOH , Assignment 28, Paragraph 10).

7. Repeat the **experiment** of Paragraph 6 with a dilute solution of AgNO_3 . The precipitated oxide, Ag_2O , dissolves

in excess of the reagent with the formation of the complex ammonia ion, $\text{Ag}(\text{NH}_3)_2^+$. **Question.** Which solution has the greater concentration of Ag^+ , a saturated solution of Ag_2O or a solution of the complex ion containing excess of NH_4OH ?

8. Add nitric acid drop by drop to the solution of $\text{Ag}(\text{NH}_3)_2^+$ prepared in Paragraph 7 until the solution is acid. This is in a sense the reverse of the experiment of the last paragraph but it will be observed that no precipitate of Ag_2O forms in this case. The addition of H^+ , of course, produces NH_4^+ in the solution and the non-precipitation of the silver oxide may be explained by the solubility of the oxide in ammonium salts (cf. Assignment 28, Paragraphs 8 and 9). To a slighter degree the same effect may be observed with $\text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$. For example, if NH_4OH is added to a dilute CuSO_4 solution until the blue of the $\text{Cu}(\text{NH}_3)_4^{++}$ is present but some of the precipitate of $\text{Cu}(\text{OH})_2$ still remains, the addition of 4 *M* NH_4Cl to the solution will cause the precipitate to dissolve and the blue of the solution to deepen.



9. The experiments above have illustrated the solubility of certain hydroxides and oxides in ammonium hydroxide due to the greater stability of the complex ammonia ions. The following **experiment** is an example of the solubility of a slightly soluble salt in ammonia. Prepare some silver chloride by the addition of HCl to a dilute solution of AgNO_3 . The solubility of silver chloride is somewhat less than that of silver oxide. Treat the solid precipitate with excess 1 *N* NH_4OH . Acidify the resulting solution with nitric acid.

10. **Questions.** When AgCl is dissolved in excess NH_4OH solution, what is the principal positive ion, and the principal negative ion, in the resulting solution? When 0.1

mole of AgCl is dissolved and the final volume is 100 cc. what is the approximate concentration of each of these ions?

11. We shall next consider the action of NH_4OH solution on silver iodide, a salt which is much less soluble in water than either silver oxide or silver chloride. Solid AgI , suspended in water, is in equilibrium with Ag^+ and I^- in the saturated solution. When NH_4OH is added some Ag^+ must react with it to form $\text{Ag}(\text{NH}_3)_2^+$, and some solid AgI must dissolve to establish again the solubility equilibrium. We can therefore predict that AgI must be more soluble in NH_4OH solution than in water, but it is not safe to predict that a large amount of it will dissolve. **Experiment.** Prepare a solution of silver oxide or silver chloride in NH_4OH and add to this solution a few drops of 0.1 *N* potassium iodide solution. In another experiment collect some solid silver iodide on a filter paper, wash it with water, and treat it with 1 *N* NH_4OH solution. Devise and try an experiment with the solution thus prepared to determine whether an appreciable amount of AgI has dissolved.

12. Predict what will happen when silver chloride is treated with a solution of potassium iodide. Try the **experiment**.

13. When $\text{Cu}(\text{OH})_2$ is dissolved in excess NH_4OH solution, what is the principal negative ion in the final solution? **Note.** It is important to realize that $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$, and $\text{Ag}(\text{NH}_3)_2\text{OH}$ are soluble, fairly strong bases.

14. The ions of the alkali metals, as Na^+ , K^+ , etc.; those of the alkaline earth metals, as Ca^{++} , Sr^{++} , and Ba^{++} ; and many other positive ions do not combine with NH_3 to form complex ions. **Question.** Will a difficultly soluble salt, as CaCO_3 , dissolve in NH_4OH solution to a greater extent than in water?

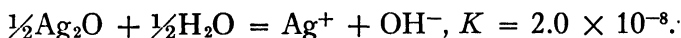
15. **Problems.** (1) Write equations for the net reactions in the following experiments:

- (a) A few drops of NH_4OH solution are added to a solution containing Zn^{++} .
- (b) Excess NH_4OH solution is added to a solution containing Zn^{++} .
- (c) An ammoniacal solution of silver chloride is acidified with nitric acid.

(2) The solubilities of AgCl and AgI in water are about 10^{-5} and 10^{-8} moles per liter, respectively. In two experiments with NH_4OH solution each substance is found to be ten thousand times more soluble than in water. How many grams of each have dissolved in 1 liter of the NH_4OH solutions?

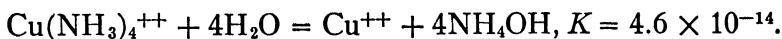
(3) Give two examples of complex ions other than those with ammonia.

(4) *The solubility product of Ag_2O is



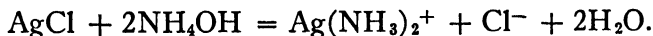
Calculate the concentration of OH^- in a saturated solution of the oxide in water.

(5) *The constant for the dissociation of the cupric ammonia complex ion is



What is the concentration of Cu^{++} in a solution which contains 0.1 M $\text{Cu}(\text{NH}_3)_4^{++}$ and 1 M NH_4OH ?

(6) *The solubility product of AgCl is 1.7×10^{-10} and the dissociation constant for $\text{Ag}(\text{NH}_3)_2^+$ is 6.0×10^{-8} . Calculate the constant for the reaction



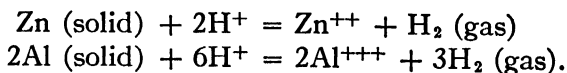
(7) *Calculate the corresponding constant for AgI which has a solubility product of 8.5×10^{-17} .

Assignment 30

Oxidation and Reduction. Replacement Reactions. Table of Oxidizing and Reducing Couples

Special Material: Fine copper wire, "quantitative" filter paper, 0.1 *N* silver nitrate solution. A two-holed rubber stopper to fit a small flask, thistle tube, clamp. Metallic lead, copper, and zinc.

1. In Assignment 30 we shall consider examples of **oxidation** and **reduction** reactions. In these reactions definite transfers of electrons from one substance to another occur and as a result new substances are formed in which there is a change in the **oxidation state** of the elements involved. These reactions are easily distinguished from other reactions such as the formation of weak electrolytes or the precipitation of slightly soluble salts in which there are no changes in oxidation states of the elements forming the compounds. In Assignment 4 we studied the reactions of certain metals such as zinc and aluminum with acids, the net reactions being:



Questions. Write under each term in the above equations the number which represents the oxidation state of each element. What numerical changes in the oxidation states occur in each reaction? Which elements have lost electrons and which have gained electrons? In each reaction, what

substance is (a) the **oxidizing agent** and (b) the **reducing agent**? Which substances have been oxidized and which reduced?

2. In the first of the above reactions the oxidation of Zn to Zn^{++} and the reduction of 2H^+ to H_2 consist simply in the transfer of two electrical charges from two hydrogen atoms to one zinc atom, which in reality is the transfer of two electrons from the zinc atom to the two hydrogen atoms. In the present Assignment we shall study a number of examples which are characterized by such an interchange of electrical charges. The reaction between copper and silver ion will first be studied quantitatively and then a number of other cases will be taken up qualitatively.

3. **Experiment.** Obtain at the office 110 cc. of 0.10 *N* silver nitrate, and a special filter paper which burns to give an ash of negligible weight. Clean a piece of fine copper wire and weigh about 0.3 g. to 5 mg. Cover the copper wire with 110 cc. of 0.10 *N* silver nitrate solution and let it stand until the copper has disappeared.¹ The precipitate formed is metallic silver. **Questions.** What substance is responsible for the color of the final solution? What is the color of silver ion? Heat a porcelain crucible, let it cool, and weigh to 5 mg. Collect the silver by filtering through the special filter paper and wash the precipitate until the washings are colorless. (Save the filtrate, and place in it another piece of copper in order to recover the rest of the silver.) Fold the filter paper so that it will fit into the crucible, heat with a small flame until it is dry, and then with a larger flame until the paper is completely consumed. Let the crucible cool and again weigh to 5 mg. Repeat the heating, cooling, and weighing until the weight is constant to 5 mg.

4. **Calculations.** Calculate (a) the weight of silver formed in the experiment; (b) the weight of silver precipitated by one gram atom of copper. Compare the latter number with the atomic weight of silver. What is the formula of cupric ion?

¹ While waiting proceed with Paragraph 6, etc.

5. **Questions.** Give the formulas of silver nitrate, silver sulfate, cupric nitrate, and cupric sulfate. If one gram molecule of silver ion has associated with it 96,500 coulombs of positive electricity what quantity of electricity is associated with one gram molecule of cupric ion? With a gram molecule of nitrate ion? Write the equation for the action of silver ion on copper. How would the result of this experiment have been influenced by replacing the silver nitrate with silver sulfate solution?

6. **Experiment.** Into 10 cc. of N $\text{Cu}(\text{NO}_3)_2$ place a piece of lead.

7. Repeat the **experiment** with a solution of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, and zinc.

8. Write the equations for all the reactions between metals and positive ions which you have studied in Paragraphs 3, 6, and 7. **Questions.** The negative ion present in each experiment is not shown in the equation; what experimental fact is thereby implied? If in one of the above experiments the dry salt had been used instead of its solution, would the reaction occur sufficiently rapidly at room temperature to be detected? Try an experiment, if necessary, with lead and solid copper sulfate.

9. **Experiment.** Determine by experiment which of the metals used in this Assignment will dissolve readily in dilute hydrochloric acid (or sulfuric acid).

10. Arrange the metals used in these experiments in the order in which they will replace each other from solution. After referring to your lecture notes state where hydrogen belongs in this **replacement series**. From this replacement series predict what will happen when:

Silver nitrate solution	is treated with lead,
Copper nitrate	“ “ “ “ zinc,
Copper nitrate	“ “ “ “ silver.

Experiment. Test the correctness of your predictions.

11. Now rewrite the series in the same order, substituting

in each case the equation for the **half-reaction**: element equals ion plus electron, e. g., $\text{Cu} = \text{Cu}^{++} + 2e^-$. Your table is now a **table of oxidizing and reducing couples** and this table may be extended to include not merely positive elements and their ions but all substances which undergo oxidation and reduction (LH Appendix II). Note that in your table, as now arranged, the reduced form of each couple may be oxidized by the oxidized form of any couple below it, e. g., Zn is oxidized by H^+ , Cu^{++} , and Ag^+ . **Questions.** Which is the stronger reducing agent, Zn or H_2 ? Cu or Ag? Which is the stronger oxidizing agent, Zn^{++} or Cu^{++} ?

12. Replacement series for the halogens. Experiment. Make a small gas generator and charge the flask with about 2 g. of manganese dioxide. Pour 5 cc. of concentrated HCl into the flask and warm gently until a continuous stream of chlorine is slowly evolved.¹ Pass a few bubbles of the gas through a very dilute solution of sodium bromide, prepared by diluting a few drops of the laboratory solution with 5 cc. of water. Shake the solution with 1 cc. of carbon bisulfide (or carbon tetrachloride). The brown color in the non-aqueous layer is characteristic of bromine.

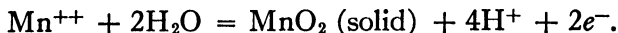
13. Experiment. To 1 cc. of potassium iodide solution add a drop of bromine water. Shake with carbon bisulfide. The violet color is characteristic of iodine.

14. Questions. For each of the above experiments write the equation for the reaction which has taken place. Point out the changes in oxidation numbers and the transfer of electrons. Predict what reaction, if any, will occur when (a) chlorine gas is passed through KI solution, (b) bromine is added to KCl solution, and (c) iodine is added to KBr solution.

15. Write the equations for the half-reactions, two molecules of halide ion equals one molecule of halogen plus two electrons, and arrange these couples in order of increasing strengths of the halogens as oxidizing agents.

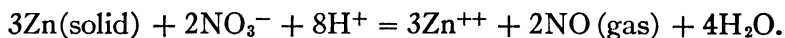
¹ Caution. Do not breathe the gas. Use a fume-closet or work out of doors.

16. In the reaction between manganese dioxide and hydrochloric acid in Paragraph 12 manganous ion, Mn^{++} , was formed. Write the equation for the reaction. The half-reaction for the manganous ion-manganese dioxide couple is



At 25° C. chlorine and manganese dioxide in 1 M H^+ are of very nearly equal strengths as oxidizing agents; but higher concentrations of hydrogen ion favor the reaction carried out above (Paragraph 12), as does also the greater volatility of the chlorine at the higher temperature. Predict the effect of adding bromine to a strongly acid solution of Mn^{++} .

17. **Action of nitric acid on zinc, copper, and silver. Experiment.** Treat about 0.3 g. of zinc with 2 N HNO_3 in a small beaker, covered with a watch-glass. If the reaction is slow warm the mixture. The net reaction under these experimental conditions is



Show how this equation is related to the equations of the two half-reactions: $Zn = Zn^{++} + 2e^-$ and $NO + 2H_2O = NO_3^- + 4H^+ + 3e^-$.

18. Repeat the **experiment** with about 0.3 g. of copper. This reaction and that with silver are similar to the one between zinc and nitric acid, and the change from Zn to Zn^{++} corresponds exactly to the change from Cu to Cu^{++} and from $2Ag$ to $2Ag^+$. Write the equations for the reactions. **Question.** How is the speed of the reaction between nitric acid and the metals affected by a change in temperature and by a change in the concentration of the acid?

19. **Action of bromine on zinc, copper, and silver.** The halogens, chlorine, bromine, and iodine, react directly with many metals. To illustrate this action we will use bromine because its aqueous solution is a convenient reagent. The

solution of chlorine in water does not keep well, while iodine is a solid which is only slightly soluble in water. **Experiment.** Treat a small piece of zinc with bromine water. After a few minutes pour the solution into a porcelain dish, and heat it to boiling to expel any bromine that is present. To a portion of the solution add a few drops of silver nitrate: AgBr, like AgCl and AgI, is a slightly soluble salt. What evidence have you that a reaction takes place between zinc and bromine? Repeat the **experiment** with copper and bromine water. Silver, also, reacts with bromine.

20. While it is desirable to assign a definite place in one table to each oxidizing and reducing couple which you study, it must be kept in mind that the oxidizing or reducing power of a substance depends upon its concentration and that, if two couples are close together, an equilibrium may be established in which all of the substances are present at appreciable concentrations and that the reaction may be made to take place in either direction by changing the experimental conditions. It must also be remembered that in many cases the speed of the reaction is slow even though there is a large difference in the oxidizing and reducing power of the two couples, as, for example, the slow action of dilute nitric acid upon hydrogen. **Question.** Give examples in which the action of hydrogen ion upon electropositive metals is also slow.

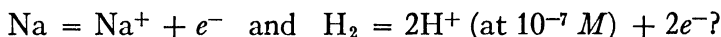
21. Summarize your results in a table of oxidizing and reducing couples arranged to show the relative strengths of all the oxidizing and reducing agents considered in the Assignment. In order to fix the position of certain couples you will need additional experimental results, as, for example, the fact that nitric acid will not oxidize manganous ion Mn^{++} . Formulate such additional experiments and ask your instructor for the experimental results. Indicate in your table the couples which react slowly at ordinary temperatures.

22. Summarize the behavior of Na, K, Ca, Zn, Cu, and

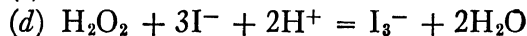
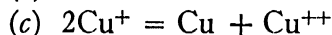
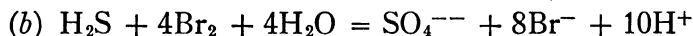
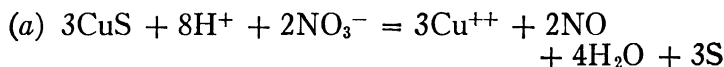
other metals discussed in the lectures by dividing the metals into the three following classes:

- I. Those which react readily with water. Hydrogen is evolved.
- II. Those which react readily with HCl or H₂SO₄ solution, but not with water. Hydrogen is evolved.
- III. Those which dissolve readily in HNO₃ or Br₂ solution, but not in HCl, H₂SO₄, or water. H₂ is not evolved.

What can you say regarding the relative strengths as reducing agents of the couples



23. **Problems.** (1) Break up each of the following reactions into the half-reactions or couples.



(2) What is the oxidation number of manganese in the following compounds: MnSO₄, Mn(OH)₃, HMnO₃⁻, Mn₃O₄, KMnO₄, Na₂MnO₄, and Mn(CN)₂⁻?

(3) *What is the atomic weight of the electron? What then is the weight of (a) one faraday of electricity, (b) one coulomb of electricity?

Assignment 31

Electrical Cells. Electromotive Force as a Measure of the Tendency of a Reaction to Occur

Special Material: High resistance voltmeter. Porous cup. Thin strips of the metals, zinc, copper, and silver. Graphite rods.

1. **The conversion of chemical into electrical energy.** The reactions studied in the preceding Assignment may be utilized to convert chemical into electrical energy. In each of the reactions an interchange of electrical charges has taken place; and the problem in the construction of an electrical cell is to arrange the substances involved in the reaction in such a way that this interchange of electricity can take place only through an external conductor such as a wire joining the electrodes. Thus, in the reaction between zinc and cupric ion, zinc is changed to zinc ion and gives up two electrons per atom, and cupric ion is changed to copper by the gain of two electrons per atom. When zinc is placed directly in a solution of a cupric salt the electrical changes both occur at the surface of the zinc and the transfer of electricity cannot be directly detected; but when we arrange the materials so that the copper electrode dips into a copper sulfate solution contained in a porous cup, and this is placed in a vessel containing zinc sulfate solution and the zinc electrode, then no reaction takes place. If now we join the two electrodes by a wire, electricity is able to make a complete circuit through the wire and the solution: at the

zinc electrode the half-reaction $\text{Zn} = \text{Zn}^{++} + 2e^{-}$ takes place, while at the copper electrode the half-reaction $\text{Cu}^{++} + 2e^{-} = \text{Cu}$ occurs. The total change in the cell is, of course, the same as when zinc acts directly on copper ion.

2. Draw a diagram of the electrical cell described above.

Questions. What substances carry the electricity from one electrode to the other through the solution? Toward which electrode does the cupric ion move when the cell is operating? The zinc ion? The sulfate ion? Which electrode is the **anode** and which the **cathode**?

3. In a similar way the reaction between chlorine and bromide ion may be used to generate electrical energy; but, to lead the current into and out of the solution, we must use some substance, as graphite, which conducts electricity and is not attacked by chlorine or bromine. In one part of this electrical cell there would thus be a graphite rod dipping into a solution which contains bromide ion and bromine, and in the other part a graphite rod in a solution of chloride ion and chlorine. The two solutions must be separated, e. g., by a porous cup, in order to prevent the chlorine from reacting directly with the bromide ion. When the graphite electrodes are joined by a wire a current will flow, and at the one electrode bromide ion will change to bromine while at the other electrode chlorine will change to chloride ion. Draw a diagram of the cell and write the equations for the reaction at the electrodes. **Questions.** In which direction will the electrons flow through the wire when the circuit is closed? Toward which electrode will the various ions in the solution move?

4. **The electromotive force of chemical cells.** In each of the cells discussed above the electrical force which causes the electrons to flow through the external circuit may be measured by suitable electrical instruments. This **electromotive force** is usually expressed in volts and affords a direct method of measuring the difference in the relative oxidizing and reducing powers of the couples used to construct the

cells. In Assignment 30 you concluded from chemical evidence that Cu^{++} was a stronger oxidizing agent than Zn^{++} and likewise that Cl_2 was stronger than Br_2 . These results were qualitative but, by measuring the electromotive force of the two cells, you can determine quantitatively the electrical force exerted by the electrons in passing from metallic zinc to cupric ion and from bromide to chlorine.

5. Experiment. Suitable cells may be constructed by placing one electrode and its solution in a porous tube and inserting it in a 60 cc. bottle containing the other electrode and its solution. A cell so constructed should have a sufficiently low internal resistance to be measured with a voltmeter¹ provided of course that the electrode reactions are rapid. Electromotive force values may be obtained with all of the couples listed in your table of Paragraph 21, Assignment 30, except for those of nitric acid and hydrogen. The nitric acid electrode is slow and non-reversible and cannot be measured directly. A reversible hydrogen electrode may be made by using a platinum black surface but even then the reaction is too slow to give sufficient current to be measured directly with a voltmeter. Difficulty will also be met with the manganese dioxide electrode if the oxide is not in an active form.

Four or five students may work together and apportion the construction of the cells among the group. Each student may secure from the storeroom the materials necessary for the construction of one cell. A good plan is to include the $\text{Zn}-\text{Zn}^{++}$ couple in each cell, preferably in the outer compartment; and to use equal concentrations of the salt solutions in the two parts of the cell. Summarize the results obtained by the group, recording also the concentrations used in each cell.

Compare these results with those calculated by difference from the **standard potentials** of half-cells tabulated in

¹ An inexpensive high resistance voltmeter which may be attached to the wall is suitable for these measurements.

LH, Appendix II. In general your results will be about 0.1 volt too low on account of polarization effects and the electromotive force which exists at the junction of the two electrolytes. Larger discrepancies may arise if the concentrations differ greatly from those to which the standard potentials refer.

6. Concentration effects. Experiment. Prepare a cell having as one electrode the Cu—Cu⁺⁺ couple. Measure the voltage of the cell and then add (NH₄)₂S solution in small excess to the copper solution, which will precipitate CuS, and again measure the voltage. Explain the result in terms of the change in concentration of the cupric ion. When sulfide is present, what substance is reduced at the cathode?

7. Electrolysis. If two platinum electrodes are placed in molal sulfuric acid and the circuit closed, a current flows through the cell when an external electromotive force above about 1.3 volts is inserted in the circuit. Such a process is called **electrolysis**. A knowledge of the strength of oxidation-reduction couples makes possible the prediction of the electrode reactions, since at the anode the substance most easily oxidized is oxidized and at the cathode the most easily reduced substance is reduced. In the present example the half-reaction at the anode is $\text{H}_2\text{O} = \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^-$ and at the cathode $2\text{H}^+ + 2e^- = \text{H}_2$. If sodium hydroxide were used in place of sulfuric acid, the reactions would be: at the anode $2\text{OH}^- = \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^-$ and at the cathode $2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$. **Question.** What is the net cell reaction in each case?

8. Experiment. Predict what will happen if a sulfuric acid solution is electrolyzed between copper electrodes. Try the experiment using 2 copper electrodes in a small beaker and applying about 2 volts external e.m.f., which may be obtained by combining in series two or more of the cells constructed in Paragraph 5. Write equations for the half-reaction at each electrode and the net cell reaction.

9. **Problems.** (1) How many (a) faradays, (b) coulombs of electricity are involved in the conversion of 1 mole of cupric ion to copper?

(2) How many coulombs of electricity would be required to form 10 liters of chlorine, measured under standard conditions, from chloride ion?

(3) For how many seconds could a cell, in which the reaction $\text{Zn} = \text{Zn}^{++} + 2e^-$ is occurring, produce a current of 1 ampere, if the initial weight of the zinc electrode were 10 grams?

(4) Write equations for the electrode reactions which occur upon the electrolysis with inert electrodes of solutions of (a) AgNO_3 and $\text{Cu(NO}_3)_2$, (b) NaI and NaCl .

(5) Which type of reaction, reduction or oxidation, always occurs at the anode? What is the sign of the anode in the internal part of the circuit? In the external part?

(6) *The general expression for the reversible potential of the $\text{H}_2\text{—H}^+$ couple at 25°C . is

$$E = E^\circ - \frac{0.059}{2} \log \frac{C_{\text{H}^+}^2}{P_{\text{H}_2}}$$

where C_{H^+} is the molal concentration of H^+ and P_{H_2} is the pressure of H_2 in atmospheres. Calculate E for the couple when C_{H^+} is 10^{-7} and P_{H_2} is 1.

Assignment 32

Preparation and Properties of Colloids

Special Materials: Sugar, gelatine, commercial sodium silicate, rosin in alcohol, benzene, methyl alcohol, cottonseed oil, formaldehyde, 0.1 *N* H_3AsO_3 , 0.01% AuCl_3 , H_2SO_4 solution, 0.1 *N* $\text{H}_2\text{C}_2\text{O}_4$, concentrated (20–30%) FeCl_3 solution.

Reference. Hildebrand, Chapter XIX.

1. Before starting this Assignment the student should read carefully the reference on dispersed systems in order to acquire a reasonable working knowledge of the fundamental concepts of these systems. In the following experiments it is assumed that the student is familiar with the relation of size of particles to the colloidal state and with the terminology commonly employed.

PREPARATION OF COLLOIDS BY CONDENSATION METHODS

2. If a chemical reaction in solution produces a substance at a higher concentration than the saturation value of that substance, a precipitate generally results; but if the conditions are such as to retard the growth of the many crystal nuclei which first form, the result is a colloidal suspension. The important factors which control this retardation of growth are temperature, concentration of reacting substances, the electrification of the particles by the adsorption of ions, and the presence of substances which form protective coverings about the particles. Examples will be given in which the colloids are formed by oxidation and reduction reactions, metathesis, hydrolysis, and change in the

nature of the solvent; and the conditions determining their stability will be investigated.

3. **Ferric oxide.** Boil about 200 cc. of water in a flask and add concentrated ferric chloride until a deep red-brown color is obtained. The resulting colloid is quite stable but its stability may be still further increased by dialysis. (How could you prove that the deeply colored liquid is a colloidal rather than a true solution?) The sol is charged positively. How could this be determined by cataphoresis? When the liquid is cool pour about 10 cc. into each of two test-tubes and add to one an equal volume of 0.01 *M* NaCl and to the other 0.01 *N* Na₂SO₄. Explain the result in terms of the neutralization of the charges on the colloid. Repeat the coagulation test with the sodium sulfate, adding first a few drops of 0.5 per cent gelatine solution to the solution. Explain.

4. **Arsenious sulfide.** Pass hydrogen sulfide through 100 cc. of 0.1 *N* H₃AsO₃. The resulting sol is negatively charged. Try the coagulating effect of the following reagents: 0.01 *N* NaCl, 0.01 *N* BaCl₂, 0.01 *N* AlCl₃, and 2 *N* HCl. A 0.1 *N* AsCl₃ solution contains a high concentration of hydrochloric acid owing to hydrolysis. What prediction would you make regarding the result of passing hydrogen sulfide into this solution?

5. **Cupric hydroxide.** Add a few drops of 6 *N* NaOH to a solution of cupric sulfate. Repeat using a cupric sulfate solution to which a small amount of cane sugar has been added.

6. **Sulfur.** Pass hydrogen sulfide through a solution of sulfurous acid. Write the equation for the reaction. Try the effect of boiling and of the addition of solid salt in coagulating the colloid. With what other examples of the formation of colloidal sulfur are you familiar?

7. **Rosin.** Pour a few cc. of a solution of rosin in alcohol into 50 cc. of water. Repeat using 50 cc. of 1 *N* NaOH in place of water.

8. **Gold.** Heat 20 cc. of a 0.01 per cent gold chloride solution, add a few drops of 1 *N* Na_2CO_3 to neutralize excess acid, and then add drop by drop with stirring a 5 per cent formaldehyde solution. Repeat adding a few drops of a 1 per cent gelatine solution to the gold chloride before adding the formaldehyde. How can you explain the difference between the ruby and the blue gold solutions in terms of the size of the particles in the two cases? Add 10 per cent sodium chloride solution to some of the ruby solution. If too much gelatine has not been used the color will change from ruby to blue. Does the change in color indicate an increase in the size of the particles?

9. **Silver.** Add several cc. of 1 per cent gelatine to 20 cc. of 0.1 *N* AgNO_3 ; then add 5 cc. of 5 per cent formaldehyde solution and heat. The amber solution becomes dark brown upon standing. What commercial preparation is of similar composition?

10. **Barium sulfate.** Pour 15 cc. of *N* BaCl_2 into 15 cc. of *N* Na_2SO_4 . Determine if the precipitate runs through filter paper. Repeat the experiment; this time, however, first dilute the sodium sulfate to 300 cc., heat to boiling, and add the barium chloride slowly with stirring. What conclusions can you draw regarding the size of the crystals in the two cases?

PREPARATION OF COLLOIDS BY DISPERSION METHODS

11. In the preparation of colloids by dispersion there is a reduction in the size of the molecular aggregates. This may be carried out mechanically by grinding in a so-called colloid mill, or by the disruptive action of an electric arc under water, or chemically by the addition of a peptizing agent which acts to disperse the solid or liquid in the solvent phase. In general the factors governing stability are the same as those discussed in Paragraph 2.

12. **Cadmium sulfide.** Precipitate some cadmium sulfide. Filter and wash the precipitate. Suspend a small amount

of the sulfide in water and saturate with hydrogen sulfide. What is the peptizing agent? Try the effect of boiling off the hydrogen sulfide from one portion, and of adding ammonium chloride to another.

13. **Ferric ferrocyanide.** Precipitate some Prussian blue. Filter and wash the precipitate. Shake a small amount of the solid with oxalic acid solution. Note the color of the solution.

14. **Benzene-water emulsion.** Shake together 10 cc. portions of benzene and water. Repeat using a 50 per cent methyl alcohol-water solution instead of the pure water. How may the action of the alcohol in stabilizing the emulsion be explained?

15. **Oil-water emulsions.** Shake 1 cc. of cottonseed oil with 5 cc. portions of (1) water (2) 0.1 *N* HCl (3) 0.1 *N* NaOH and (4) 1 per cent soap solution. From the results of the experiment explain the action of soap and washing soda in removing grease. How could you determine whether the emulsion is oil-in-water or water-in-oil? Is it possible to prepare both types?

GELS

16. Although it is convenient to treat gels as a separate class, in many cases they differ from colloidal solutions only in the greater concentration of the dispersed phase; the semi-solid property results from an interlocking of the particles to give a fibrous or cell-like structure. A striking characteristic of gels is the ability to take up large quantities of the solvent. The student is doubtless familiar with many gels and their methods of preparation, such as: soap in water, soap in petroleum oil (cup grease), starch in water, gelatine in water, and pectin in sugar solution (fruit jellies).

17. **Silicic acid gel.** Dilute 10 cc. of commercial water glass with three volumes of water and pour this into an equal volume of 1 *N* HAc. Repeat using 1 *N* HCl instead of the acetic acid. Set the mixture aside to jell. In the next

laboratory period break up the gel made with the hydrochloric acid, wash with water to remove salts, and heat carefully in a pyrex beaker until only a fine sand remains. Of what commercial importance is this dehydrated silica gel? Add a drop of carbon drawing-ink to 200 cc. of water and test the absorptive power of the porous silica with some of the carbon suspension.

Section III

Introduction to the Systematic Study of Reactions of Ions in Aqueous Solutions

Assignment 41

The Properties of Sodium, Potassium, and Ammonium Ions. Tests for Chloride, Nitrate, Sulfate, Carbonate, and Sulfide

Special Material: Suitable "unknowns" for analysis; solutions may be used, in which case the student should supply two sample bottles labelled 41, I and 41, II.

Reference. For Assignment 41 and all later Assignments: *Reference Book of Inorganic Chemistry*, by Latimer and Hildebrand, to be used by means of the index to look up specific points.

Note. Write equations for all reactions.

1. In this Assignment we shall study the properties of the ions of the common acids and bases.

2. Aside from the physical properties, such as color, the properties of an ion depend on its behavior toward other substances. The study of the **chemistry of an ion** thus consists in determining whether or not various substances react with the ion, and in studying the reactions that do take place. For each reaction it is necessary to know:

- (1) The products of the reaction.
- (2) Whether the reaction takes place rapidly or slowly.
- (3) Whether the reverse reaction can be made to take place.
- (4) The nature of the equilibrium, i. e., the relative concentration of the various substances in one equilibrium state.

In this course the task is greatly simplified on account of the following considerations: Nearly all the reactions stud-

ied take place very rapidly; this is characteristic of ionic reactions, such as ionization, precipitation, neutralization, etc. Also the number of different types of reactions is not large; and, when for one type a single example is understood, additional examples should present no real difficulty. Finally an equilibrium state is reached in many cases, and a knowledge of the principles of equilibrium enables the student to predict what will happen when there is a given change in the experimental conditions. While the number of facts to be remembered is thus greatly reduced, it is necessary, however, to **memorize** such facts as: the formulas of substances, the relative solubilities of salts, the relative volatilities of various solid or liquid substances, and the relative strengths of weak electrolytes.

3. Properties of sodium ion. The chemistry of Na^+ is very simple: at moderate concentrations it does not in general react with other ions. This statement signifies that nearly all sodium compounds are relatively non-volatile, readily soluble, and strong electrolytes.

4. Flame test for sodium. Experiment. Clean an iron wire by dipping it into dilute HCl solution in a test-tube and holding the wire in the flame until it gives only a faint yellow color. (**Note.** Do not contaminate your HCl solution by dipping the iron wire into the bottle.) Try the flame test with solid sodium chloride, the laboratory solution of sodium chloride, a very dilute solution, and distilled water, cleaning the wire before each test. It is very important to note the length of time during which the intense yellow color persists. This will depend upon the amount of sodium, the temperature of the wire, and the volatility of the sodium compounds which are present. Almost every substance contains enough sodium to give a yellow flame for a few seconds but if appreciable amounts of a sodium compound are present the color should last at least 10 seconds. Before concluding that sodium is present in an "unknown" it is well to make comparative tests with (1) a known solution

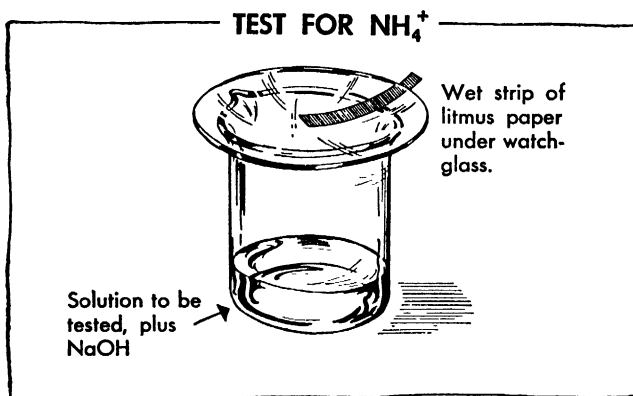
“free” from sodium and (2) the same solution containing a small amount of sodium salt. Such **control** experiments are often called **blank tests**. Repeat the experiment using the laboratory solution of sodium sulfate, and compare the length of time the color may be observed with the time found for sodium chloride solution. Chlorides generally give more satisfactory flame tests than sulfates or oxides, because of the relatively greater rate of volatilization of the chlorides.

5. Properties of potassium ion. What is the relation of potassium and sodium in the Periodic System? Potassium ion resembles sodium ion very closely. One difference, however, is the precipitation of potassium cobaltinitrite when cobaltinitrite ion, $\text{Co}(\text{NO}_2)_6^{---}$ is added to a solution containing K^+ . **Experiments.** To 1 cc. of a dilute, neutral solution of a potassium salt add a few drops of acetic acid and 0.5 to 1 cc. of the sodium cobaltinitrite reagent; let the mixture stand 10 minutes. **Note.** The cobaltinitrite ion decomposes in both alkaline and highly acid solutions. The test is more delicate if a volume of ethyl alcohol equal to about half the volume of the solution is added. A number of positive ions, e. g., Ag^+ and Cu^{++} , interfere with the test.

6. Flame test for potassium. Try the flame test with solid KCl, KCl solution, KCl solution containing a small amount of NaCl, NaCl solution, and NaCl solution containing a small amount of KCl. Use the two blue glasses to shut off the yellow color of the sodium flame and practice until the presence or absence of both potassium and sodium can be determined. **Note.** Since the flame test depends upon the amount of solid present it is well to concentrate a dilute solution by evaporation before making the test. A small direct-vision spectroscope will prove useful in flame tests, but cannot be used for sodium as the D-lines (yellow) may be observed with almost every substance.

7. Properties of ammonium ion. Ammonium ion re-

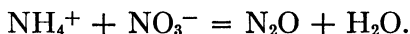
sembles sodium ion and potassium ion in that with few exceptions its compounds are soluble, strong electrolytes. Like the potassium ion it forms a precipitate with $\text{Co}(\text{NO}_2)_6^{---}$. Ammonium compounds give no flame test. The detection of NH_4^+ is facilitated by the fact that NH_4OH not only is a weak base, but is decomposed easily into NH_3 gas and H_2O . NH_3 enters into many reactions some of which have been considered in Assignment 29. **Experiment.** Try the cobaltinitrite test, using NH_4^+ instead of K^+ . **Experiment.** Note the odor of the 6 *N* NH_4OH laboratory reagent, and its effect on moist litmus



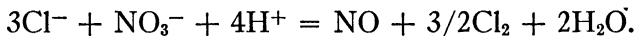
paper. Put into a beaker 0.001 mole of NH_4^+ , by taking a suitable volume of the laboratory solution of an ammonium salt. Make the solution strongly alkaline with NaOH , cover the beaker with a watch-glass and let it stand five or ten minutes. Note the odor of the gas in the beaker, and test its effect on litmus paper. Repeat the experiment with 10^{-4} mole of NH_4^+ , 10^{-5} mole of NH_4^+ , etc. What is the smallest amount of NH_4^+ you can detect by this method?

8. **Removal of ammonium compounds.** Ammonium compounds are much more volatile than those of sodium and potassium, but it is not easy to remove ammonium salts

completely by direct volatilization. A better method makes use of the reaction between NH_4^+ and NO_3^- , which yields nitrous oxide.



If chloride ion is present, the evaporation with nitric acid will also remove it by the following oxidation-reduction reaction:



Since this reaction uses up both nitrate and chloride, by adding an excess of either ion and evaporating the acid solution the other ion may be removed almost completely.

Experiment. Heat strongly in a porcelain dish until fumes are no longer given off a small amount (a few milligrams) of

- (a) solid NH_4Cl ,
- (b) solid NH_4Cl to which one or two cc. of concentrated HNO_3 has been added,
- (c) a mixture of the solids NH_4Cl and KCl , to which one or two cc. of concentrated HNO_3 has been added. Test the residue in (c) for ammonium ion and for chloride ion (the test for chloride ion is discussed in Paragraph 10). Suggest a method other than the flame test for determining the presence of K^+ in a solution which contains both K^+ and NH_4^+ .

9. Properties of H^+ and OH^- . Aside from the tendency of H^+ and OH^- to unite with each other to form water, each of these ions reacts with many other ions to form weak electrolytes. We have already noted the reactions of H^+ with Ac^- , CO_3^{--} , and HCO_3^- and of OH^- with NH_4^+ . In Assignment 28 the reactions of OH^- to form slightly soluble hydroxides or oxides have been studied. In Assignment 24 you have developed a method of estimating the concentration of H^+ and OH^- by means of indicators.

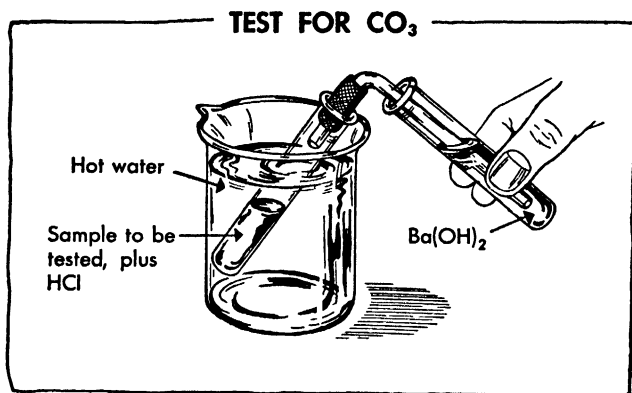
10. Test for chloride ion. A few chlorides are slightly soluble, e. g., AgCl , Hg_2Cl_2 . **Experiment.** To 1 drop portions of solutions of NaCl , $\text{Ba}(\text{OH})_2$, Na_2CO_3 , and Na_2SO_4

add 1 cc. of water, shake, and add a drop of AgNO_3 solution. In each case, record your observations, noting the color of the precipitate. Repeat the **experiment**, but acidify each solution with HNO_3 before adding the AgNO_3 . From your results state how you would test an unknown solution for chloride ion. **Note.** Ba(OH)_2 was used instead of NaOH because Cl^- is usually present in the laboratory NaOH solutions. **Experiment.** Test a dilute solution of your NaOH for Cl^- . **Experiment.** Make up solutions of various concentrations of Cl^- and repeat the test with them, to determine if it can be used to decide whether the concentration of Cl^- is large or small.

11. **Test for nitrate.** Try the following experiment with a solution which contains nitrate ion and with one free from nitrate ion, first acidifying with 6 N H_2SO_4 if the solution is alkaline. Into a small (10 $\times$ 75 mm.) test-tube put about 0.5 cc. of the solution to be tested, and add 0.5 cc. of 1 N ferrous sulfate, FeSO_4 . If there is a precipitate, centrifuge the mixture and discard the precipitate. Hold the test-tube in a slanting position and add carefully from a dropper 1 cc. of concentrated H_2SO_4 . The concentrated acid sinks to the bottom of the tube and a dark brown ring forms on its surface when nitrate is present. **Note.** The formula of the brown substance is FeNO^{++} . It decomposes rapidly when the mixture is hot. If the result of the test is negative and the test-tube feels hot to the hand (owing to the heat liberated when the concentrated H_2SO_4 mixes with the solution), repeat the test more carefully. **Experiment.** Make up solutions of various concentrations of NO_3^- , and repeat the test with them.

12. **Test for sulfate ion.** A few sulfates are slightly soluble, e. g., BaSO_4 , SrSO_4 , PbSO_4 . **Experiment.** To dilute solutions of NaCl , NaOH , Na_2CO_3 , and Na_2SO_4 add a few drops of $\text{Ba(NO}_3)_2$ solution. Now add HNO_3 until each solution is distinctly acid. From your results state how you would test an unknown solution for SO_4^{--} .

13. **Test for carbonate. Experiment.** Fit a small test-tube with stopper and delivery tube. Place a small amount of any carbonate in the tube and add a few cc. of 6 *N* HCl. Insert the stopper and pass the gas given off into a clear solution of $\text{Ca}(\text{OH})_2$.¹ If only a small amount of carbonate is present the CO_2 will not pass over into the $\text{Ca}(\text{OH})_2$ solution. A satisfactory test may be obtained in this case by



placing the test-tube in a beaker of boiling water, or by adding a small piece of zinc to the cold mixture in the test-tube. The CO_2 is carried over with the dissolved air and steam in the first method, and with the hydrogen gas in the second.

14. **Relative volatility of common acids.** The displacement of H_2CO_3 by the less volatile HCl has been illustrated in the previous paragraph. Sulfuric acid is also less volatile than HCl and HNO_3 , and the evaporation of a chloride or nitrate with excess of H_2SO_4 results in its conversion into a solid sulfate. H_2S is gaseous at room temperature, and its high volatility is the basis for the common test for sulfide ion.

¹ Instead of $\text{Ca}(\text{OH})_2$ solution, $\text{Ba}(\text{OH})_2$ solution may be used; BaCO_3 like CaCO_3 , is a slightly soluble substance.

15. Test for sulfide. Experiment. To 1 drop of Na_2S solution add an excess of H_2SO_4 , and test the evolved gas by holding over the mouth of the test-tube a piece of filter-paper moistened with CuSO_4 solution or $\text{Pb}(\text{NO}_3)_2$ solution. Repeat the experiment with smaller concentrations of sulfide. (The test may fail when it is applied to such slightly soluble sulfides as Ag_2S or HgS . The treatment of these slightly soluble substances will be taken up in subsequent Assignments.) **Question.** How would you test for chloride in a solution known to contain sulfide?

16. Problems. (1) What is the charge on each of the 4 positive and 6 negative ions considered in this Assignment? Write the formulas of the twenty-four possible compounds, each of which contains one positive and one negative constituent. Name each of the twenty-four substances, state whether it is a solid, liquid, or gas at room temperature, whether it is readily soluble in water or not, and whether it is a strong or weak electrolyte.

(2) What is the oxidation state of sodium in (a) solid sodium sulfate, (b) metallic sodium?

(3) A solid unknown was dissolved in water and the solution was found to give distinct tests for Na^+ , K^+ , Cl^- , and SO_4^{--} . What mixtures of solid salts might have been used in preparing the unknown?

(4) Outline experiments to decide whether or not each of the following contains the impurity named:

- (a) Barium chloride impurity in barium hydroxide solution.
- (b) Potassium chloride in solid sodium chloride.
- (c) Potassium chloride in solid ammonium chloride.
- (d) Ammonium chloride in solid potassium chloride.
- (e) Sodium nitrate in solid sodium sulfate.
- (f) Sodium carbonate in sodium hydroxide solution.

(5) In each of the following it is assumed that two solutions are mixed each of which contains one of the substances

at moderate concentration, say 0.1 *M*. Mark the cases in which no reaction takes place. In the others write the equation for the reaction. In (a), (b), (c) state what solutions you would use in the experiment.

- | | |
|---|---|
| (a) Ac^- and Cl^- | (g) K^+ and CO_3^{--} |
| (b) NH_4^+ and Na^+ | (h) K^+ and Ac^- |
| (c) NH_4OH and H^+ | (i) Ag^+ and Cl^- |
| (d) NH_4OH and K^+ | (j) Ba^{++} and Cl^- |
| (e) H^+ and Ac^- | (k) Ba^{++} and CO_3^{--} |
| (f) K^+ and OH^- | (l) H^+ and S^{--} |

17. Analysis Nos. 41, I and II. Analyze the **unknowns** for the four positive and six negative constituents considered in this Assignment. Try to distinguish between large amounts, small amounts, and traces. **Report** your results.

Assignment 42

Calcium

1. In Assignment 42 we shall study the chemistry of calcium with special reference to the properties of calcium ion, Ca^{++} , and its more common slightly soluble compounds. The chloride, nitrate, and sulfide are readily soluble salts.

2. **Metallic calcium.** What is the standard potential of the $\text{Ca}-\text{Ca}^{++}$ couple (LH)? From this value and your lecture notes on calcium, state what would happen when the metal is placed in water. What reaction would occur at the cathode if a solution of CaCl_2 were electrolyzed?

3. **Calcium hydroxide.** Review Assignment 28, Paragraphs 6 to 8.

4. **Calcium carbonate.** The solubility of CaCO_3 in water at room temperature is very small, viz., 0.00013 mole per liter. **Questions.** What is the concentration of calcium ion in this saturated solution, (1) in moles per liter, (2) in equivalents per liter? What solutions would you mix in order to form a precipitate of calcium carbonate? Try the **experiment.** Continue the experiment with very dilute solutions of a calcium salt in order to determine if this reaction can be used as a delicate **test for calcium ion.** In the more dilute solutions, if a precipitate does not form at once, heat to boiling and let stand 10 minutes. If the liquid is turbid compared with water a precipitate has formed.

5. **Experiment.** For use in Paragraph 6, prepare some CaCO_3 , nearly free from soluble salts, as follows: dilute

1 cc. of 1 N CaCl_2 with about 10 cc. of water and add 1.5 cc. of 1 N Na_2CO_3 solution. Heat the mixture to boiling, centrifuge, and wash the solid two or three times with water. From the volumes of the CaCl_2 and Na_2CO_3 solutions used, which reagent was added in excess? Name all the ions which must have been present in appreciable amount in the supernatant liquid.

6. **Experiment.** Treat a portion of the CaCO_3 precipitate with hydrochloric acid solution in small excess. Repeat the experiment with nitric acid. The gas given off is carbon dioxide, CO_2 . What substances are present in the final solution in each case after the solution has been boiled to expel the CO_2 ? **Note.** CO_2 is moderately soluble in cold water and the solution contains carbonic acid, H_2CO_3 , which is a weak acid. CO_2 gas will not be evolved until the concentration of carbonic acid in the solution becomes sufficiently high. **Questions.** How is the equilibrium between solid CaCO_3 and its ions disturbed by the addition of a strong acid (a) in small amount, (b) in excess. (Review Assignment 27.) What is the analogy between this example and the action of an acid on solid $\text{Ca}(\text{OH})_2$, and on solid silver acetate? What is the reason for the difference between these results and that obtained when dilute nitric acid is added to silver chloride or barium sulfate?

7. **Calcium oxalate. Experiment.** Prepare some CaC_2O_4 by treating a solution containing calcium ion with ammonium oxalate solution. Test the action of excess of a strong acid, as HCl or HNO_3 , on CaC_2O_4 . **Question.** Is oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, a weak or a strong acid?

8. **Experiment.** Determine if the precipitation of CaC_2O_4 is a delicate test for calcium by treating very dilute solutions of Ca^{++} with ammonium oxalate solution and a little ammonium hydroxide (to make sure that the mixture is not acid). Observe the same precautions as in the test for calcium by means of CO_3^{--} . **Note.** The solubility of calcium oxalate in water is somewhat less than that of calcium carbonate.

9. Calcium sulfate. Experiment. To 2 cc. of 1 *N* CaCl_2 solution add 0.5 cc. of 6 *N* H_2SO_4 . If no precipitate appears at once, heat the solution gently and let it stand. Centrifuge. Test one portion of the supernatant liquid for SO_4^{--} . Test another portion of the liquid for Ca^{++} by adding NH_4OH until the solution is no longer acid, then adding $(\text{NH}_4)_2\text{CO}_3$ solution and warming the mixture. **Questions.** What conclusion do you draw with regard to the solubility of CaSO_4 in water? Which is the less soluble, (1) CaSO_4 or CaCO_3 , (2) CaSO_4 or BaSO_4 ?

10. Predict what will take place when solid CaSO_4 is heated with excess Na_2CO_3 solution? **Experiment.** Test your prediction by boiling some solid CaSO_4 with normal Na_2CO_3 solution. Test the filtrate for SO_4^{--} . Wash the precipitate with water, and test it for carbonate.

11. **Experiment.** Test whether the reverse reaction will take place in a neutral solution, by heating solid CaCO_3 with sodium sulfate solution, filtering and testing the precipitate and filtrate. **Question.** Would the same result have been obtained if H_2SO_4 had been used instead of Na_2SO_4 ?

12. **Flame test for calcium. Experiment.** Determine whether calcium salts give a characteristic flame test. Try the experiment with both CaCl_2 and CaSO_4 . Can you distinguish the flame with calcium chloride from that with sodium or potassium salts?

13. Arrange the compounds of calcium (which you have studied) according to their solubilities in water, distinguishing readily soluble, moderately soluble, and slightly soluble substances. Point out the compounds which are much more soluble in dilute hydrochloric or nitric acids than in water. **Note.** The solubilities of most common salts are given in LH, Appendix XIX. Do not try to remember the actual solubilities, but make lists of the readily soluble and slightly soluble salts of each metal studied and memorize these lists. The term "slightly soluble" is preferable to "insoluble."

14. Give as many methods as you can of testing for Ca^{++} in a solution which is known to contain H^+ , Na^+ , K^+ , and NH_4^+ .

15. **Problems.** (1) What is the minimum volume of water needed at 18° to dissolve 1 gram of calcium carbonate?

(2) Can the following substances be present at moderate concentrations in the same solution? If not, what is formed?

- | | |
|---|--|
| (a) H^+ and NO_3^- | (e) H^+ and $\text{C}_2\text{O}_4^{--}$ |
| (b) H^+ and OH^- | (f) Ca^{++} and CO_3^{--} |
| (c) H^+ and SO_4^{--} | (g) Ca^{++} and HCO_3^- |
| (d) H^+ and CO_3^{--} | (h) Ca^{++} and NH_4OH |

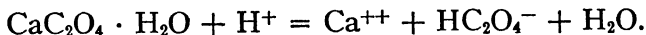
(3) How would you prepare:

- Solid CaCO_3 from solid $\text{Ca}(\text{OH})_2$?
- Solid CaSO_4 from solid CaCO_3 ?
- Solid CaC_2O_4 from solid CaSO_4 ?
- Solid CaCl_2 from solid $\text{Ca}(\text{NO}_3)_2$? (Two methods, cf. Assignment 41, Paragraph 8 for one method.)
- Solid CaSO_4 from solid $\text{Ca}(\text{NO}_3)_2$? (Two methods, cf. Assignment 41, Paragraph 14 for one method.)

(4) What is the position of calcium in the Periodic System? Name the elements in the alkaline earth group. Write a brief note illustrating gradations of properties in this group (cf. LH V).

(5) Give the formulas of 3 additional calcium compounds which are not readily soluble in water.

(6) *The solubility product of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is 2.3×10^{-9} and the 2nd ionization constant of $\text{H}_2\text{C}_2\text{O}_4$ is 6.4×10^{-5} . Calculate the constant for the equilibrium



(7) *The solubility product of CaCO_3 is given as 4.8×10^{-9} and the solubility as 1.3×10^{-4} . How can you account for the apparent discrepancy?

Assignment 43

Zinc. Hydrogen Sulfide and Its Salts

Special Material: Potassium cobalticyanide paper.

Note. Write equations for all reactions.

1. **Zinc metal. Question.** What are the oxidation states of zinc? From your knowledge of the potential of the $\text{Zn}-\text{Zn}^{++}$ couple (cf. Assignments 30 and 31), state what reaction may be expected with metallic zinc and a solution of (a) H^+ , (b) Cl_2 solution, (c) Cu^{++} .

2. **Zinc ion.** Zinc chloride, nitrate, sulfate, and acetate are soluble strong electrolytes. What is the color of zinc ion in these solutions? The properties of the slightly soluble compounds, $\text{Zn}(\text{OH})_2$, ZnCO_3 , and ZnS and the complex ion $\text{Zn}(\text{NH}_3)_4^{++}$ will be considered.

3. **Zinc hydroxide, zincate ion, and zinc ammonia complex ion.** Review your notes on Assignment 28, Paragraphs 10 and 11, and Assignment 29.

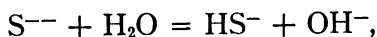
4. **Zinc carbonate. Experiment.** To 2 cc. of 0.1 *N* ZnSO_4 solution add a slight excess of Na_2CO_3 solution. Repeat the experiment adding NaHCO_3 solution. Collect the precipitates in centrifuge cones, wash with water, and test portions of the precipitates for carbonate. Try the action of ammonium hydroxide on these precipitates.

5. **Note.** Since a Na_2CO_3 solution contains both carbonate and hydroxide (by hydrolysis), its addition in excess to a solution of a positive ion of a metal may precipitate (a) a pure carbonate, (b) a pure hydroxide, (c) a mixture

of the carbonate and hydroxide, or (*d*) a basic carbonate in a definite compound of the oxide or hydroxide and carbonate. The precipitate obtained depends upon the relative solubilities of the various possible compounds. In the case of Ca^{++} , the carbonate is formed as it is much less soluble than the hydroxide. However with Zn^{++} the precipitate is a basic carbonate. In other cases to be considered later the precipitate is the pure hydroxide. Since NaHCO_3 solutions are much less basic than Na_2CO_3 solutions, this reagent will be more likely to precipitate a pure carbonate, and this is the case with Zn^{++} . Carbon dioxide, of course, gives no precipitate with solutions of zinc salts.

6. Zinc sulfide. Experiment. Prepare 5 cc. of 0.1 *N* solution of Zn^{++} . Add 0.5 cc. of 6 *N* H_2SO_4 and pass in H_2S gas ¹ until the liquid is saturated. To determine this, close the end of the test-tube or flask, shake thoroughly, and test the odor cautiously. Now add 2 cc. of 1 *N* NaAc solution, and again saturate with H_2S gas. Note the color of the precipitate. **Question.** What effect has the addition of Ac^- in this experiment on the concentration of H^+ ? **Experiment.** Collect some of the ZnS in a centrifuge cone, wash it with water, and try the test for S^{--} .

7. Hydrogen sulfide and its salts. The solubility of H_2S at 1 atmosphere pressure in water at 25° C. is about 0.1 *M*. The problem of the composition of solutions of the acid and its salts is analogous to that of carbonic acid, discussed in Assignment 27. The first ionization constant, $K_1 = 1.1 \times 10^{-7}$, corresponding to $\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$ is only slightly smaller than that of H_2CO_3 , but the second ionization constant, $K_2 = 1 \times 10^{-15}$, is very much smaller. Therefore solutions of Na_2S are much more hydrolyzed than those of Na_2CO_3 . In 1 *M* Na_2S the reaction,

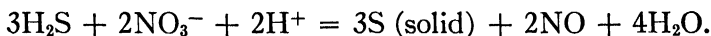


¹ Caution. H_2S is poisonous. Do not breathe the gas. Use a fume-closet or work out of doors.

reaches equilibrium when about 90 per cent of the sulfide is hydrolyzed. The hydrolysis of solutions containing both NH_4^+ and S^{--} is practically complete, a 1 M $(\text{NH}_4)_2\text{S}$ solution contains only $10^{-6} M$ S^{--} . It is also important to keep in mind the large change in the concentration of S^{--} with change in the H^+ concentration. A saturated solution of H_2S in $10^{-4} M$ H^+ contains $10^{-15} M$ S^{--} and in $0.3 M$ H^+ $10^{-22} M$ S^{--} . As a consequence the solubility of ZnS will change by a factor of 10^7 with this change in H^+ concentration. **Questions.** On the basis of this discussion and your results in Paragraph 6, what prediction could you make as to the result of adding (a) $(\text{NH}_4)_2\text{S}$ reagent ($\text{NH}_4\text{OH} + \text{HS}^-$) to a solution of ZnSO_4 , (b) excess 1 M HCl to a precipitate of ZnS . Verify your results by **experiments**. What evidence have you that ZnS is considerably less soluble than ZnCO_3 ?

8. **Experiment.** To a solution containing $\text{Zn}(\text{NH}_3)_4^{++}$, add $(\text{NH}_4)_2\text{S}$ solution. **Note.** Since NH_4OH is present in excess the same result would have been obtained by using H_2S gas instead of $(\text{NH}_4)_2\text{S}$ solution. State which has the smaller concentration of Zn^{++} ion, a solution containing the complex ion, or a solution saturated with the sulfide. From the fact that the sulfide is much less soluble than the carbonate, predict the action of H_2S on mixtures of zinc carbonate and water. Test your answer by an **experiment**.

9. **Experiment.** Test the action of H_2S on solutions of nitric acid of different concentrations, 0.1 N , 2 N , and 6 N . Saturate each solution with H_2S gas and heat the mixture almost to boiling. The white precipitate formed is solid sulfur and the principal reaction is



The equilibrium is so far to the right that the reverse reaction does not have to be considered. **Questions.** What evidence is furnished by your experiments that this is a slow reaction? How is the speed affected by the concentra-

tion of the nitric acid, and by the temperature? **Note.** Because of this reaction, nitric acid in a strongly acid solution will remove sulfide ion from the solution more completely than will H^+ alone, since it destroys the H_2S which is in equilibrium with sulfide ion. This agrees with the experimental fact that nitric acid is a better solvent for difficultly soluble sulfides than sulfuric or hydrochloric acid, but we do not wish to imply that the mechanism may not be the direct oxidation of the solid sulfide by the nitric acid.

Write the equation for the action of HNO_3 on ZnS .

10. *The precipitation of zinc as the ammonium phosphate, $ZnNH_4PO_4$, and as the potassium (or sodium) zinc ferrocyanide, $K_2Zn_3[Fe(CN)_6]_2$, is important in quantitative analysis. The former is precipitated from a solution containing Zn^{++} and NH_4^+ by excess of the reagent $(NH_4)_2HPO_4$. The latter precipitates upon the addition of the ferrocyanide reagent to a solution of Zn^{++} but the composition of the precipitate varies considerably, depending upon the concentration of H^+ and NH_4^+ in the solution.

11. **Cobalt zincate.** Cobalt and zinc oxides unite at high temperatures to form a green solid solution. This reaction is frequently used as a confirmatory test on a precipitate which may contain zinc. The test may conveniently be carried out as follows. **Experiment.** Place a drop of a solution of zinc chloride on a small piece of the special cobalt paper. Ignite the paper in a casserole by turning the bunsen burner flame directly on the paper. Heat the ash with the flame until all the carbon is burned out. If zinc is present the ash will turn to a light green color. The cobalt paper contains the compound $K_3Co(CN)_6$. Aluminum compounds give a blue ash of cobalt aluminate.

12. **Problems.** (1) What will be the solid residue when each of the following solutions is evaporated to dryness?

- (a) A solution containing Zn^{++} and NO_3^- at large concentrations and H^+ and SO_4^{--} at small concentrations.

(b) A solution containing Zn^{++} , H^+ , and Cl^- at large concentrations and NO_3^- at small concentration.

(2) How would you convert

(a) ZnS to ZnCl_2 ?

(b) ZnCl_2 to ZnSO_4 ?

(c) Na_2ZnO_2 to ZnS ?

(d) ZnCO_3 to $\text{Zn}(\text{NO}_3)_2$?

(3) What difference in the precipitate would you expect if Zn^{++} were treated with solutions of (a) Na_2CO_3 , (b) NaHCO_3 ?

(4) *From the data in Paragraph 7, calculate for a saturated solution of H_2S the value of the constant

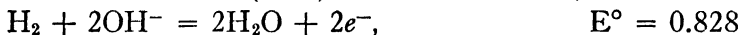
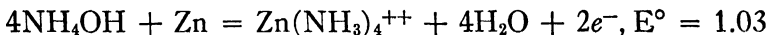
$$C_{\text{H}^+}^2 C_{\text{S}^{--}} = K.$$

(5) *Calculate the $C_{\text{S}^{--}}$ in a saturated H_2S solution containing 1 M H^+ .

(6) *The solubility product of ZnS is 4.5×10^{-24} . Calculate the maximum concentration of Zn^{++} in a saturated solution of H_2S in 0.3 M H^+ . What would occur if H_2S is passed into a 1 M Zn^{++} solution in 0.3 M H^+ ?

(7) *Zinc may be precipitated by cathodic reduction in dilute acid solutions. Explain.

(8) *From the following potentials,



predict what reaction should occur when zinc is placed in a solution of NH_4OH .

Assignment 44

Copper

Special Material: Copper foil.

1. **Oxidation states. Experiment.** Place a strip of copper foil (cleaned in dilute H_2SO_4) in a solution of CuSO_4 and note if there is any evidence that a reaction occurs. **Questions.** What conclusion can you draw regarding the equilibrium in the reaction



Which is the better oxidizing agent, Cu^+ or Cu^{++} ? Better reducing agent, Cu or Cu^+ ? Solid cuprous oxide is stable with respect to the decomposition



What can you state regarding the relative solubilities of Cu_2O and CuO ? What would be observed if Cu_2O were dissolved in H_2SO_4 ? **Experiment.** Place a strip of copper foil in a solution of CuCl_2 . The film formed on the surface is CuCl . Explain the difference in the result of this experiment and that with Cu and CuSO_4 . **Note.** If a mixture of Cu and solid CuCl_2 is treated with 6 *N* HCl , a high concentration of complex cuprous chloride ions, as CuCl_3^{--} , is formed. Upon dilution a precipitate of CuCl is obtained. The properties of Cu^+ are quite similar to those of Ag^+ , but they will not be studied in detail. The following paragraphs deal with the chemistry of Cu^{++} .

2. **Cupric ion. Questions.** What is the color of (a) cupric sulfate solution, (b) anhydrous cupric sulfate, (c) concentrated cupric chloride solution? Cupric ion in aqueous solutions is doubtless $\text{Cu}(\text{H}_2\text{O})_4^{++}$. What is the color of this ion? The more important slightly soluble compounds of Cu^{++} are the hydroxide, carbonate, and sulfide.

3. **Cupric hydroxide and cupric ammonia complex.** Review your notes on cupric hydroxide, Assignment 28, and cupric ammonia ion, Assignment 29.

4. **Cupric carbonate. Experiment.** Test the action of Na_2CO_3 solution on a dilute solution of CuSO_4 . The precipitate is a basic carbonate. Even with NaHCO_3 solution it is difficult to precipitate a pure carbonate (cf. Assignment 43, Paragraph 5). Test the solubility of the basic carbonate in NH_4OH .

5. **Cupric sulfide. Experiment.** To 5 cc. of 0.1 *N* CuSO_4 add 0.5 cc. of 6 *N* H_2SO_4 (which will make the solution about 0.3 *N* H^+) and saturate with H_2S . Centrifuge, dilute the supernatant liquid with an equal volume of water, and again saturate with H_2S to be sure the precipitation is complete. Wash the precipitate with water and use it for the experiments in Paragraph 6.

6. **Methods of dissolving slightly soluble cupric salts.** CuS is the most common cupric salt which is difficult to dissolve. **Experiment.** (1) Test the solubility of CuS in 1 *N* NH_4OH . What would be the result of adding $(\text{NH}_4)_2\text{S}$ solution to $\text{Cu}(\text{NH}_3)_4^{++}$? (2) Try the sulfide test on CuS . Repeat the test, this time adding a small piece of zinc to the test-tube along with the CuS (warm the tube). (3) Test the solubility of CuS in hot 2 *M* nitric acid. The black residue which remains is sulfur which is colored by a little CuS .

7. **Problems.** (1) How would you prepare:

(a) Solid CuCl_2 from solid CuSO_4 ?

(b) Solid CuSO_4 from solid CuS ?

(c) Solid $\text{Cu}(\text{OH})_2$ from $\text{Cu}(\text{NH}_3)_4^{++} + \text{SO}_4^{--}$?

(d) Solid CuS from a solution of CuSO_4 and ZnSO_4 ?

(2) *If the concentration of S^{--} is $1 \times 10^{-22} M$ in a $0.3 N \text{H}^+$ solution saturated with H_2S and the solubility product of CuS is 4×10^{-38} , how complete was the precipitation of copper in the experiment in Paragraph 5?

Assignment 45

Silver

1. Oxidation states. In aqueous solutions the only important oxidation state is the +1, although appreciable concentrations of the ion Ag^{++} , and to a lesser extent AgO^+ , may be formed by the action of very powerful oxidizing agents, e. g., O_3 upon Ag^+ . **Questions.** Which is the more powerful oxidizing agent, Ag^+ or (a) Cu^{++} , (b) H^+ , (c) Cl_2 ? Which is the more powerful reducing agent, Ag or (a) Cu , (b) H_2 , (c) Zn ?

2. Silver oxide and silver ammonia complex ion. Review your notes on Assignment 28, Paragraph 5, and Assignment 29, Paragraph 7.

3. Silver carbonate. Experiment. Test the action of NaHCO_3 solution upon a dilute solution of Ag^+ . The precipitate is Ag_2CO_3 . Test the solubility of some of the precipitate in NH_4OH , and treat another portion with 1 *N* NaOH solution.

4. Silver sulfide. Experiment. Acidify 2 cc. of 0.1 *N* AgNO_3 with about 2 drops of 6 *N* HNO_3 and saturate with H_2S . Collect the precipitate in a centrifuge cone, and test its solubility in (1) NH_4OH , and (2) hot 2 *N* HNO_3 . Write the equation for the reaction.

5. Silver sulfate. Experiment. To 1 cc. of 0.1 *N* AgNO_3 add 1 cc. of *N* Na_2SO_4 . **Note.** Ag_2SO_4 was expected to precipitate, since its solubility in pure water is 0.025 *M* at 20°. The solubility of a salt, however, is increased by the addition of strong electrolytes, and the percentage increase

is large when a multiply charged ion, as SO_4^{--} , is involved. **Question.** Will sulfate interfere with your chloride test?

6. Silver chloride. Methods of dissolving slightly soluble silver salts. The slight solubility of silver chloride makes Ag^+ a convenient reagent for the detection of Cl^- , and Cl^- a convenient reagent for the detection of Ag^+ . It also makes AgCl a substance difficult to bring into solution for analysis. **Experiment.** To 5 cc. of 0.1 *N* AgNO_3 add a few drops of 6 *N* HCl , collect the precipitated AgCl in a centrifuge cone, and wash it thoroughly with water. Use portions of the precipitate for the following tests.

(1) Treat AgCl with an excess of 6 *N* HCl . The solubility of the precipitate is due to the formation of AgCl_2^- and higher complexes such as AgCl_3^{--} . Pass some H_2S into the solution of the complex chloride. What can you state regarding the relative solubilities of AgCl and Ag_2S ?

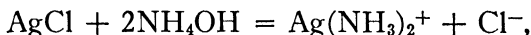
(2) Place a small amount of AgCl in a porcelain dish, add 3 or 4 cc. of concentrated HNO_3 , and evaporate the mixture to dryness. Add a little water, and determine whether the solution now contains any silver nitrate. Compare the result with that in the experiment in which KCl was evaporated with nitric acid, in Assignment 41. What explanation can you offer for the result obtained?

(3) Place a small amount of AgCl in a porcelain dish with 3 or 4 cc. of concentrated H_2SO_4 , and evaporate until the dense white fumes of SO_3 appear. When the dish is cool, add water cautiously, and test the solution for Ag^+ .

(4) Test the solubility of AgCl in NH_4OH solution, and in $\text{Na}_2\text{S}_2\text{O}_3$ solution.

7. Silver bromide and iodide. The solubility of the silver halides decreases with increasing weight of the halogen. The conversion of the white AgCl into the yellow AgI may be readily observed upon the addition of I^- to solid AgCl . The bromide and iodide are also soluble in excess of the corresponding halide with the formation of complex silver halide ions.

8. In the following list the more important slightly soluble compounds and complex ions of silver have been arranged in order of the decreasing concentration of Ag^+ in equilibrium with the solid or complex ion when an excess (1 M concentration) of the negative ion or complex forming molecule is present: Ag_2SO_4 , AgAc , AgNO_2 , Ag_2CO_3 , Ag_2CrO_4 , $\text{Ag}(\text{NH}_3)_2^+$, Ag_2O , AgCl , AgBr , $\text{Ag}(\text{S}_2\text{O}_3)_2^{--}$, AgCN , AgI , $\text{Ag}(\text{CN})_2^-$, and Ag_2S . The complex ions AgCl_2^- , AgBr_2^- , and AgI_2^- have not been included as their exact position is somewhat uncertain because of the existence of ions of greater halogen content. Two substances which are close together in the list may both be present in large amount at equilibrium and the reaction may be made to go in either direction by the addition of an excess of one of the reagents. Thus it has been shown that the reaction,



proceeds sufficiently so that a precipitate of AgCl may be completely dissolved in excess of NH_4OH . The order given above, however, indicates that if AgCl and 1 M $\text{Ag}(\text{NH}_3)_2^+$ are both present in equilibrium, the concentration of NH_4OH must be greater than the concentration of Cl^- . If two substances are far apart in the list, the equilibrium will be displaced greatly in one direction. Thus Ag_2S is not appreciably soluble in NH_4OH solution while Ag_2SO_4 would be completely converted to AgI by excess of I^- .

9. **Problems.** (1) Diagram a cell to use the reaction



Write the electrode reactions and indicate the direction of flow of electrons in the external circuit and the direction of motion of the ions in the electrolyte (cf. Assignment 31, Paragraphs 1 and 2). What would be the direction of flow of electrons if AgI were substituted for the AgCl (cf. LH, Table of oxidation-reduction potentials)?

(2) Calculate the number of moles of each substance

present, after reaction, in a solution made by adding 0.01 mole of H_2S , 0.05 mole of NaCl , and 0.04 mole of AgNO_3 to 500 cc. of water. Calculate the concentrations.

(3) The solubility product, $C_{\text{Ag}^+} \times C_{\text{Cl}^-}$, for silver chloride is 1.7×10^{-10} . Calculate the solubility of AgCl in moles per liter. What is the concentration of Ag^+ in equilibrium with AgCl in a solution containing 0.01 M Cl^- ?

(4) How would you convert (a) Ag_2S to Ag_2CO_3 , (b) AgCl to Ag_2O , (c) $\text{Ag}(\text{NH}_3)_2^+$ to AgCl ?

(5) *The solubility product of silver oxide, $C_{\text{Ag}^+} \times C_{\text{OH}^-}$, is 2.0×10^{-8} and for silver carbonate, $C_{\text{Ag}^+}^2 \times C_{\text{CO}_3^{--}}$, 8.2×10^{-12} . Calculate the solubility of each in water. Calculate the equilibrium constant for the reaction



Note. It is recommended that Assignment 61 follow Assignment 45.

Assignment 46

Iron

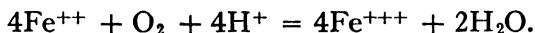
1. Oxidation states of iron. The important oxidation states of iron are the +2 and +3. The corresponding ions in acid solution are Fe^{++} , ferrous, and Fe^{+++} , ferric. **Questions.** From the existence of solutions of ferrous salts as strong electrolytes, what can you conclude regarding the equilibrium state in the reaction,



Predict what would happen if iron were placed in a solution of a ferric salt. What are the two oxidation-reduction couples involved in the reaction? **Experiment.** Treat iron filings with 3 *N* H_2SO_4 . Heat the mixture to speed up the reaction. Filter. The ferrous sulfate solution may not be concentrated enough to show the green color of ferrous ion. Now add a few drops of bromine water to the solution, and boil off any excess of bromine. The yellow color of the acid solution is characteristic of ferric bromide or chloride. To a few cc. of *N* FeCl_3 add some KI solution.

With these results as a basis, arrange the various couples involved in a series with the strongest oxidizing couple at the bottom.

The oxygen of the air slowly oxidizes Fe^{++} to Fe^{+++} .



The rate of this reaction decreases with increasing concentration of H^+ . **Question.** What can you say regarding the

rate of oxidation of Fe^{++} by NO_3^- in dilute acid, and the effect of increasing the concentration of H^+ (refer to the procedure for the nitrate test)?

2. Direct measurement of cells, using the electrodes, $\text{Fe}—\text{Fe}^{++}$, and $\text{Fe}^{++}—\text{Fe}^{+++}$ (with a graphite rod), may be made by several members of the class, using the methods discussed in Assignment 31.

3. **Ferrous ion.** Ferrous ion forms slightly soluble compounds with hydroxide, carbonate, sulfide, oxalate, and phosphate. It forms no ammonia complex ion but does form a complex ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$. The complex with nitric oxide, FeNO^{++} , has been mentioned in connection with the nitrate test.

4. **Ferrous hydroxide. Experiment.** Prepare a small amount of the hydroxide by precipitation with NaOH . Filter and allow the precipitate on the filter paper to stand in the air. The oxidation to $\text{Fe}(\text{OH})_3$ is quite rapid. Ferrous hydroxide is not appreciably soluble in excess of 1 *N* NaOH .

5. **Ferrous carbonate. Experiment.** Test the action of Na_2CO_3 solution on a solution of Fe^{++} . The precipitate is FeCO_3 .

6. **Ferrous sulfide. Experiment.** To about 1 cc. of 1 *N* FeSO_4 add 10 cc. of 6 *N* HAc , dilute to 50 cc., and saturate with H_2S . Now make alkaline with NH_4OH and saturate again with H_2S . FeS is somewhat more soluble than ZnS .

7. **Ferric ion.** Ferric ion forms slightly soluble compounds with hydroxide, phosphate, and arsenate. The carbonate is completely hydrolyzed. Among the more important complex ions are $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CNS})^{++}$ (deep red) and higher complexes of thiocyanate up to $\text{Fe}(\text{CNS})_6^{3-}$, FeF_6^{3-} , and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$.

8. **Ferric hydroxide.** Review your notes on hydrous ferric oxide, Assignment 28. **Experiment.** Treat small quantities of dilute solutions of FeCl_3 with (a) NH_4OH in small amount and in excess (b) 1 *M* NaOH in small amount and in excess. Ferric hydroxide is appreciably soluble in

concentrated NaOH but the solubility in 1 M OH^- is small.

9. Hydrolysis of Fe^{+++} . A 1 M solution of $\text{Fe}(\text{NO}_3)_3$ is highly acid (around 0.02 M H^+) by hydrolysis. Although the first step of the hydrolysis is doubtless the formation of $\text{Fe}(\text{OH})^{++}$, the equilibrium is complicated by the presence of more highly hydrolyzed positive ions and colloidal particles. The ferric oxide colloid is remarkably stable. Its color varies from yellow to deep red, and much of the color of solutions of ferric salts is due to its presence. **Experiment.** Prepare colloidal ferric oxide by the technique described in Paragraph 3 of Assignment 32. Does filtration of this solution lead to any separation? Does centrifugation? **Experiment.** Dissolve a small amount of solid $\text{Fe}(\text{NO}_3)_3$ in water. Slowly add HNO_3 to the solution and note the change in color. **Note.** Solutions of FeCl_3 do not become colorless with the addition of HCl as the complex ferric chloride ions are themselves colored. **Experiment.** To 10 cc. of 1 N FeCl_3 in a beaker add gradually 1 N Na_2CO_3 solution, with stirring, until a permanent precipitate is obtained. This is an example of complete hydrolysis to form the hydroxide. **Questions.** How would the equation for the net reaction differ if a small amount of FeCl_3 were added to a large amount of Na_2CO_3 solution? What is the color of Fe^{+++} ?

10. Reactions of Fe^{++} and Fe^{+++} with $\text{Fe}(\text{CN})_6^{-4}$ and $\text{Fe}(\text{CN})_6^{-3}$. **Experiment.** Test dilute solutions of Fe^{++} and Fe^{+++} with a few drops of (a) $\text{Na}_4\text{Fe}(\text{CN})_6$ solution and (b) $\text{Na}_3\text{Fe}(\text{CN})_6$ solution. Record the observations in these four experiments. Consult LH for a discussion of the substances formed. **Question.** How would you use these tests to prove the presence of both Fe^{++} and Fe^{+++} in the same solution?

11. Reaction of Fe^{+++} with H_2S and HS^- . **Experiment.** To a few drops of FeCl_3 solution add 1 cc. of 6 N HCl and about 20 cc. of water, and saturate the solution with H_2S

gas. Boil the mixture in a porcelain dish to coagulate the precipitated sulfur and expel the H_2S , filter, and at once test a portion of the clear solution for Fe^{+++} . Treat the remainder of the solution again with H_2S if Fe^{+++} seems to be present. Test the action of $(\text{NH}_4)_2\text{S}$ upon a dilute solution of Fe^{+++} . The precipitate is mainly Fe_2S_3 but may contain some FeS and S . **Question.** What would be the result of treating Fe_2S_3 with excess HCl ?

12. **Problems.** Try experiments when necessary.

(1) How would you transform

- (a) ferric chloride to ferric sulfate;
- (b) ferric sulfate to ferric chloride;
- (c) ferrous sulfate to ferric sulfate;
- (d) ferric sulfate to ferrous sulfate?

(2) Ferric alum, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is an example of a **double salt** and $\text{K}_3\text{Fe}(\text{CN})_6$, while also a double salt is often called a **complex salt**. What are the principal ions present in solutions of each of these salts?

(3) Suggest a method of preparing $\text{Fe}(\text{OH})_3$ and ZnS from a single portion of a solution which contains Fe^{++} , Zn^{++} , H^+ , and SO_4^{--} .

(4) Suggest an explanation for the removal of rust spots by oxalic acid.

(5) Write the equation for the net reaction which occurs when Fe_3O_4 dissolves in HCl .

(6) *The solubility product of FeCO_3 is 2×10^{-11} and that of $\text{Fe}(\text{OH})_2$ 1.6×10^{-15} . Which is the more soluble in water (neglect the hydrolysis of CO_3^{--})? Which would give the smaller concentration of Fe^{++} , FeCO_3 with excess of 1 M CO_3^{--} or $\text{Fe}(\text{OH})_2$ with excess of 1 M OH^- ?

(7) *The equilibrium constant for the reaction,

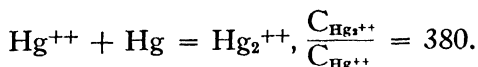


is 10^{-41} . What is the concentration of Fe^{+++} in a 1 M Fe^{++} solution in equilibrium with Fe ?

Assignment 47

Mercury

1. Oxidation states. Mercury forms the positive ions, Hg_2^{++} , mercurous, and Hg^{++} , mercuric. For the equilibrium,



Since the ratio of the two concentrations is not large, a solution of Hg_2^{++} always contains a low concentration of Hg^{++} even if metallic Hg is present. The equilibrium is readily reversible and may be shifted in either direction by the removal of one of the ions to form a slightly soluble compound or a stable complex ion. **Questions.** What are the two couples involved in the equilibrium? Which couple has the higher oxidizing potential? From the nature of the equilibrium would you say the potentials of the two couples are close together or far apart? Before continuing the study of these couples it will be necessary to develop methods of testing for Hg_2^{++} and Hg^{++} .

2. Mercurous chloride and mercuric chloride. Experiment. To 5 cc. of water add 3 or 4 drops each of 0.1 N $\text{Hg}_2(\text{NO}_3)_2$ and 6 N HCl . Repeat the experiment with 0.1 N $\text{Hg}(\text{NO}_3)_2$, and give a method of distinguishing between soluble mercurous and mercuric salts. **Note.** Mercuric chloride is one of the few examples of weak salts. The concentration of Hg^{++} in 0.1 M HgCl_2 is about $10^{-8} M$. In solutions containing excess chloride ion, the complex ion HgCl_4^{--} is formed.

3. **Reaction of Hg_2^{++} and Hg^{++} with stannous ion.** Tin forms two series of compounds, stannous and stannic, in which the oxidation state of tin is +2 and +4 respectively. Stannous ion, Sn^{++} , is a good reducing agent since it is easily oxidized to Sn^{++++} . The chlorides of tin are both soluble in water; and the common stannous salt laboratory reagent is SnCl_2 solution to which HCl has been added to prevent the precipitation of a basic salt. **Experiment.** To 1 cc. of 0.1 N $\text{Hg}(\text{NO}_3)_2$ and 5 cc. of water add from a dropper one drop of SnCl_2 solution. Divide the mixture into two portions and to one portion add SnCl_2 until it is present in excess. Observe the difference in appearance of finely divided mercury and a large drop of the metal. Outline a method of testing for the presence of mercuric mercury in a solution containing Hg_2^{++} and Hg^{++} after first removing the Hg_2^{++} . Try your method with a dilute solution of $\text{Hg}_2(\text{NO}_3)_2$ and $\text{Hg}(\text{NO}_3)_2$.

4. **Reduction of Hg_2^{++} and oxidation of Hg .** By **experiments** with some of the metals you have studied and small amounts of $\text{Hg}_2(\text{NO}_3)_2$ solution determine approximately the position of Hg — Hg_2^{++} in your table of oxidizing and reducing agents. In these experiments any metallic mercury formed can usually be seen on the surface of the metal, but the solution may also be tested for the dissolved metal after precipitating the mercurous mercury with HCl . From your result predict whether metallic mercury will dissolve in dilute sulfuric acid, and test your prediction. **Note.** Hg dissolves in hot 2 N HNO_3 .

5. **Oxidation of Hg_2^{++} and of Hg_2Cl_2 .** **Experiment.** Try an experiment to determine how rapidly hot 2 N HNO_3 oxidizes Hg_2^{++} . Repeat the experiment with hot concentrated HNO_3 . **Experiment.** Collect some Hg_2Cl_2 in a centrifuge cone. Treat a small portion in a porcelain dish with hot 2 N HNO_3 , and another portion with hot 2 N HNO_3 to which some HCl has been added. Repeat the experiments, if necessary, with more concentrated HNO_3 , and note

whether the speed of oxidation is increased by the presence of HCl. **Experiment.** Treat a small portion of Hg_2Cl_2 with bromine water, and test the solution as before for mercuric mercury after boiling it to expel bromine.

6. **Slightly soluble salts of mercuric mercury. Experiment.** Test the action of each of the following reagents on a dilute solution of $\text{Hg}(\text{NO}_3)_2$. Save the precipitates for use in 7.

- (a) H_2SO_4 or a soluble sulfate in acid solution.
- (b) Na_2CO_3 . The precipitate is a basic carbonate.
- (c) NaOH . The precipitate is HgO .
- (d) NH_4OH . When a chloride is present the precipitate is $\text{Hg}(\text{NH}_2)\text{Cl}$, ammonobasic mercuric chloride, which is closely related to $\text{Hg}(\text{OH})\text{Cl}$, basic mercuric chloride. Analogous but more complex substances are precipitated in the absence of chloride. What is the charge on the OH radical? On the NH_2 radical? Cf. LH VIII.
- (e) H_2S in acid solution. If this precipitation is carried out in a solution containing a high concentration of chloride ion, the initial precipitate is a white mercuric chloro-sulfide, $2\text{HgS} \cdot \text{HgCl}_2$. Continued treatment with H_2S converts it to the black mercuric sulfide.

7. Test the action of dilute HCl or HNO_3 on each of the precipitates just obtained (except HgS). The HgNH_2Cl dissolves slowly in H^+ and more readily if NH_4^+ is also present at concentrations above 0.5 *M*.

8. At low acid concentration, the soluble ionized mercuric salts hydrolyze to form precipitates of basic salts. **Experiment.** Add some solid $\text{Hg}(\text{NO}_3)_2$ to 5 cc. of water. Heat the solution.

9. **Experiment.** Collect some HgS in a centrifuge cone and wash it with water. Transfer part of the precipitate to a porcelain dish, add 2 *N* HNO_3 , boil the mixture for about a minute,¹ and filter. Test filtrate for Hg^{++} . Repeat the

¹ By long boiling or the use of more concentrated acid the black sulfide is converted into a white, slightly soluble substance which is a double salt of mercuric nitrate and sulfide.

experiment with hot 2 *N* HNO₃ to which some HCl has been added. Suggest an explanation for the result of this experiment. Repeat the **experiment** with bromine solution instead of HNO₃.

10. Other reactions of mercurous ion. Experiment. Treat a dilute solution of Hg₂(NO₃)₂ with each of the following reagents:

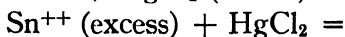
- (a) H₂SO₄ or a soluble sulfate in acid solution.
- (b) Na₂CO₃. Hg₂CO₃ readily decomposes upon warming into Hg, HgO, and CO₂.
- (c) NaOH. The precipitate is Hg₂O, which on heating, decomposes into Hg and HgO.
- (d) NH₄OH. The precipitate is a mixture of metallic mercury and an ammonobasic mercuric salt; see 6 (d).
- (e) H₂S in acid solution. The precipitate is a mixture of Hg and HgS.

11. From the results of your experiments in Paragraphs 5, 7, and 9, give methods for dissolving each of the precipitates obtained in 10. Try experiments whenever you are doubtful of your method.

12. Table of reactions for mercurous ion and mercuric ion. Summarize in a table for future reference the reactions of Hg₂⁺⁺ and Hg⁺⁺ with the following reagents: HCl, a strong oxidizing agent as Br₂, a strong reducing agent as SnCl₂ (in small amount and in excess), and the reagents used in Paragraphs 6 and 10. Below this table classify the precipitates according to reagents used in dissolving them and point out the considerations that led to the choice of each reagent. Be sure that you can write the equation for each reaction.

13. Problems. Try experiments when necessary.

(1) Complete the following equations, and indicate what you would observe in the corresponding experiments:



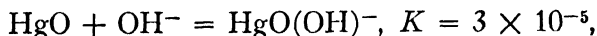
(2) What reaction is possible between a sulfide and hydrochloric acid? What reactions between a sulfide and nitric acid? In connection with your answers discuss the following experimental facts: CuS dissolves readily in hot 2 *N* HNO₃ but not in hot 2 *N* HCl.

(3) Compare the action of hot 2 *N* HNO₃ on CuS (Assignment 44) and HgS, and state what conclusion can be drawn with regard to the relative solubilities of these two sulfides in water. Outline a method of preparing pure HgCl₂ and pure CuSO₄ from a mixture of the freshly precipitated sulfides.

(4) Suggest methods of making the following preparations:

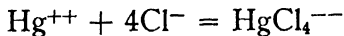
- (a) HgO from Hg(NO₃)₂.
- (b) Hg(NO₃)₂ from HgSO₄.
- (c) Hg(NO₃)₂ from Hg₂(NO₃)₂.
- (d) Hg₂(NO₃)₂ from Hg(NO₃)₂.

(5) *From the equilibrium data,



calculate the concentration of HgO(OH)⁻ in a saturated solution of HgO in 1 *M* NaOH.

(6) *For the reaction



the equilibrium constant is given as 9×10^{15} . Calculate the concentration of Hg⁺⁺ in a solution made by dissolving 0.01 mole of HgCl₂ in a liter of 1 *M* HCl.

Note. It is recommended that Assignment 62 follow Assignment 47.

Assignment 48

Aluminum

Special Material: Aluminum foil, aluminon paper.

1. Aluminum is a highly electropositive metal, but is rendered comparatively inert by an oxide coating on the surface. **Experiment.** Place a small strip of thin aluminum foil in a hot solution of HgCl_2 . The surface of the foil is quickly coated by an amalgam. Remove the foil after about 2 minutes and place it in a test-tube of boiling water. The evolution of hydrogen is readily observed.

2. **Aluminum and aluminate ions.** The only oxidation state of aluminum is the +3. The hydroxide is amphoteric and dissolves in acids to form Al^{+++} and in bases to form AlO_2^- (or H_2AlO_3^-). All of the common salts of Al^{+++} are soluble.

3. **Aluminum hydroxide. Experiment.** To very dilute solutions of an aluminum salt add NH_4OH a few drops at a time until, after shaking, the odor of ammonia is just perceptible. Warm the mixture, centrifuge, and discard the supernatant liquid. This is a delicate test for Al^{+++} . The fresh gelatinous precipitate is hydrous $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ [or $\text{AlO}(\text{OH})$] but upon standing it forms $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

4. When a solution of an aluminum salt is treated with a soluble carbonate or sulfide, the hydroxide of aluminum is precipitated. Explain.

5. **Experiment.** To a dilute solution of an aluminum salt add NaOH solution, drop by drop, with shaking, until the precipitate of aluminum hydroxide just redissolves. To the

resulting solution of sodium aluminate add some solid ammonium salt, and heat the mixture. Note what happens, and write the equation for the reaction.

6. **Aluminon test.** Aluminum hydroxide forms lakes with many dyes. **Experiment.** Secure from the office a strip of aluminon test paper. This contains a dye (ammonium salt of aurintricarboxylic acid) and ammonium acetate. Moisten the paper with a drop of AlCl_3 solution and hold over the mouth of an NH_4OH reagent bottle for 10 sec. Then wash it with $(\text{NH}_4)_2\text{CO}_3$ solution. Determine if you can use the test to distinguish between AlCl_3 and ZnCl_2 . A number of positive ions interfere with the test.

7. **Problems.** (1) Write the equation for the net reactions in the following: (a) Al is dissolved in NaOH , (b) a solution of sodium aluminate is slowly acidified with HCl , (c) Na_2S solution is added to AlCl_3 solution until a precipitate is formed.

(2) How could you prepare separate samples of (a) ZnS and $\text{Al}(\text{OH})_3$ from a solution containing Zn^{++} and Al^{+++} , (b) $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ from a solution containing Fe^{++} and Al^{+++} ?

(3) In the test for Al^{+++} , Paragraph 3, students frequently observe a flocculent precipitate when no Al^{+++} is present. An inspection of the NH_4OH reagent will disclose the fact that the precipitate came from the reagent. What was it?

Assignment 49

Chromium. Peroxides

Special Material: Sodium peroxide.

1. **Oxidation states.** Chromium is somewhat less electropositive than zinc, but, like aluminum, is rendered inert by an oxide coating. It forms the positive ions, Cr^{++} , chromous, and Cr^{+++} , chromic. The former is such a powerful reducing agent that it decomposes water with the evolution of H_2 . Chromic ion is very similar to Al^{+++} in its reactions. Chromate, CrO_4^{--} , and dichromate, $\text{Cr}_2\text{O}_7^{--}$, both belong to the +6 oxidation state; the former exists in alkaline solutions and the latter in acid. Dichromate in molal acid is an oxidizing agent of about the same strength as chlorine.

2. **Chromic hydroxide and chromite ion.** Repeat the experiments in Paragraphs 3 and 5, Assignment 48, using a chromic salt instead of an aluminum salt.

3. **Chromate ion and dichromate ion.** Note the colors of solutions of sodium (or potassium) chromate and dichromate. What is the color of CrO_4^{--} ? Of $\text{Cr}_2\text{O}_7^{--}$? **Experiment.** Add dilute HNO_3 or H_2SO_4 to a small quantity of a chromate solution. Add dilute NaOH or NH_4OH to a dichromate solution; acidify the solution obtained. From the equation for the reaction involved state how the equilibrium concentration of CrO_4^{--} in dilute acid solution varies with the concentration of H^+ .

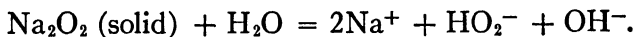
Arrange the ions of +3 and +6 chromium in a table to

show the principal substances present in (a) an acid solution, (b) an alkaline solution. State what would happen if a chromite solution were gradually acidified.

4. **Reduction of $\text{Cr}_2\text{O}_7^{--}$ and of CrO_4^{--} . Experiment.** Test the action of H_2S on very dilute solutions of a dichromate in the presence of sulfuric acid, heat the mixture to boiling, and filter off the precipitate (sulfur). Make the filtrate alkaline with NH_4OH . Repeat the **experiment** with H_2S and a very dilute solution of a chromate in the presence of NaOH ; heat, centrifuge, and wash the precipitate. Acidify the filtrate. **Experiment.** Determine the action of hot concentrated HCl on $\text{Cr}_2\text{O}_7^{--}$, and of Cl^- on CrO_4^{--} in alkaline solution.

5. **Oxidation of chromite ion. Experiment.** Prepare a small quantity of a chromite solution. To a portion of this add bromine solution; boil the solution to remove any free bromine that may remain. **Question.** What happens when chlorine is passed into a cold solution of NaOH ? Write the equation for the oxidation of CrO_2^- by ClO^- . **Experiment.** Boil a small quantity of a chromic salt solution with concentrated HNO_3 , or with aqua regia.

6. **Peroxides.** Sodium peroxide is a salt of the weak acid H_2O_2 . It is soluble in water and hydrolyzes completely to form HO_2^- .



The solution decomposes rapidly even at room temperature and almost with explosive violence at high temperatures.

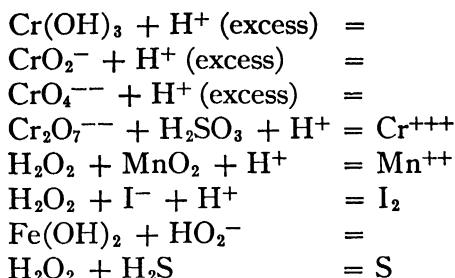


Na_2O_2 is a very powerful oxidizing agent and should be handled carefully. **Caution.** Never place it on paper. **Experiment.** Try the reaction of Na_2O_2 on a suspension of $\text{Cr}(\text{OH})_3$ or on a CrO_2^- solution.

7. Hydrogen peroxide in a cold dilute acid solution decomposes only very slowly. It is a good oxidizing agent, for

example, it oxidizes I^- readily to I_2 . Hydrogen peroxide is also a fairly good reducing agent. **Experiment.** To an acid solution of $Cr_2O_7^{--}$ add H_2O_2 solution. The deep blue color which first forms is a peroxy-acid of chromium, but the final product is Cr^{+++} . Write the half-reactions (in acid solutions) for H_2O_2 as (a) an oxidizing agent, (b) a reducing agent.

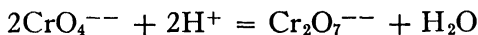
8. **Problems.** (1) Complete the following equations and state what would be observed in the corresponding experiments:



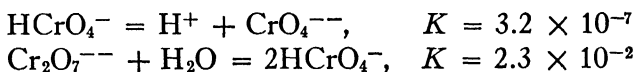
(2) State how you would prepare $Cr_2O_7^{--}$ from Cr^{+++} .

(3) Concentrated NH_4OH solution has a slight solvent action on $Cr(OH)_3$, but the hydroxide can be reprecipitated by adding an ammonium salt and warming the mixture. Explain.

(4) *Calculate the equilibrium constant for the reaction



from the following data.



What is the concentration of CrO_4^{--} in a solution which is 1 M with respect to H^+ and $Cr_2O_7^{--}$?

Assignment 50

Lead

Special Material: Lead dioxide. Strips of lead.

1. **Oxidation states.** The potential of the Pb—Pb^{++} couple is 0.126 volts. **Question.** Which is the better oxidizing agent, Pb^{++} or H^+ , Pb^{++} or Cu^{++} , Pb^{++} or Zn^{++} ? The dioxide, PbO_2 , in acid solution is one of the most powerful oxidizing agents. Plumbous hydroxide is amphoteric. The dioxide is only very slightly soluble in concentrated HNO_3 but freshly precipitated hydrous dioxide dissolves readily in concentrated NaOH .

2. **Tests for Pb^{++} .** **Experiment.** Prepare 10 or 20 cc. portions of 0.01, 0.001, and 0.0001 N $\text{Pb}(\text{NO}_3)_2$. Test 1 cc. portions of each solution with the following reagents:

- (a) HCl .
- (b) NaOH in small amount.
- (c) NaOH in excess.
- (d) NH_4OH in small amount.
- (e) NH_4OH in excess.
- (f) Na_2CO_3 . The precipitate is $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$. The normal carbonate is precipitated by NaHCO_3 .
- (g) H_2S in 0.3 N H^+ solution. If this precipitation is carried out in a hot solution containing a high concentration of Cl^- , the initial precipitate is the orange-red lead chloro-sulfide, $3\text{PbS} \cdot 2\text{PbCl}_2$. Continued treatment with H_2S converts it to the black lead sulfide.
- (h) Na_2S or $(\text{NH}_4)_2\text{S}$.
- (i) H_2SO_4 (dilute).
- (j) Na_2CrO_4 .

From the results of these experiments, arrange the slightly soluble salts in order of decreasing concentration of Pb^{++} in the saturated solution. Try additional experiments if necessary. Also locate the position in the list of HPbO_2^- in dilute sodium hydroxide, by determining which of the precipitates will dissolve in dilute NaOH .

3. Methods for dissolving slightly soluble lead salts. State which of the precipitates obtained in Paragraph 2 you would expect to dissolve in 2 N HNO_3 . **Experiments.**

(1) Prepare some PbS , collect it in a centrifuge cone, and test portions of it with (a) hot 2 N HCl , (b) hot 2 N HNO_3 .

(2) Prepare some PbCl_2 and test its solubility in cold water and in hot water.

(3) Collect some PbCrO_4 and test its solubility in (a) hot dilute HNO_3 , (b) hot concentrated HCl , and (c) dilute NaOH .

(4) Collect some PbSO_4 and investigate the effect upon it of (a) dilute NaOH , (b) H_2S , and (c) boiling with 1 N Na_2CO_3 solution. Test the liquid prepared in (c) for sulfate ion, and dissolve the solid in HNO_3 and test it for Pb^{++} .

4. Lead dioxide, PbO_2 . Experiment. Treat a small portion of PbO_2 with hot 6 N HCl . What gas is evolved? Repeat the experiment with HNO_3 instead of HCl .

5. Suggest experiments to determine the position of the couples $\text{Pb}—\text{Pb}^{++}$ and $\text{Pb}^{++}—\text{PbO}_2$ (H^+) in the table of oxidizing and reducing agents. How would the position of the latter couple vary with the concentration of H^+ ? If time permits verify your conclusion.

6. Lead storage battery. Several members of the class may make a storage battery and demonstrate its operation. First prepare three zinc-copper cells as in Assignment 31. These cells in series will give about 3 volts. Place two strips of lead in a small beaker containing 3 M H_2SO_4 . Electrolyze with the 3 volt potential until a heavy brown coat appears on the anode. Measure at once the voltage of the cell. Write the equations for the electrode reactions

and the cell reaction when the storage battery is being discharged. Which electrode is the anode when the battery is (a) discharging, (b) charging?

7. Problems. (1) Outline methods for making the following transformations:

- | | |
|---|---|
| (a) PbSO_4 to PbS . | (d) PbO_2 to $\text{Pb}(\text{NO}_3)_2$. |
| (b) PbS to PbSO_4 . | (e) PbSO_4 to $\text{Pb}(\text{NO}_3)_2$. |
| (c) PbCO_3 to PbCrO_4 . | |

(2) Name three amphoteric hydroxides. What would be observed on gradually acidifying a solution of sodium plumbite? Of sodium plumbate?

(3) When "red lead," Pb_3O_4 , is heated with HNO_3 or H_2SO_4 it is transformed into PbO_2 and a plumbous salt. Write the equation for the net reaction with each acid.

Assignment 51

Tin. Acidic Sulfides

Special Material: Metallic tin.

Reference. Hildebrand, Chapter XIII.

1. **Oxidation states.** Tin forms the ions, Sn^{++} , stannous, and Sn^{++++} , stannic. The corresponding hydroxides (or hydrous oxides) are amphoteric. **Question.** From the number of charges on the ions which hydroxide would you predict is the more readily soluble in H^+ ? **Note.** Although we have written Sn^{++++} , the principal ion in hydrochloric acid solutions is SnCl_6^{--} , and hydrolyzed ions such as SnOH^{+++} or $\text{Sn}(\text{OH})_2^{++}$ are doubtless present in nitrate and sulfate solutions even at high acid concentrations.

Tin dissolves slowly in H^+ to form stannous ion but the latter is not oxidized by H^+ to stannic. With these facts as a basis what conclusion can you draw regarding the following equilibrium?



In alkaline solutions stannite is unstable with respect to its decomposition into stannate and tin, but the decomposition appears to be repressed by high concentrations of OH^- .



2. **Ammonium polysulfide solution.** Alkaline sulfide solutions readily dissolve sulfur to form polysulfide (cf. LH). The polysulfide is a fairly strong oxidizing agent. **Experiment.** Prepare some colorless ammonium sulfide solution by passing

H_2S into 6 *N* NH_4OH . Acidify a portion of the $(\text{NH}_4)_2\text{S}$ solution at once. To another portion add a very small amount of powdered sulfur and note the change in color. Acidify the resulting polysulfide solution (or a small quantity of the laboratory ammonium polysulfide solution).

Questions. What can you state regarding the stability of polysulfide in acid solution? Colorless ammonium sulfide solutions become colored upon standing in contact with the air. Explain.

3. **Acid sulfides.** The variation of the acidic and basic properties of oxides (and hydroxides) was discussed in Assignment 28. Similar variations are found in the sulfides. Thus a basic sulfide reacts readily with H^+ , while a sulfide with acidic properties is soluble in excess of S^{--} (or SH^-). Stannic sulfide is an example of such a sulfide, and forms thiostannate ion, SnS_3^{--} (or HSnS_3^-). Stannous sulfide is not soluble in excess of $(\text{NH}_4)_2\text{S}$ but is oxidized by polysulfide to thiostannate.

4. **Reactions of Sn^{++} and Sn^{++++} .** **Experiment.** Prepare 0.1 *N* solutions of stannous chloride and of stannic chloride, and determine the action of the following reagents on each of these solutions:

- (a) H_2S in cold 0.3 *N* HCl solution. These tests are delicate and characteristic.
- (b) H_2S in hot 3 *N* HCl . **Note.** Native SnS_2 may fail to dissolve, even in hot 3 *N* HCl . It can be tested for sulfide by adding to the test-tube a small piece of zinc along with the SnS_2 .
- (c) NH_4OH in small amount and in excess.
- (d) NaOH in small amount and in excess. If there is a precipitate after adding NaOH in excess, centrifuge, acidify the liquid with HCl or H_2SO_4 , and test it for tin.
- (e) $(\text{NH}_4)_2\text{S}$ after NH_4OH has been added.
- (f) Ammonium polysulfide after NH_4OH has been added. Centrifuge to remove any precipitate that may remain undissolved, and acidify with HCl .

- (g) A soluble carbonate. Centrifuge, wash the precipitate, and test it for carbonate.
- (h) A good oxidizing agent in dilute acid solution, such as bromine.
- (i) A good reducing agent in dilute acid solution, as zinc.
- (j) HgCl_2 solution in small amount and in excess.

5. Action of concentrated HNO_3 on Sn. Experiment.

Treat a small piece of tin with concentrated HNO_3 in a casserole. Evaporate the mixture **just to dryness**: to avoid heating the residue strongly, evaporate the last portions of the liquid by moving the casserole back and forth through a small flame. Warm the residue with dilute HNO_3 , filter, and test the filtrate for tin. **Note.** Stannic acid, or hydrous stannic oxide, when prepared in this way by the action of concentrated HNO_3 on Sn or on a compound of tin, does not dissolve in HNO_3 . **Experiment.** Suggest and try methods of dissolving this substance (cf. LH).

6. **Problems.** (1) If a solution were known to be either SnCl_2 or SnCl_4 how would you identify it?

(2) How would you test for SnCl_2 in a solution of SnCl_4 ?

(3) What happens when HCl is added gradually to a solution of (a) sodium stannite, (b) sodium stannate, (c) sodium stannite after it has been treated with a powerful oxidizing agent, as sodium peroxide, Na_2O_2 , or hypochlorite, (d) sodium thiostannate?

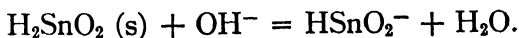
(4) How would you prepare (a) sodium polysulfide solution, (b) sodium thiostannate solution from SnS_2 , (c) sodium thiostannate solution from SnS , (d) SnS_2 from sodium thiostannate?

(5) HgS has weakly acidic properties. It is much more soluble in Na_2S solutions than in $(\text{NH}_4)_2\text{S}$. Explain.

(6) *From the solubility product,



calculate the constant for the reaction



Assignment 52

Chemistry of Manganese. The Use of Permanganate in Quantitative Analysis

Special Materials: Standardized KMnO_4 . Samples of unknown oxalates. Burets and clamps.

1. Manganese forms the ions: Mn^{++} , manganous; Mn^{+++} , manganic; MnO_4^{--} , manganate; and MnO_4^- , permanganate. A solution of the tetrachloride MnCl_4 , a weak salt, may be prepared in cold concentrated hydrochloric acid but the salts of the oxygen acids with +4 manganese are completely hydrolyzed to the dioxide even in concentrated acid solutions. In this Assignment the properties of the compounds of the various oxidation states will be studied, and an example will be given of the use of permanganate solutions in quantitative analysis.

2. Manganous ion forms sparingly soluble compounds with sulfide, hydroxide, carbonate, ferrocyanide, and phosphate. **Experiment.** Form a precipitate of the hydroxide and determine whether it is sufficiently soluble to dissolve in solutions of ammonium salts. Saturate an acid solution of Mn^{++} with hydrogen sulfide and then add ammonium hydroxide. With which group of ions will Mn^{++} precipitate in the standard scheme of analysis?

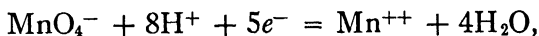
3. Expose a small amount of manganous hydroxide to the air for some time: manganic hydroxide is formed. Dis-

solve the compound in sulfuric acid: manganese dioxide is precipitated. Explain.

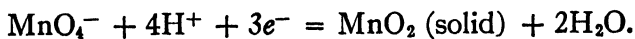
4. To a dilute alkaline solution of permanganate add manganese dioxide. What change in color of the solution takes place upon standing a few minutes? Pour off two portions of the resulting solution. To one add sulfuric acid. Write the equation for the reaction which occurs and discuss the conditions for its reversibility. To the other portion add bleaching powder.

5. Try the effect of adding KMnO_4 drop by drop to (a) neutral, (b) acid ($0.5\ M\ \text{H}_2\text{SO}_4$) solutions of manganous sulfate. Is the reaction favored by a high or low concentration of H^+ ? Add one drop of manganous sulfate solution to a tube containing Pb_3O_4 or PbO_2 in $3\ N$ sulfuric acid. Boil the solution. What evidence for the formation of MnO_4^- is obtained?

6. The importance of KMnO_4 in volumetric analysis depends upon its ability to oxidize quantitatively a very large number of substances (cf. LH XVIII). When permanganate is reduced in acid solution to Mn^{++} it is evident from the equation,



that five equivalents of negative electricity are given up by the reducing agent per mole of MnO_4^- . A mole of MnO_4^- may then in such reactions be considered to be **5 equivalents** of oxidizing agent, and a **normal oxidizing solution of KMnO_4** is defined as $\frac{1}{5}\ M$ when the reduction product is Mn^{++} . This conforms to the general practice in volumetric analysis of expressing all concentrations of oxidizing or reducing agents in terms of the number of equivalents of the oxidizing or reducing agent per liter. In certain reactions (neutral solution) MnO_4^- is reduced to MnO_2 according to the equation



If a permanganate solution is 1 *N* when Mn^{++} is the reduction product, what is the normality of the solution when MnO_2 is the reduction product? How many moles of I_2 would be liberated by adding 50 cc. of 0.8 *N* KMnO_4 to excess KI solution in the presence of acid?

7. Standardization of KMnO_4 solutions. The starting point in the standardization of any solution for use in volumetric analysis is an exact weight of some pure compound. Commercial KMnO_4 is not of sufficient purity to permit the standardization of KMnO_4 solution by weighing out the salt directly. The substances usually used are (1) $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, (2) pure iron, (3) $\text{Na}_2\text{C}_2\text{O}_4$ or $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The first of these may be dissolved and titrated directly with permanganate, the ferrous iron being oxidized to ferric. When pure iron is the standard it is necessary to first oxidize it to the ferrous state with acid. Oxalate is oxidized to carbon dioxide, $\text{C}_2\text{O}_4^{--} = 2\text{CO}_2 + 2e^-$. Of these standards the sodium oxalate is considered the most desirable. In making up a solution of potassium permanganate, the salt should be dissolved in hot water and filtered through asbestos (why not paper?) to remove MnO_2 . **Question.** What weight of $\text{Na}_2\text{C}_2\text{O}_4$ would it be necessary to take in order to use 50 cc. of 0.1 *N* KMnO_4 ?

8. Determination of an unknown oxalate. Secure from the storeroom a quantity of standardized permanganate solution (about 0.1 *N*) and a sample of unknown oxalate. In a 400 cc. beaker dissolve in 200–250 cc. of hot water (80–90° C.) a quantity of the unknown which will require about 40 cc. of the permanganate solution. (This may be determined by a preliminary titration.) Add 30 cc. of 6 *N* H_2SO_4 . Titrate at once, stirring the solution vigorously. The permanganate must not be added more rapidly than 10–15 cc. per minute and the last cc. must be added dropwise with care to allow each drop to decolorize before the next is added. The end-point is of course the character-

istic permanganate color. Report the per cent C_2O_4 in the sample.

9. Problems. (1) Outline a method by which the reaction between permanganate and oxalate could be used to determine the amount of calcium in a limestone.

(2) How could permanganate be used to determine the iron in a sample containing Fe_2O_3 ?

(3) What quantity of permanganate would be required to titrate 10 cc. of a 3 per cent (by weight) H_2O_2 solution?

Section IV

Qualitative Analysis

Assignment 61

The Development of a Scheme of Analysis for a Limited Number of Positive Ions

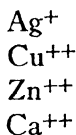
(To follow Assignment 45)

Special Material: "Unknowns" for analysis, Paragraph 10; the student should supply 2 clean sample bottles labelled 61, I and 61, II.

1. In this and the following two Assignments we shall consider the general problem of the analysis of a solution containing the positive ions studied in Assignments 41 to 51. The extension of a system of analysis to include a larger number of elements offers no difficulty in principle, but it can become exceedingly time-consuming—mainly on account of the many experiments which must be made in order to prove that the proposed methods are satisfactory. The experiments in these Assignments are designed to illustrate and emphasize general principles, and only a limited number of elements are included. If you have occasion to make an analysis for elements not included in this course, reference should be made to a standard textbook such as E. H. Swift's *A System of Chemical Analysis*. If you have mastered the general principles, it should not be difficult for you to use such a text, provided you work through the procedures first with known solutions and examine the chemistry involved.

2. **Table of reactions.** (Most of the material in this Paragraph may be written up at home before undertaking the later experimental work.) In planning the analysis of a

solution containing several positive ions, it is necessary to have clearly in mind the chemical properties of those ions. Prepare a tabular summary of the reactions between dilute solutions of the ions



and the following reagents:

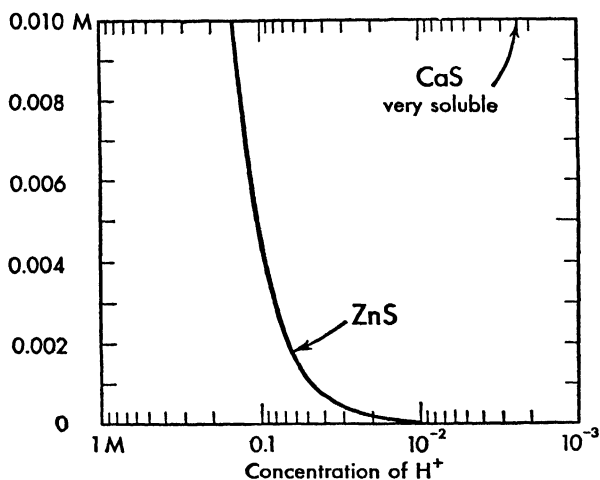
- (a) NaOH solution in excess.
- (b) NH_4OH solution in excess.
- (c) H_2S in 0.3 N H^+ solution.
- (d) A soluble sulfide such as Na_2S , or $(\text{NH}_4)_2\text{S}$ in NH_4OH solution.
- (e) HCl or a soluble chloride.
- (f) H_2SO_4 or a soluble sulfate.
- (g) A soluble carbonate.
- (h) A soluble chromate.
- (i) A metal which is a good reducing agent, e. g., Fe, Zn, or Al.

When no reaction takes place, mark X at the proper place in your table. When a reaction does occur, write the formula of the substance formed, mark the precipitates by underlining their formulas, and note the colors. Refer freely to your laboratory notes for the information you need, and try additional experiments whenever necessary, e. g., when your laboratory notes are incomplete or seem to be incorrect. **Question.** Would Na^+ , K^+ , or NH_4^+ react with any of the reagents in the preceding list?

3. One conceivable method of analysis would be to have a series of special reagents, each reagent sensitive to one particular ion and that ion only. Then, if seven ions were to be considered, the original solution would be divided into seven separate portions, and each portion would be tested with one of the special reagents. This sort of technique is

impracticable because such highly specific reagents do not, in general, exist.

Instead, in systematic qualitative analysis the method has been adopted of treating a single portion of the unknown solution with a succession of reagents. This process divides the ions present into groups, divides each of these groups into subgroups, and so on, until finally each kind of ion is found in a separate portion of the solution. It is then easy to prepare any desired pure compound of each metal.



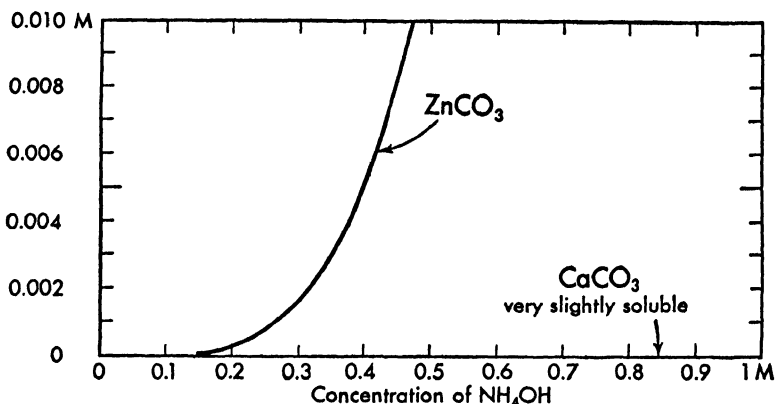
Solubility of CaS and ZnS in water saturated with H₂S, at various concentrations of ⁺H.

4. As an illustration we shall discuss the preparation of pure salts of zinc and calcium from a solution containing Zn⁺⁺ and Ca⁺⁺. The Table in Paragraph 2 shows the following differences between zinc and calcium ions, which may be utilized for their separation:

(1) CaS is so soluble in water that it cannot be prepared from an aqueous solution, while ZnS is sparingly soluble in any solution whose H⁺ concentration is less than about 10⁻² M. (The accompanying graph shows the solubility of ZnS at various hydrogen ion concentrations, as computed

from the solubility product of ZnS and the ionization constants of H_2S). If the solution containing Zn^{++} and Ca^{++} is adjusted to an acidity of less than $10^{-2} M$ (say, by the addition of NH_4OH) and H_2S is passed into it, the Ca^{++} will remain in solution and the zinc will be practically completely precipitated as ZnS .

(2) Both ZnCO_3 and CaCO_3 are sparingly soluble in water. Zn^{++} forms a complex ion with ammonia, so that zinc carbonate is readily soluble in NH_4OH . Ca^{++} does not form a complex ion with ammonia and its carbonate is quite



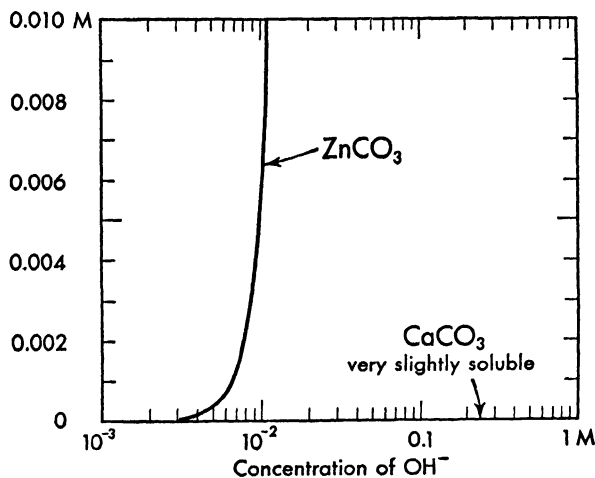
Solubility of CaCO_3 and ZnCO_3 in $1 M \text{CO}_3^{--}$, at various concentrations of NH_4OH .

unaffected by NH_4OH . (The solubility of ZnCO_3 in ammonium hydroxide of various concentrations is shown in the accompanying graph, as computed from the solubility product of ZnCO_3 and the equilibrium constant for the formation of $\text{Zn}(\text{NH}_3)_4^{++}$.) If the solution containing Zn^{++} and Ca^{++} is treated with a solution containing NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, the calcium precipitates as carbonate and the zinc remains in solution as $\text{Zn}(\text{NH}_3)_4^{++}$.

(3) Zn^{++} is converted into zincate ion by excess of a strong base, so that ZnCO_3 dissolves readily in NaOH solution. CaCO_3 is unaffected by NaOH solution. (The solubil-

ity of ZnCO_3 at various concentrations of OH^- is shown in the accompanying graph, as computed from the solubility product of ZnCO_3 and the equilibrium constant for the formation of ZnO_2^{--} .) If the solution containing Zn^{++} and Ca^{++} is treated with a solution of NaOH and Na_2CO_3 , the calcium precipitates as CaCO_3 and the zinc remains in solution as ZnO_2^{--} .

5. With the aid of your Table of Reactions plan several methods of separating silver ion from calcium ion. By



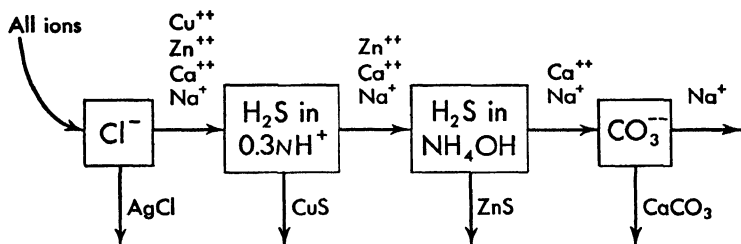
Solubility of CaCO_3 and ZnCO_3 in 1 M CO_3^{--} , at various concentrations of OH^- .

combining one of your proposed methods with one of the methods for separating zinc ion from calcium ion, devise a "scheme of analysis" for these three positive ions, silver, zinc, and calcium. What will cupric ion do if treated by your scheme of analysis? Modify your scheme to include a separation of cupric ion. Where would sodium ion be found in a solution analyzed by your scheme?

Show your scheme of analysis for the five positive constituents to your instructor. Test your scheme by applying it to dilute solutions (about 1 drop of 1 N reagent in 5 cc.

of water) of (a) a silver salt alone, (b) a zinc salt alone, (c) a cupric salt alone, and (d) a calcium salt alone. In each experiment a satisfactory test should be obtained for the metal known to be present, and blanks in the tests for all the others.

6. One of the most satisfactory schemes, and the one used in practically all text-books, is the following:



(In this flow-sheet the reagent used in each separation is enclosed in a box, the precipitate resulting from the treatment is written along the downward arrow, and the solution along the horizontal arrow.)

Procedure for the Separation of the Chloride Group.

To the unknown solution add 1 *N* HCl or 1 *N* NH_4Cl , one drop at a time, until no more precipitate forms. Avoid adding a large excess of the chloride reagent. Centrifuge the mixture. The precipitate is AgCl , and the solution contains Cu^{++} , Zn^{++} , Ca^{++} , and Na^+ .

Procedure for the Separation of the Hydrogen Sulfide Group. Add a drop of methyl violet indicator to the unknown solution, and adjust the H^+ concentration to approximately 0.3 *N* by adding a drop or two of dilute HCl or dilute NH_4OH as required. Put the solution into a small flask and saturate it with H_2S gas (cf. Appendix 1F). Centrifuge the mixture. The precipitate is CuS and the solution contains Zn^{++} , Ca^{++} , and Na^+ . It is well to pass H_2S into the solution a second time, to be sure all the CuS has been precipitated.

Procedure for the Separation of the Ammonium Sulfide Group. Boil the solution for a short time in an open beaker, to expel the H_2S . Add a few cc. of NH_4OH solution, enough to give the solution an odor of ammonia. Put the solution into a small flask and saturate it with H_2S . Place the flask in a beaker of boiling water for a few minutes, in order to coagulate any colloidal sulfides. Centrifuge the mixture. The precipitate is ZnS and the solution contains Ca^{++} and Na^+ . It is well to pass H_2S into the solution a second time, to be sure all the ZnS has been precipitated.

Procedure for the Separation of the Carbonate Group. To the solution add a few cc. of $(\text{NH}_4)_2\text{CO}_3$ reagent, warm the mixture and then allow it to stand for some time. Centrifuge: the precipitate is CaCO_3 and the solution contains Na^+ .

7. When an unknown solution has been analyzed according to a scheme of analysis and some result is inconclusive, owing for example to the small size of the precipitate, a **confirmatory test** is made whenever possible. Thus a confirmatory test for silver may be carried out by dissolving the AgCl in NH_4OH and reprecipitating the chloride by acidifying; copper may be confirmed by dissolving the CuS in hot nitric acid and adding NH_4OH to obtain the deep blue complex ion; zinc may be confirmed by dissolving the ZnS in acid and then forming the green cobalt zincate; and a flame test may be used to confirm the presence of calcium or sodium.

8. **Alternative schemes of analysis.** Devise schemes of analysis for the positive ions considered in this Assignment, to meet the specifications listed below. Write each scheme in the form of a flow sheet like that in Paragraph 6. It is not necessary to write out the full details of each procedure.

(1) 1 *N* NaOH is the first reagent used.

(2) A solution of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ is the first reagent used.

(3) The unknown is first treated with metallic iron.

(4) A scheme which does not use H_2S .

9. Problems. (1) What negative ions need not be tested for in solutions which contain the following positive ions:

(a) H^+ , (b) Ca^{++} , (c) Zn^{++} , (d) Cu^{++} , (e) Ag^+ ?

(2) Point out the errors in the following reports:

(a) A solution known to contain Ag^+ was reported to contain SO_4^{--} because BaCl_2 gave a white precipitate which did not dissolve in HNO_3 .

(b) A pure sodium salt which dissolved in water to give an alkaline solution was reported to be a sulfate because a white precipitate was obtained on the addition of $\text{Ba}(\text{NO}_3)_2$.

(c) Chloride was reported absent in a solution known to contain NH_4OH because no precipitate formed when AgNO_3 was added.

10. Analyses 61, I and II. Test for the positive and negative constituents:

H^+ , Ag^+ , Cu^{++} , Zn^{++} , Ca^{++} , Na^+ , K^+ , NH_4^+ ,
 OH^- , Cl^- , NO_3^- , SO_4^{--} , CO_3^{--} , S^{--} .

Record at once each experiment and observation and write down any conclusion that has bearing on the identification. Try to distinguish between large amounts, small amounts, and traces of the different constituents. When you report the result of an analysis to your laboratory instructor show him your note book record.

Assignment 62

Iron and Mercury in the Scheme of Analysis. Methods of Dissolving Difficultly Soluble Substances

(To follow Assignment 47)

Special Material: "Unknowns" for analysis, Paragraph 11.

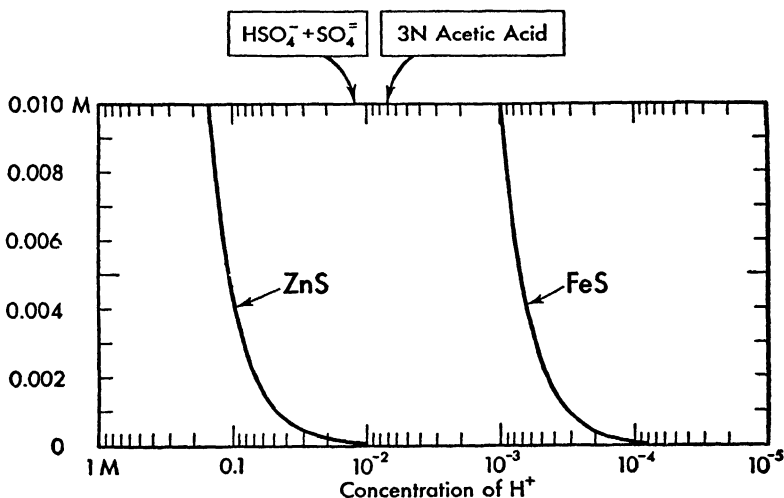
1. Extend your Table of Reactions (Assignment 61, Paragraph 2) to include Fe^{++} and Fe^{+++} , Hg_2^{++} and Hg^{++} .

2. **Separation of ZnS from FeS.** Since FeS and ZnS will precipitate together from an ammoniacal solution, it is necessary to devise a scheme for their separation. This is more difficult than one would surmise from a study of the individual ions. One obvious method would be to dissolve the sulfides in HCl, boil off the H_2S , oxidize the Fe^{++} to Fe^{+++} by boiling with nitric acid or with bromine, and then add an excess of NH_4OH in the hope that this will precipitate $\text{Fe}(\text{OH})_3$ but will hold the zinc in solution as $\text{Zn}(\text{NH}_3)_4^{++}$. Another method of treating the solution containing Fe^{+++} and Zn^{++} which has been prepared from the sulfides would be to add an excess of NaOH, in the hope of precipitating $\text{Fe}(\text{OH})_3$ but keeping the zinc in solution as HZnO_2^- . However, in both of these procedures the $\text{Fe}(\text{OH})_3$ carries with it much of the zinc. We shall discuss below two other procedures, which do give satisfactory separations of zinc from iron.

(1) Advantage may be taken of the difference in solubility of ZnS and FeS: the solubility products of the sulfides

are 4.5×10^{-24} and 1×10^{-19} respectively. The accompanying graph shows the computed solubilities of the two sulfides in water saturated with H_2S , at various acidities. We observe from the graph that if the H^+ concentration is maintained at 10^{-2} N , ZnS is only sparingly soluble but FeS is easily soluble. This acidity can be obtained by use of a buffer solution containing equimolar HSO_4^- and SO_4^{--} , or by use of rather concentrated acetic acid.

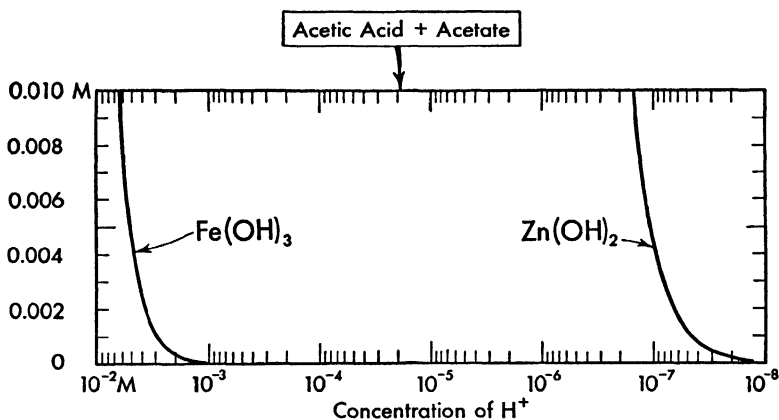
(2) Advantage may be taken of the difference in solubility of $\text{Fe}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$: the solubility products of the



Solubility of ZnS and FeS in water saturated with H_2S , at various concentrations of H^+ .

hydroxides are 4×10^{-38} and 4.5×10^{-17} respectively. The accompanying graph shows the computed solubilities of the two hydroxides, as a function of the acidity of the solution. We observe that over a wide range of H^+ concentration $\text{Fe}(\text{OH})_3$ is only sparingly soluble while $\text{Zn}(\text{OH})_2$ is easily soluble. A convenient buffer solution for the separation contains equimolar acetic acid and sodium acetate, giving a H^+ concentration of $1.8 \times 10^{-5} \text{ N}$.

Experiment. Prepare some solid ZnS and some solid FeS , and investigate the effect on each of boiling it with a buffer solution prepared by adding 0.5 cc. of 6 N H_2SO_4 to 10 cc. of 1 N Na_2SO_4 . Prepare solutions containing Fe^{+++} and Zn^{++} respectively, make them approximately 1 M with respect to acetic acid and 1 M with respect to sodium acetate, and boil them for five or ten minutes.

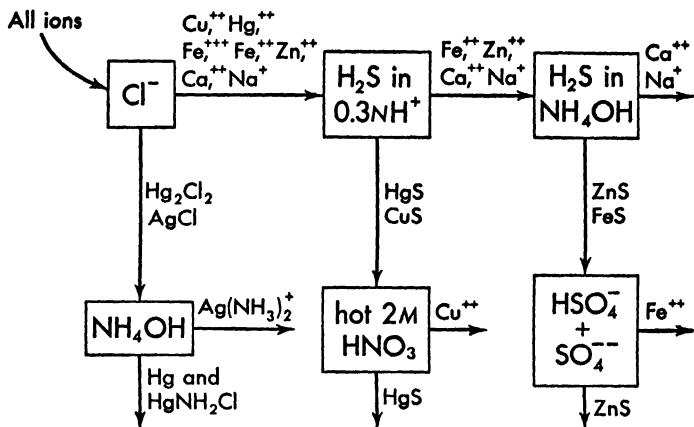


Solubility of $\text{Fe}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$, at various concentrations of H^+ .

3. Separation of CuS from HgS . **Experiment.** Test the solubility in hot 2 M HNO_3 of (a) CuS alone, and (b) a mixture of CuS and HgS . Why is the sulfur residue black when CuS alone is tested? Devise a confirmatory test for Hg^{++} . **Question.** What mistake has been made if in the analysis of a pure mercuric salt a heavy black precipitate is obtained with sulfide in the NH_4OH solution?

4. Separation of AgCl from Hg_2Cl_2 . **Experiment.** Investigate the effect of NH_4OH on (a) AgCl , (b) Hg_2Cl_2 , and (c) a mixture of the two.

5. The standard scheme of analysis. The scheme of analysis given in Paragraph 6 of Assignment 61 can be extended in the following way to include the ions of mercury and iron:



Procedure for the Separation of Silver from Mercurous Mercury. To the washed precipitate of AgCl and Hg_2Cl_2 in the centrifuge cone, add a few cc. of 6 *N* NH_4OH and then centrifuge. A black precipitate at this point is a mixture of Hg and HgNH_2Cl . The supernatant liquid contains the $\text{Ag}(\text{NH}_3)_2^+$, which can be reconverted to AgCl by acidifying.

Procedure for the Separation of Copper from Mercuric Mercury. To the washed precipitate of CuS and HgS in the centrifuge cone add a few cc. of 2 *M* nitric acid, place the centrifuge cone in a beaker of boiling water for about ten minutes, and then centrifuge. The supernatant liquid, which contains the Cu^{++} , can be withdrawn and tested for Cu^{++} by the addition of NH_4OH . HgS is unattacked by the hot nitric acid, so remains as a precipitate, which can be dissolved in a mixture of hot HNO_3 and HCl . The reaction with stannous chloride is a suitable confirmatory test for Hg^{++} .

Procedure for the Separation of Iron from Zinc. To the washed precipitate of ZnS and FeS in the centrifuge

cone, add a few cc. of bisulfate-sulfate buffer (as prepared in Paragraph 2), place the cone in a beaker of boiling water for a few minutes, and then centrifuge. The FeS will dissolve under this treatment, while the ZnS will be almost unattacked. The ferrous ion in the supernatant liquid can be reconverted to FeS by the addition of $(\text{NH}_4)_2\text{S}$ reagent.

6. Alternative schemes of analysis. Where will the ions Hg_2^{++} , Hg^{++} , Fe^{++} , and Fe^{+++} appear in the schemes of analysis you devised in Paragraph 8, Assignment 61? Extend or revise your schemes to include these additional ions.

DIRECTIONS FOR THE ANALYSIS OF SOLIDS

7. Analysis of an unknown solid. Treat a small portion (a few milligrams) of the solid with water in a small test-tube. If the solid does not dissolve readily in cold water, heat the water to boiling. When you are in doubt as to whether any of the solid has dissolved, you can evaporate a few drops of the clear solution to dryness on a watch-glass; or you can add to a portion of the clear solution a drop of Na_2CO_3 solution, which will precipitate the carbonate of practically any metal whose ion may be present.

If the solid does not dissolve in water, try preliminary experiments (such as are suggested in the next Paragraph) with small quantities of the powdered substance until you find a suitable solvent.

When a method for dissolving the substance has been found, dissolve about 0.1 gram of it in 10 cc. of the solvent, and treat the resulting solution according to the scheme of analysis. Set aside the remaining solid, portions of which may later be used in testing for NH_4^+ and the negative constituents, and for making confirmatory tests.

Before precipitating the copper group with H_2S , be sure the concentration of H^+ is approximately 0.3 *N*. **Question.** Outline two methods for adjusting the H^+ concentration to 0.3 *N*.

8. Methods of dissolving a difficultly soluble, pure substance. Observations in these preliminary experiments with small quantities of the solid may be of great assistance in identifying the substance. (In the following, some substances are mentioned which will not be encountered in the Analyses in this Assignment, Paragraph 11.)

(1) Treatment with dilute acid. First try 1 *N* HNO_3 ; boil if necessary. If not soluble try hot 1 *N* HCl . Anhydrous oxides generally dissolve more rapidly in HCl than in HNO_3 but an oxide like Fe_2O_3 may require a long time. If HCl is used, the slightly soluble chlorides, AgCl and Hg_2Cl_2 , may be formed. Similarly BaSO_4 or PbSO_4 might form if H_2SO_4 were used. The treatment with HNO_3 will also dissolve salts which, although soluble in water, readily hydrolyze (unless acid is present) to form slightly soluble basic salts. This is particularly true of some salts of mercuric ion.

(2) Treatment with hot concentrated HCl . If chlorine is evolved a very powerful oxidizing agent is present, such as MnO_2 , PbCrO_4 , or PbO_2 . Concentrated HCl dissolves AgCl readily, with formation of complex negative ions, but the chloride precipitates again when water is added to dilute the acid.

(3) Treatment with hot concentrated HNO_3 , a powerful oxidizing agent. The rapid formation of brown gases indicates the presence of a reducing agent. There is a residue of sulfur after the action of nitric acid on a sulfide, and the solution will contain some SO_4^{--} .

(4) Treatment with either (a) a mixture of concentrated HCl and HNO_3 (aqua regia) or (b) bromine water. A few substances, as HgS , are dissolved more readily by these reagents than by concentrated HNO_3 (which is really a more powerful oxidizing agent) on account of the formation of weak electrolytes or complex ions.

Note. Before using for analysis a solution containing concentrated acid evaporate it almost to dryness to remove

the excess of acid, and add water. Question. What happens when H_2S is passed into concentrated HNO_3 or aqua regia?

(5) Treatment with Na_2CO_3 solution to form a carbonate. Some slightly soluble salts of strong or only slightly weak acids may be transformed into carbonates which will then dissolve in dilute HNO_3 . Use a concentrated solution of Na_2CO_3 in a porcelain dish, cover the dish with a watch-glass, and boil for several minutes. Filter and retain the filtrate to test for the negative constituent. Treat the residue with dilute HNO_3 , filter if necessary, and analyze this solution for the positive constituent. Review the action of Na_2CO_3 solution on CaSO_4 , Assignment 42; and, **experiment**, try the above procedure with BaSO_4 .

(6) Treatment with NH_4OH or with NaOH . If an otherwise insoluble salt dissolves in NH_4OH , it is obviously a compound of a positive ion which forms an ammonia complex. If it dissolves in NaOH , it is a compound of an element whose hydroxide is amphoteric. Salts which have been dissolved in these alkaline solutions can be converted to the sulfides by $(\text{NH}_4)_2\text{S}$ and these sulfides dissolved by oxidation with concentrated HNO_3 .

(7) Certain intractable substances can be brought into solution only by a more drastic treatment than any discussed above. For example, most silicate minerals will dissolve in HF , with the evolution of gaseous SiF_4 . Insoluble oxides and phosphates such as those of titanium and zirconium may be rendered soluble by treatment with molten $\text{K}_2\text{S}_2\text{O}_7$. Some alloys, such as those of the platinum metals, and some acid-resistant steels, require treatment with molten Na_2O_2 .

9. When the unknown is a mixture of solid salts, the same method of procedure may be followed in order to determine a method of dissolving the solid completely. However, it is often convenient to analyze separately the portions dissolved in the different operations. For example,

the mixture might consist of one salt which dissolves readily in water or dilute HNO_3 , and a second salt which does not. If this method is followed, care should be taken to dissolve the first salt completely before continuing the experiments with the residue. **Note.** Frequently when a mixture of two salts, as AgNO_3 and NaCl , is treated with water a reaction takes place.

10. Problems. (1) What reagent would you use to dissolve each substance in the following list?

- | | |
|-------------------------|------------------------------|
| (a) Ag | (j) $\text{Fe}(\text{OH})_3$ |
| (b) AgCl | (k) Hg_2Cl_2 |
| (c) BaCrO_4 | (l) HgS |
| (d) BaSO_4 | (m) PbCl_2 |
| (e) CaCO_3 | (n) PbCrO_4 |
| (f) CuO | (o) PbO_2 |
| (g) CuS | (p) PbSO_4 |
| (h) brass (Cu-Zn alloy) | (q) SnO_2 |
| (i) Fe | (r) SnS_2 |

(2) A strongly ammoniacal solution was tested for silver (a) by acidifying with HNO_3 and adding a little HCl , (b) by acidifying with HCl . A white precipitate formed in (a) but not in (b). Explain.

(3) At equilibrium in the reaction, $\text{BaSO}_4 + \text{CO}_3^{--} = \text{BaCO}_3 + \text{SO}_4^{--}$, the ratio of the concentration of SO_4^{--} to that of CO_3^{--} is 0.01. What weight of BaSO_4 can be converted into BaCO_3 by a single treatment with 50 cc. of M Na_2CO_3 ?

11. Analyses 62, I, II, and III. In addition to the positive and negative constituents considered in Assignment 61, test for Fe^{++} , Fe^{+++} , Hg_2^{++} , and Hg^{++} . Before starting your unknowns, test your scheme of analysis for the positive constituents with a solution made by adding 1 drop of 1 N solution of each of the ions (as nitrates) to about 10 cc. of water.

Assignment 63

Lead, Tin, Aluminum, Chromium, and Barium in the Scheme of Analysis

(To follow Assignment 51)

Special Material: "Unknowns" for analysis, Paragraph 9.

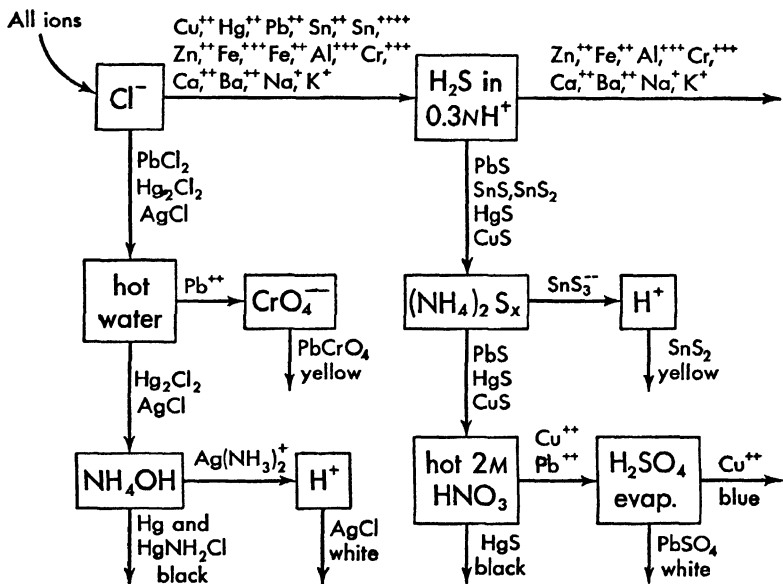
1. Extend your Table of Reactions to include Pb^{++} , Sn^{++} and Sn^{++++} , Cr^{+++} , and Ba^{++} . State what would be observed if a solution containing these five ions were treated by the scheme of analysis you used in Assignment 62.

2. **Lead in the scheme of analysis.** Suggest a method of determining whether a white precipitate obtained with HCl contains any PbCl_2 . What would be the result of treating a mixture of HgS , CuS , and PbS with hot 2 N HNO_3 (cf. Assignment 62, Paragraph 3)? Give two reactions which are characteristic of Pb^{++} but not of Cu^{++} , and one reaction which is characteristic of Cu^{++} but not of Pb^{++} . Suggest a method of separating lead from copper and mercury, i. e., of including lead in the scheme of analysis. **Experiment.** Test your method with known solutions.

3. **Tin in the scheme of analysis.** Suggest a method of removing SnS and SnS_2 from a precipitate which also contains PbS , CuS , and HgS . **Note.** While colorless $(\text{NH}_4)_2\text{S}$ solution does not dissolve PbS , CuS , or HgS , some CuS dissolves in ammonium polysulfide, and much HgS in concentrated Na_2S . The use of polysulfide may be avoided if Sn^{++} is known to be absent in the original unknown or if it has been oxidized to the +4 state. **Experiment.** Try your

procedure on various mixtures of the tin sulfides with PbS, CuS, and HgS. Your method should include the reprecipitation of SnS_2 from the thiostannate solution. Try a blank test with copper present but no tin.

4. **The standard scheme of analysis: chloride group and hydrogen sulfide group.** The scheme of analysis given in Paragraph 5 of Assignment 62 can be extended in the following way to include the ions of lead and tin:



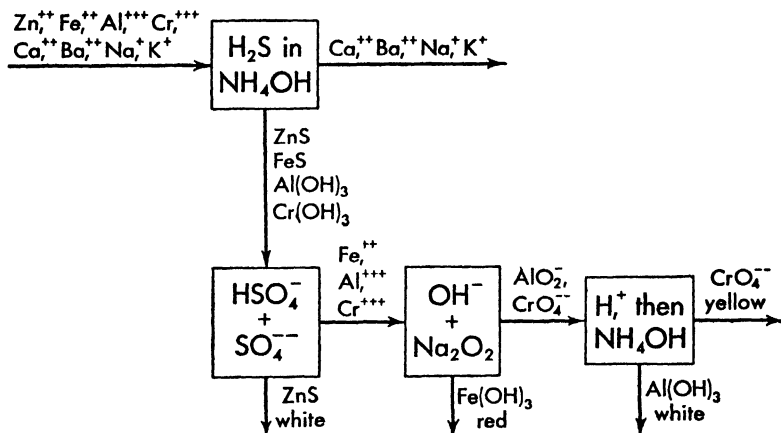
Procedure for the Separation of Lead from Silver and Mercurous Mercury. To the washed precipitate of AgCl , Hg_2Cl_2 , and PbCl_2 in the centrifuge cone, add distilled water. Put the cone into a beaker of boiling water and leave it until the mixture is thoroughly heated, then centrifuge the hot mixture briefly and remove the hot supernatant liquid at once. The liquid contains the Pb^{++} , which can be converted into PbCrO_4 by the addition of a drop of sodium chromate solution.

AgCl and Hg_2Cl_2 are unaffected by the treatment with hot water.

Procedure for the Separation of Stannous and Stannic Tin from Copper, Lead, and Mercuric Mercury. To the centrifuged and washed mixture of sulfides resulting from the H_2S precipitation in $0.3\text{ }N\text{ H}^+$, add 1 to 5 cc. of ammonium polysulfide reagent. Warm the mixture for several minutes, then centrifuge it and withdraw the supernatant liquid, which contains the tin as SnS_3^{--} . The tin can be precipitated as SnS_2 by acidifying the solution of thiostannate. HgS and PbS are unaffected, and CuS is only slightly attacked, by the ammonium polysulfide reagent.

Procedure for the Separation of Lead from Copper. The supernatant liquid resulting from the treatment of HgS , CuS , and PbS with hot $2\text{ }M$ nitric acid will contain the Pb^{++} and Cu^{++} . Remove this liquid from the unattacked HgS , put it in a casserole, and add 1 cc. of concentrated H_2SO_4 . Heat the casserole over a flame while keeping it continuously in swirling motion, until the solution has so far evaporated that dense white fumes of SO_3 appear. Allow the casserole to cool, then pour into it (caution!) 5 cc. of water. Allow the solution to stand for about ten minutes, then centrifuge it. The lead appears as a white precipitate of PbSO_4 , while the Cu^{++} remains in solution. The supernatant liquid can be removed and NH_4OH added to it to obtain the blue tetrammine cupric ion. **Note.** This separation may be omitted if lead has already been found in the chloride group, since in that case its presence has already been established. The addition of NH_4OH to a solution containing Pb^{++} and Cu^{++} will precipitate the white $\text{Pb}(\text{OH})_2$ and leave in solution the blue $\text{Cu}(\text{NH}_3)_4^{++}$.

5. **The standard scheme of analysis: ammonium sulfide group.** The scheme of analysis given in Paragraph 5 of Assignment 62 can be extended farther to include the ions of chromium and aluminum:



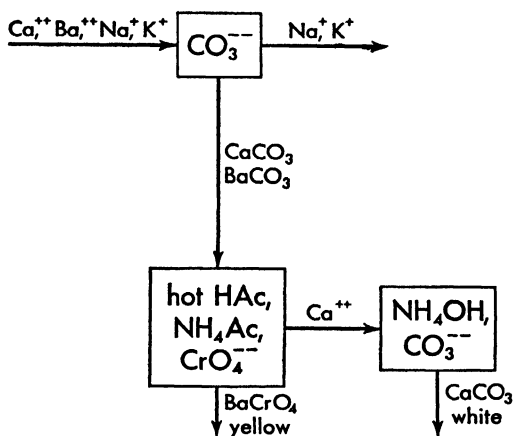
Procedure for the Separation of Iron from Aluminum and Chromium. The treatment with bisulfate sulfate buffer solution, which leaves ZnS but dissolves FeS , dissolves also the hydroxides of aluminum and chromium. Withdraw the supernatant liquid containing Fe^{++} , Al^{+++} , and Cr^{+++} , place it in a centrifuge cone, and add 2 cc. of 6 *N* NaOH . Sprinkle into the solution a few tenths of a gram of powdered Na_2O_2 . Place the cone in a beaker of hot water and allow it to boil, with stirring, until no more bubbles of oxygen are evolved. By this treatment iron will be precipitated as $\text{Fe}(\text{OH})_3$, and aluminum and chromium will remain in solution as AlO_2^- and CrO_4^{2-} respectively.

Procedure for the Separation of Aluminum from Chromium. To the solution containing AlO_2^- and CrO_4^{2-} add 6 *N* acid until the solution is just acidic, then add NH_4OH until the solution is just alkaline. Heat the mixture for a few minutes, then centrifuge it.

Aluminum will form a flocculent precipitate of $\text{Al}(\text{OH})_3$, while chromium will remain in the supernatant liquid as the yellow CrO_4^{--} . The presence of chromium may be confirmed by, for example, acidifying the solution and adding H_2O_2 to form peroxychromic acid; or by passing H_2S into the ammoniacal solution to convert the chromate to $\text{Cr}(\text{OH})_3$, centrifuging and washing the precipitate, treating it with NaOH solution and Na_2O_2 to obtain the chromate which is now free from sulfate, acidifying with HNO_3 , and adding Pb^{++} to precipitate the yellow PbCrO_4 .

Experiment. Treat by the preceding scheme solutions containing one drop of 1 *N* (a) aluminum nitrate, (b) chromic nitrate, and (c) ferrous sulfate. Each ion should give satisfactory tests with those procedures designed to detect it, and blanks with the other procedures.

6. The standard scheme of analysis: carbonate group. The following extension of the scheme of analysis provides for the detection of barium ion:



Procedure for the Separation of Barium from Calcium. To the centrifuge cone containing the washed precipitates of CaCO_3 and BaCO_3 resulting from the

ammonium carbonate treatment, add 2 cc. of hot 3 *N* acetic acid, or more if necessary to dissolve the carbonates. Add 4 cc. of 1 *N* NH_4Ac , then add 3 cc. of 1 *N* Na_2CrO_4 dropwise, keeping the solution hot. Let the hot solution stand for a few minutes, then centrifuge it. This treatment precipitates the barium as BaCrO_4 , while leaving the Ca^{++} in solution. The supernatant liquid can be withdrawn, made ammoniacal, and treated with ammonium carbonate to precipitate the calcium as CaCO_3 .

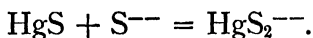
Experiment. Test the preceding scheme with solutions containing one drop of 1 *N* (a) barium chloride, and (b) calcium nitrate.

7. Alternative schemes of analysis. Where will the ions Pb^{++} , Sn^{++} , Sn^{++++} , Al^{+++} , Cr^{+++} , and Ba^{++} appear in the schemes of analysis you devised in Paragraph 6, Assignment 62? Extend or revise your schemes to include these additional ions.

8. Problems. (1) Point out the errors in the following reports:

- (a) Mercury is reported to be present because a black residue remained when the sulfides of the copper group were boiled with 2 *N* HNO_3 .
- (b) Lead is reported to have been found in the silver group but not in the copper group.
- (c) In the analysis referred to in (b) a black precipitate was observed in testing for the zinc group, although no test for iron was obtained. What errors in the method of analysis would produce this result?
- (d) Aluminum is reported to be present in the zinc group, but the note book shows the following records: on precipitating the zinc group a greenish precipitate was obtained on the addition of NH_4OH ; later a yellow solution resulted when Na_2O_2 was added; when this solution was acidified the color changed from yellow to blue to green; on the addition of NH_4OH a precipitate was formed.

(2) The concentration of S^{--} in 1 M Na_2S is 0.08 M , and in 1 M $(NH_4)_2S$ is 1.8×10^{-6} M . Calculate the solubility of HgS in each reagent. $K = 100$ for the reaction

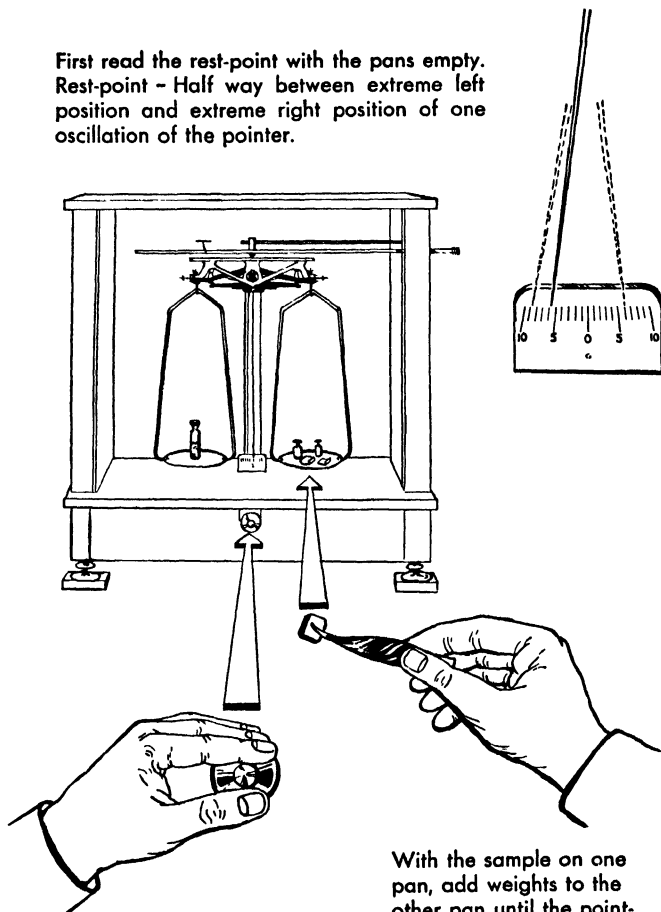


9. **Analyses Nos. 63, I, II, and II.** Test for all the positive and negative constituents you have studied. Verify your results by experiments with known substances.

Appendices

USE OF THE BALANCE

First read the rest-point with the pans empty.
Rest-point - Half way between extreme left position and extreme right position of one oscillation of the pointer.



Keep the beam and pans arrested while adding or removing weights, and when the balance is not in use.

With the sample on one pan, add weights to the other pan until the pointer is back to its original point of rest.
Handle the weights with weight-forcips only.

Appendix I

Special Laboratory Directions

A. USE OF THE BALANCE.

1. The bearings from which the beam swings, which are usually knife-edges of polished agate, might be damaged by careless misuse. When the balance is not in use, or when you are placing weights or objects upon the pans, always raise the beam off its knife-edges, never allow it to remain swinging. Raise or lower the beam carefully by turning the knob in the center of the base.

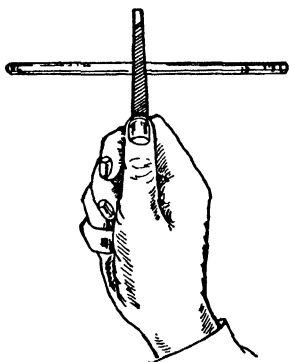
2. Before making a weighing, determine the rest point with the pans empty, by the following procedure: Set the beam in gentle motion by fanning the pan with your hand, or by jiggling the pan-release slightly. Allow the pointer to swing, and average the reading of a swing to one side and the next swing to the other side. (This is the "double-swing" method. Among other methods are the "single-swing," in which the first swing is read when the pans are released, and the "triple-swing," which averages two swings on one side, then averages that result with one swing on the other side.)

3. Objects such as crucibles or pieces of metal may be placed directly on the balance pan. Powders or liquids must be weighed in containers, such as weighing bottles. Objects should be weighed at room temperature, to avoid setting up air currents in the balance case.

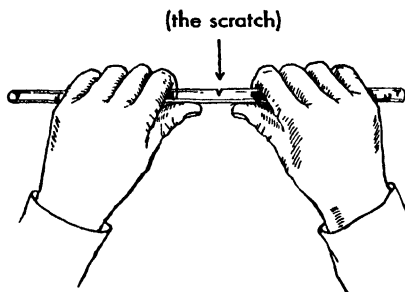
4. Add weights methodically, trying the largest first. The large brass weights are labeled in grams, the small weights in milligrams. Handle the weights with weight-forceps only. (For more precise weighing, a platinum wire "rider" may be used, which travels along a calibrated scale atop the beam.)

5. The weight of a substance is determined by adding up the weights in the pan, when the pointer has been brought to the original rest-point as nearly as possible. (If the pointer cannot be brought back exactly to the original rest-point, it is possible to take the deviation into account; to do this, it is necessary to know the "sensitivity" of the balance, which is the number of scale divisions the pointer is displaced by an excess weight of one milligram.)

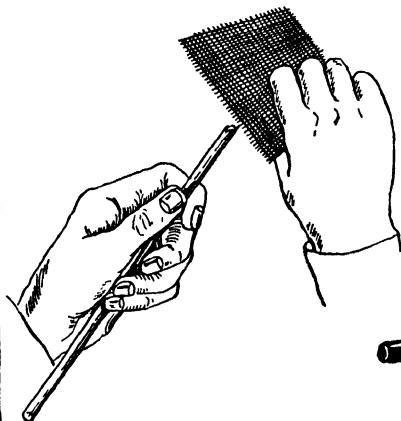
TO CUT GLASS TUBING



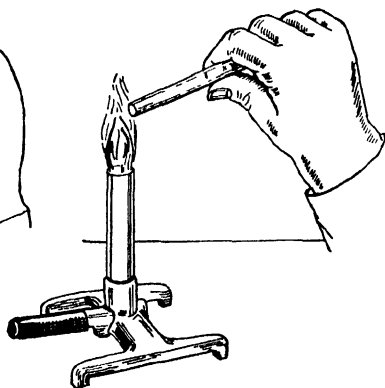
With one stroke of a sharp
file make a scratch,



...snap the tubing,



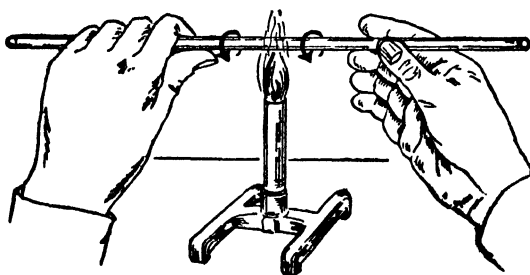
even up any rough end
with your wire gauze



...and fire-polish the ends.

TO BEND GLASS TUBING

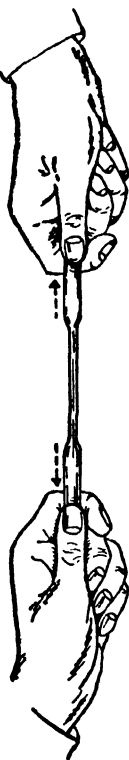
Heat a section of tubing until it is soft,
rotating so as to heat it uniformly,



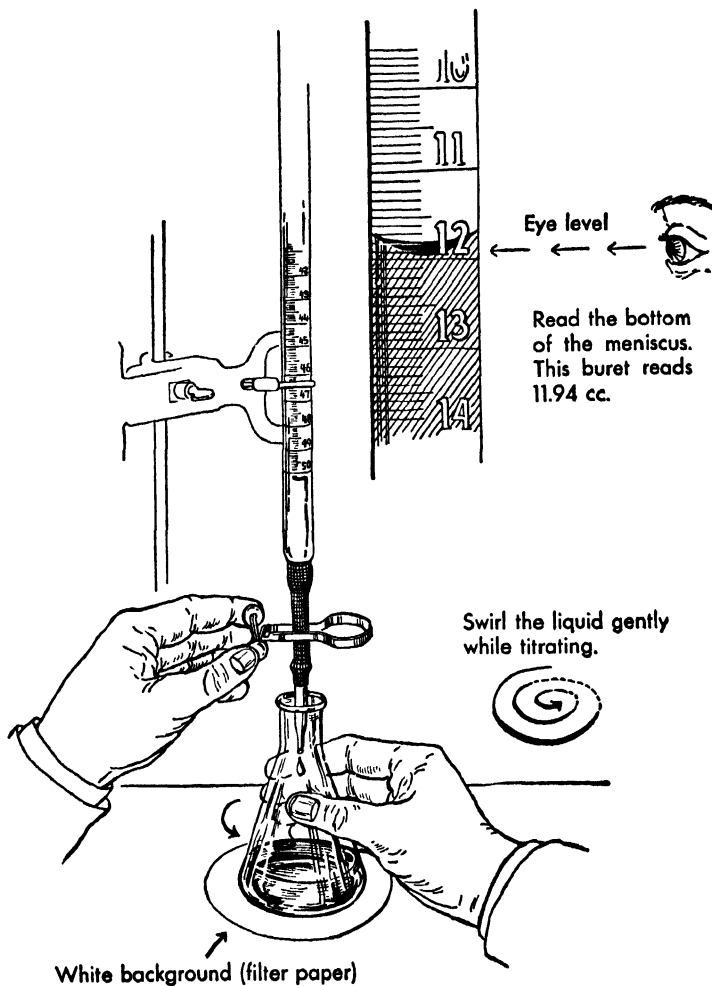
take it out of the flame and bend
it gradually. A good bend is not
pinched in.



To make a dropper tip: hold the heated
tubing vertically and pull.



USE OF BURETS



C. USE OF BURETS.

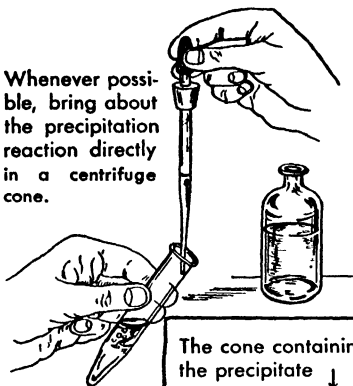
1. It is essential that the buret be clean so that no drops of liquid will adhere to the inside of the tube. This point may be checked before the buret is used, by filling it with distilled water and draining it. If the buret is not clean, exchange it at the office. When you have finished using a buret, rinse it with water repeatedly before returning it to the office. Before using a buret for a titration, rinse it with several small portions of the solution which it is to deliver.

2. A ground glass stopcock may be used to control the flow of liquid. The simpler burets, however, use a piece of rubber tubing closed with a pinch-clamp or containing a glass bead. It is necessary to make sure that no bubble of air is trapped in the small end of the tube. With the rubber fitting, this may be done by tilting the tip upward and allowing some of the liquid to flow through the cock.

3. The graduations on the buret are to 0.1 cc. and readings should be estimated to 0.01 cc. With transparent liquids it is best to record the bottom of the meniscus. To avoid parallax, the eye must be aligned horizontally with the meniscus and the buret reading. It is not worth while to adjust the volume of solution in the buret so that the initial reading will be zero or a whole number.

USE OF THE CENTRIFUGE

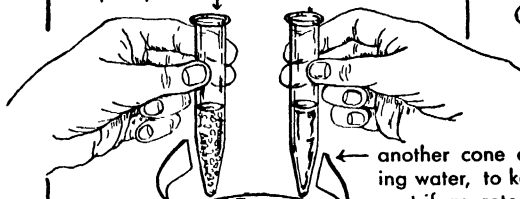
Whenever possible, bring about the precipitation reaction directly in a centrifuge cone.



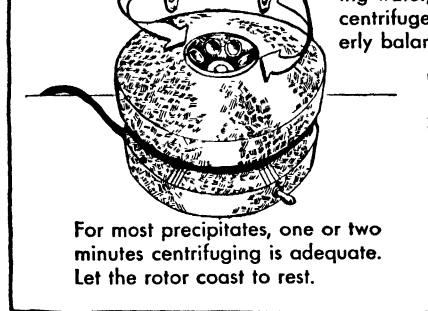
If the solution is to be heated, put the cone into a beaker of boiling water.



The cone containing the precipitate

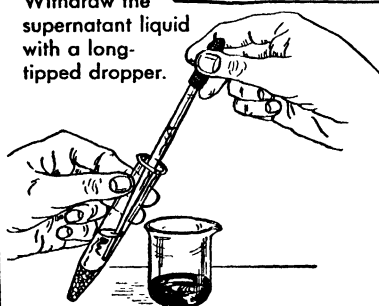


another cone containing water, to keep the centrifuge rotor properly balanced.

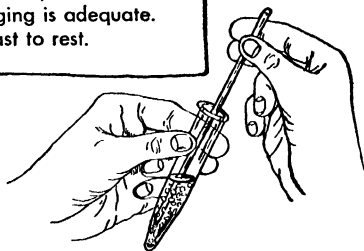


For most precipitates, one or two minutes centrifuging is adequate. Let the rotor coast to rest.

Withdraw the supernatant liquid with a long-tipped dropper.



Wash the precipitate by stirring it up with water, then re-centrifuging.



D. USE OF THE CENTRIFUGE.

1. If the centrifuge were allowed to operate with the rotor not balanced, the bearings and spindle of the machine would be damaged seriously. When you place a centrifuge cone in the rotor, always counterbalance it with another tube of the same size filled with water to about the same level.

2. To take full advantage of the technique of centrifugation, try to carry out precipitation reactions directly in centrifuge tubes whenever possible. It will seldom be necessary to transfer a precipitate out of a centrifuge cone, because you can usually dissolve the precipitate with the reagent which is to be used next in the procedure.

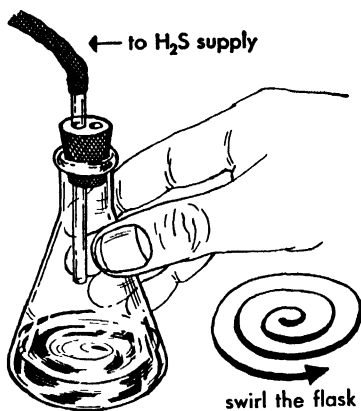
3. Be sure to stir the solution thoroughly when you add a reagent to a solution in a centrifuge cone.

4. Remove the supernatant liquid from a cone with the aid of a long-tipped dropper. Do not attempt to pour the liquid off. Always wash a centrifuged precipitate with several portions of distilled water.

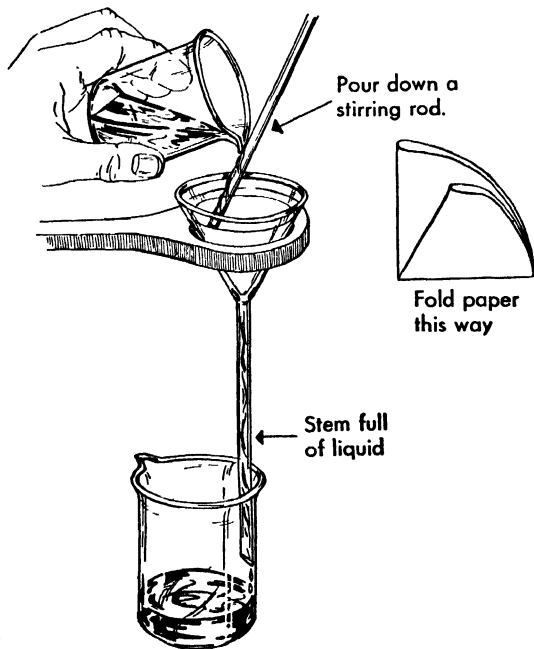
SATURATION WITH H_2S

Fill flask with H_2S ,
don't bubble H_2S
through the liquid.

Shallow layer of solution
to be saturated



FILTRATION



E. FILTRATION.

1. The filter paper is folded into halves and then into quarters. In making the fold into quarters the best angle may be not exactly 90° , since there are small variations in the shape of funnels. The best angle may be determined by trying the fit of the paper in the funnel before the final crease is made. After the filter is inserted into the funnel, it should be moistened with distilled water and pressed firmly against the glass to give a tight fit. It is helpful to tear a small corner from one fold of the paper. If no air can leak under the paper, the liquid will fill the stem of the funnel.

2. The precipitate may be removed from the filter paper by scraping it off, or by washing it off with a stream of water from the wash-bottle, or by dissolving it with a suitable reagent.

F. HYDROGEN SULFIDE SATURATION.

1. One method of saturating a solution with H_2S is to bubble the gas directly through the liquid. This has the disadvantages that the saturation may well be incomplete, and that the solution is likely to be contaminated by substances adhering to the H_2S supply tube.

2. A better method is to place the solution in a flask so as to form a shallow layer in the bottom, fill the gas space in the flask with H_2S , and swirl the solution until it is saturated. Do not shake the flask up and down.

Appendix II

Preparation of the Reagents

SOLUTIONS OF ACIDS

Acetic, 6 *N* : Mix 350 cc. of 99.5 per cent acid with 650 cc. of water.

Hydrochloric, 12 *N* : Use the c. p. acid, s. g. 1.19.

Hydrochloric, 6 *N* : Dilute 12 *N* acid with an equal volume of water.

Nitric, 16 *N* : Use the c. p. acid, s. g. 1.42.

Nitric, 6 *N* : Dilute 3 volumes of 16 *N* acid with 5 volumes of water.

Sulfuric, 36 *N* : Use the c. p. 95 per cent acid, s. g. 1.84.

Sulfuric, 6 *N* : Pour 1 volume of 36 *N* acid into 5 volumes of water.

SOLUTIONS OF BASES

Ammonium hydroxide, 15 *N* : Use the c. p. solution, s. g. 0.90.

Ammonium hydroxide, 6 *N* : Dilute 2 volumes of 15 *N* NH_4OH with 3 volumes of water.

Barium hydroxide, 0.4 *N* : Heat 60 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with 1 liter of water, cool, and decant or filter the solution.

Calcium hydroxide, saturated solution in contact with small excess of solid $\text{Ca}(\text{OH})_2$.

Potassium hydroxide, 6 *N* : Dissolve about 350 g. of c. p. KOH in water and dilute to 1 liter; or use 27 per cent solution, s. g. 1.25.

Sodium hydroxide, 6 *N* : Dissolve about 250 g. of c. p. NaOH in water and dilute to 1 liter. Or dissolve 1 part of commercial NaOH in about 1.45 parts by weight of water to give a 12 *N* solution of s. g. 1.39, let the mixture stand for several days, syphon off the clear solution, and dilute with an equal volume of water.

Note. It is recommended that each locker be supplied with at least five reagents: 6 *N* HCl, HNO_3 , H_2SO_4 , NH_4OH , and NaOH.

SOLUTIONS OF SALTS AND SPECIAL REAGENTS

Aluminum chloride, 1 *N* : 60 g. (0.33 mole) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ per liter.

Aluminum nitrate, 1 *N* : 125 g. (0.33 mole) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ per liter.

Aluminum sulfate, 1 *N* : 111 g. (0.165 mole) of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ per liter.

Ammonium acetate, 1 *N* : 77 g. (1.0 mole) of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ per liter.

Ammonium carbonate, 6 *N* : Dissolve 250 g. of ammonium carbonate in enough cold 6 *N* NH_4OH to make 1 liter.

Ammonium chloride, 4 *N* : 206 g. (4 mole) of NH_4Cl per liter.

Ammonium chloride, 1 *N* : 53 g. (1 mole) of NH_4Cl per liter.

Ammonium nitrate, 1 *N* : 80 g. (1 mole) of NH_4NO_3 per liter.

Ammonium oxalate, 0.5 *N* : 35 g. (0.25 mole) of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ per liter.

Ammonium polysulfide, 6 *N* : Dissolve 25 g. of sulfur in 1 liter of 6 *N* $(\text{NH}_4)_2\text{S}$.

Ammonium sulfate, 1 *N* : 66 g. (0.5 mole) of $(\text{NH}_4)_2\text{SO}_4$ per liter.

Ammonium sulfide, 6 *N* : Pass H_2S into 6 *N* NH_4OH , cooled with ice, until saturated; add an equal volume of 6 *N* NH_4OH .

Arsenious acid, for Assignment 32: Boil 10 g. As_2O_3 with a liter of water for one-half hour and filter.

Barium chloride, 1 *N* : 120 g. (0.5 mole) of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter.

Barium nitrate, 0.5 *N* : 66 g. (0.25 mole) of $\text{Ba}(\text{NO}_3)_2$ per liter.
Use hot water.

Bromine water, saturated : Shake bromine with water; leave small excess of bromine.

Cadmium chloride, 1 *N* : 92 g. (0.5 mole) of CdCl_2 per liter.

Calcium chloride, 1 *N* : 110 g. (0.5 mole) of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ per liter.

Calcium nitrate, 1 *N* : 118 g. (0.5 mole) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per liter.

Calcium sulfate, 0.03 *N* : Saturated solution.

Chromium nitrate, 1 *N* : 79 g. (0.33 mole) of $\text{Cr}(\text{NO}_3)_3$ per liter.

If commercial liquid reagent is used, calculate weight from percentage composition.

Copper nitrate, 1 *N* : 148 g. (0.5 mole) of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter.

Copper sulfate, 1 *N* : 125 g. (0.5 mole) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter.
Use hot water.

Ferric chloride, 1 *N* : 90 g. (0.33 mole) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ per liter.

Ferric chloride, 20–30 per cent of FeCl_3 , for Assignment 32.

- Ferric nitrate, 1 *N* : 135 g. (0.33 mole) of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ per liter.
- Ferrous sulfate, 2 *N* : Dissolve 280 g. (1 mole) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in sufficient 0.6 *N* H_2SO_4 to make 1 liter. Keep solution in contact with iron nails.
- Gold chloride, 0.01 per cent of AuCl_3 , for Assignment 32.
- Hydrogen peroxide, 3 per cent solution.
- Iodine, 0.1 *N* : Dissolve 13 g. (0.1 mole) of iodine in a solution containing 50 g. of KI per liter.
- Lead acetate, 1 *N* : 190 g. (0.5 mole) of $\text{Pb}(\text{C}_2\text{O}_2\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$ per liter.
- Lead nitrate, 0.25 *N* : 41 g. (0.125 mole) of $\text{Pb}(\text{NO}_3)_2$ per liter. Use hot water.
- Magnesium nitrate, 0.1 *N* : 13 g. (0.05 mole) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter.
- Manganous sulfate, 0.1 *N* : 75 g. (0.05 mole) of MnSO_4 per liter.
- Mercuric chloride, 0.1 *N* : 14 g. (0.05 mole) of HgCl_2 per liter.
- Mercuric nitrate, 0.1 *N* : 16 g. (0.05 mole) of $\text{Hg}(\text{NO}_3)_2$ per liter. Dissolve in minimum amount of *N* HNO_3 and dilute.
- Mercurous nitrate, 0.1 *N* : 28 g. (0.05 mole) of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ per liter. Dissolve in 0.6 *N* HNO_3 .
- Oxalic acid, 0.1 *N* : 6 g. (0.05 mole) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per liter, for Assignment 32.
- Potassium chloride, 1 *N* : 75 g. (1 mole) of KCl per liter.
- Potassium ferricyanide, 1 *N* : 110 g. (0.33 mole) of $\text{K}_3\text{Fe}(\text{CN})_6$ per liter.
- Potassium iodide, 1 *N* : 166 g. (1 mole) of KI per liter.
- Potassium permanganate, 0.1 *N* : 16 g. (0.1 mole) of KMnO_4 per liter.
- Potassium sulfate, 1 *N* : 87 g. (0.5 mole) of K_2SO_4 per liter.
- Potassium thiocyanate, 1 *N* : 97 g. (1 mole) of KCNS per liter.
- Silver nitrate, 0.1 *N* : 17 g. (0.1 mole) of AgNO_3 per liter.
- Sodium acetate, 1 *N* : 135 g. (1 mole) of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ per liter. Test with indicators before using in Assignment 25.
- Sodium acetate, 4 *N* : 544 g. (4 moles) of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ per liter.
- Sodium bicarbonate, 1 *M* : 84 g. of NaHCO_3 per liter.
- Sodium bromide, 1 *N* : 103 g. (1 mole) of NaBr per liter.
- Sodium carbonate, 1 *N* : 53 g. (0.5 mole) of Na_2CO_3 per liter.
- Sodium chloride, 1 *N* : 58 g. (1 mole) of NaCl per liter.
- Sodium chromate, 1 *N* : 171 g. (0.5 mole) of $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ per liter.

- Sodium cobaltinitrite, 0.3 *N* : Dissolve 230 g. of NaNO_2 in 500 cc. of water. Add 165 cc. of 6 *N* HAc and 30 g. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, let the mixture stand over night, filter, and dilute to 1 liter.
- Sodium dichromate, 1 *N* : 130 g. (0.5 mole) of $\text{Na}_2\text{Cr}_2\text{O}_7$ per liter.
- Sodium ferrocyanide, 1 *N* : 130 g. (0.25 mole) of $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$ per liter.
- Sodium hypochlorite, 1 *N* : Dissolve 110 g. of $\text{CaOCl}_2 \cdot 4\text{H}_2\text{O}$ and 58 g. of Na_2CO_3 per liter; filter out CaCO_3 . Use hot water.
- Sodium nitrite, 1 *N* : 70 g. (1 mole) of NaNO_2 per liter.
- Sodium sulfate, 1 *N* : 160 g. (0.5 mole) of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per liter.
- Stannic chloride, 1 *N* : 65 g. (0.25 mole) of SnCl_4 per liter. Dissolve in 3 *N* HCl. Test for Sn^{++} .
- Stannous chloride, 1 *N* : Dissolve 115 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 cc. of 12 *N* HCl and dilute to 1 liter. Keep in contact with metallic tin.
- Sulfurous acid, for Assignment 32 : Saturate water with SO_2 .
- Zinc chloride, 1 *N* : 68 g. (0.5 mole) of ZnCl_2 per liter.
- Zinc nitrate, 1 *N* : 148 g. (0.5 mole) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter.
- Zinc sulfate, 1 *N* : 144 g. (0.5 mole) of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ per liter.

SOLUTIONS OF INDICATORS

- Alizarine yellow R, 0.04 per cent solution: Dissolve 0.4 g. per liter.
- Bromcresol green, 0.04 per cent solution: Dissolve 0.4 g. in 57.2 cc. of 0.01 *N* NaOH and dilute to 1 liter.
- Bromphenol blue, 0.04 per cent solution: Dissolve 0.4 g. in 59.6 cc. of 0.01 *N* NaOH and dilute to 1 liter.
- Bromthymol blue, 0.04 per cent solution: Dissolve 0.4 g. in 64.0 cc. of 0.01 *N* NaOH and dilute to 1 liter.
- Cresol red, 0.04 per cent solution: Dissolve 0.4 g. in 69.0 cc. of 0.01 *N* NaOH and dilute to 1 liter.
- Indigocarmine, 0.04 per cent solution: Dissolve 0.4 g. per liter.
- Methyl orange, 0.04 per cent solution: Dissolve 0.4 g. per liter. Add alcohol to clear the solution if necessary.
- Methyl violet, 0.04 per cent solution: Dissolve 0.4 g. per liter.
- Phenolphthalein, 0.1 per cent solution, 1 g. per liter: Dissolve in alcohol, dilute with water to almost required volume, and clear with alcohol.

BUFFER SOLUTIONS

pH 5: Glacial acetic acid 2.0 cc., sodium acetate 5.3 g. per liter.

pH 6: 1 volume of Na_2HPO_4 stock solution (containing 11.88 g. $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ per liter), to 9 volumes of KH_2PO_4 stock solution (containing 9.08 g. KH_2PO_4 per liter).

pH 7: 6 volumes of Na_2HPO_4 stock solution to 4 volumes of KH_2PO_4 stock solution.

pH 8: 9.5 volumes of Na_2HPO_4 stock solution to 0.5 volumes of KH_2PO_4 stock solution.

pH 9: Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 38 g. per liter.

TEST PAPERS

Aluminon paper. Ashless filter paper treated with a solution containing 0.1 per cent aluminon and 1 per cent NH_4Ac , and dried at room temperature.

Cobalt paper. Filter paper treated with 1 per cent solution of $\text{K}_3\text{Co}(\text{CN})_6$.

LIQUIDS

Benzene	Chloroform ¹	Ethylene dichloride ¹
Carbon disulfide	Cottonseed oil	Formaldehyde
Carbon tetrachloride ¹	Ethyl alcohol	Methyl alcohol
	Ethyl iodide ¹	

SOLIDS

Note. Certain solids are listed which need not be regularly placed on the reagent shelves. Those marked x may be used in additional experiments planned by the instructor or students, and in the preparation of "unknowns."

Acids for Assignment 7

Benzoic
Citric
Acid sulfate of potassium or sodium
Oxalic
Tartaric

Acids for Assignment 24

Sodium acid sulfate
Sodium acid oxalate
Sodium acid phthalate
Sodium dihydrogen phosphate

¹ Suitable for "unknown" liquids in Assignment 3.

Alum (potassium aluminum sulfate)	Manganese dioxide
Aluminum, sheet, foil, granulated	Manganous nitrate
Ammonium chloride	Mercuric nitrate
Ammonium nitrate	Mercury (liquid)
xAmmonium sulfate	xNickel nitrate
Asbestos fibre, washed with 12 N HCl and water	Oxalates for Assignment 52
xBorax	Potassium oxalate
Calcium carbonate (marble)	Sodium oxalate
Calcium chloride	Potassium chlorate
Calcium filings	Potassium chloride
Calcium sulfate	xPotassium chromate
Chrom alum	Potassium cyanide
Cobalt nitrate	Potassium ferricyanide
Copper, wire, foil	Potassium nitrate
Cupric chloride	Rosin, for Assignment 32
Cupric oxide	Silver, thin foil
Cupric sulfate	xSodium acid sulfate
Cuprous oxide	Sodium bicarbonate
Ferric nitrate	Sodium bromide
Ferrous sulfate or ferrous ammonium sulfate	Sodium carbonate
Ferrous sulfide (commercial for H ₂ S generator)	Sodium chloride
Gelatine, for Assignment 32	Sodium ferrocyanide
xGlass wool	xSodium hydrogen phosphate
Graphite, rods	Sodium iodide
Iron filings or small iron nails	Sodium peroxide
Iron wire, 6-inch pieces	Sodium silicate (commercial solution)
Lead	Sodium sulfate
Lead oxides, monoxide, dioxide, and red lead	Sodium sulfite
Magnesium, wire, foil	Sodium thiosulfate
xMagnesium sulfate	xStrontium chloride
	Sugar, for Assignment 32
	xSulfides of metals studied
	Sulfur
	Tin, granulated
	Zinc, granulated, sheet

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