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Author Mahn, Lloyd E.

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38 **The Equilibria of Carbonic Acid and Its Salts** Carbon dioxide and carbonic acid, sodium hydrogen carbonate and sodium carbonate, calcium hydrogen carbonate and calcium carbonate. Temporarily hard water. Limestone cave formation. 275

E– **Recapitulation of Problems on Ionic Equilibria** A study assignment. Ionization constants. Solubility products. 279

QUALITATIVE ANALYSIS PROCEDURES

39 **The Negative Ions—Qualitative Tests** Sulfate ion, sulfite ion, sulfide ion, carbonate ion, chloride ion, bromide ion, iodide ion, phosphate ion, nitrate ion. 283

F **An Introduction to the Qualitative Analysis of the Metal Ions. Semimacro Techniques** A study assignment. 289

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41 **Precipitation with Hydrogen Sulfide. The Analysis of the Hydrogen Sulfide Group** Hydrogen sulfide as a weak dibasic acid. The precipitation of metallic sulfides. Amphoteric sulfides. The oxidation of sulfides. 297

42 **The Ammonium Sulfide Group** Precipitation with ammonium sulfide. The hydrolysis of sulfides of weak bases. Buffer action. The oxidation of chromium and manganese. 305

43 **The Alkaline Earth and Alkali Groups** Solubilities of alkaline earth salts. Precipitation with ammonium carbonate. The separation of magnesium. 315

G **The Qualitative Analysis of Cd^{++}, Bi^{+++}, AsO_3^{---}, Sb^{+++}, Ni^{++}, Co^{++}, and Sr^{++}** A study assignment. 321

44 **The Analysis of General Unknown Inorganic Substances. The Solution of Solids** Methods for the solution of difficultly soluble solids. The use of acids, oxidizing agents, reducing agents, complex ions, metathesis, and fusion processes. 323

APPENDICES

I **The Measurement of Physical Quantities** The use of dimensions, significant figures, experimental errors. 329

II **Tables of Data** Logarithms, the metric system of units, various units and conversion factors, the vapor pressure of water at different temperatures, temperature corrections for barometer readings, concentration of desk acid and base solutions, the volatility of acids, replacement series of some metals, the solubility of some common gases, general solubility rules for common salts and bases, the relative concentration of ions in 0.1 *F* solutions of electrolytes, the color changes and *p*H intervals of some important indicators, oxidation-reduction potentials, equilibrium constants, solubility products, table of ionic valences. (The periodic table and international atomic weights are given on the inside covers.) 333

Note:

A review of chemical arithmetic and fundamental mathematical operations is given in Study Assignments A and B.

A review of the rules of chemical nomenclature is given in connection with Experiments 8 and 18.

A Teacher's Manual is available to all instructors. This provides lists of supplies needed, of reagents and solutions, with directions for their preparation, and numerous suggestions to the instructor regarding individual experiments.

A Preface to the Student

This laboratory manual has been designed to correlate with the presentation of the subject in *College Chemistry, An Introductory Textbook of General Chemistry*, by Linus Pauling. References to chapters in this text will be found at the head of each experiment.

True knowledge and understanding in any field of learning depend on the careful observation and correlation of facts, and on logical deductions from them. In chemistry, these "facts" are the experimental observations of the way substances behave with respect to one another under various conditions, both in nature and in the laboratory. Out of such observations by scientists have come the "theories" and the "principles" which you are studying in your textbook. It is important that, insofar as time and reasonable laboratory facilities permit, you have the opportunity to experience this "scientific method" in your own study of chemistry. *Your laboratory work is the central core of your chemistry course.*

Here are a few suggestions which will help to give you a good start in this course:

(1) Use your ingenuity and common sense. While laboratory directions usually are quite specific, there is always abundant opportunity for clean-cut, logical, original, and imaginative thinking. These are qualities a corporation's chemical-laboratory director is seeking. The routine thinker will be assigned to the routine jobs. Ingeniousness is as important to you in the study of chemistry as in any other activity.

(2) Broaden your outlook by becoming familiar with the introductory literature of chemistry early in your course. Tabular data on the properties of substances are given in handbooks, such as: *Handbook of Chemistry and Physics*, Charles D. Hodgeman, editor in chief, Chemical Rubber Publishing Company, Cleveland, Ohio, and *Handbook of Chemistry*, N. A. Lange, Handbook Publishers, Inc., Sandusky, Ohio. Consult your instructor as to the many excellent textbooks of general chemistry and qualitative analysis which are available. A thorough, general reference work is *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, J. W. Mellor, Longmans, Green and Company, New York, 1932-1937.

(3) Familiarize yourself with the experiment you are to perform *before* you come to the laboratory. Study the "Review of Fundamental Concepts" thoroughly, and read the "Experimental Procedure." In certain experiments, you will find some "Preliminary Work" to complete before the laboratory period. Laboratory work is of much greater value and you can make more efficient use of your time if you understand beforehand what you are trying to do.

(4) Note beforehand any extra equipment required from the stockroom, and obtain all of it at once.

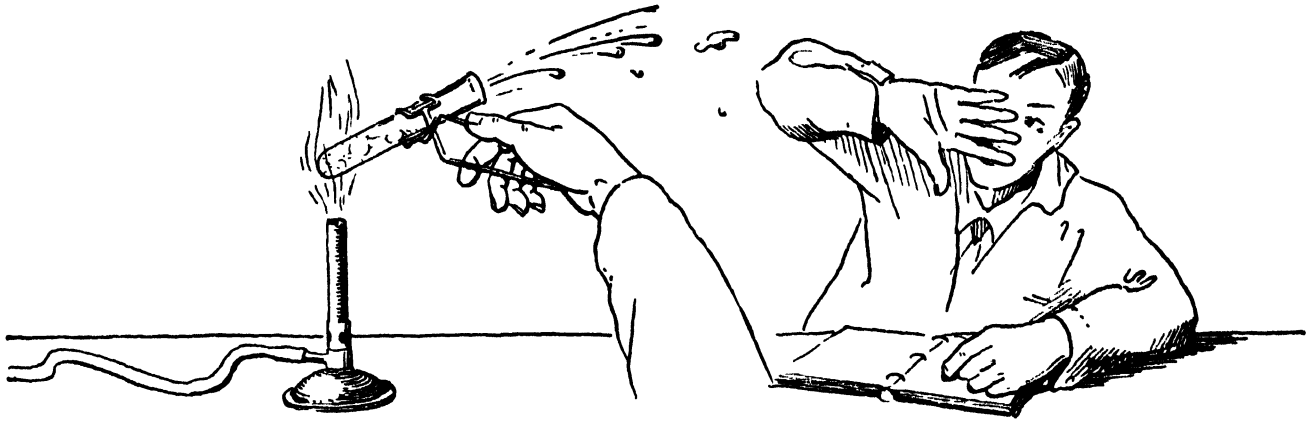
(5) You will gain self-reliance by working alone in the laboratory, except when directed to do otherwise.

(6) The "Report Sheets" are not merely a place to "put down the answers." They are intended as a stimulus and guide to your thinking. It is important that you think through and fill in these reports *as you perform the experiments.* Keep the reports, after they have been corrected by the instructor, in regular order. They thus become a more important part of this book. You will be graded in this course, however, not so much by your entries in any formal report sheet, as by *what you know about the principles underlying the experiment.*

(7) Scientists learn much by discussion with one another. Since the reports are not "tests" or "examinations," you can often profit by discussion with your classmates—but not by copying from them. The very keystone of all science rests first of all on integrity. You will also profit by frequent reference to your textbook while you are working in the laboratory. (Books are generally even more complete and reliable as sources of information than are your classmates!)

(8) The "Safety Precautions" and the "Laboratory Rules" (see pp. vii and ix) will help you to safeguard not only your interests, but those of other members of the laboratory class as well. *Know these precautions and rules and obey them.*

THE AUTHORS.



NEVER point a test tube of boiling liquid at your neighbor — it may bump.

Safety Precautions

(1) The laboratory is a place for serious work. Maintain a wholesome, businesslike attitude at all times. **Do not attempt unauthorized experiments.** Accidents and trouble will be avoided by following this rule. This is for the safety of the whole class.

(2) Any accident involving even a minor injury should be reported to the instructor at once. Beware of hot glass: glass cools very slowly and may be very hot without appearing so.

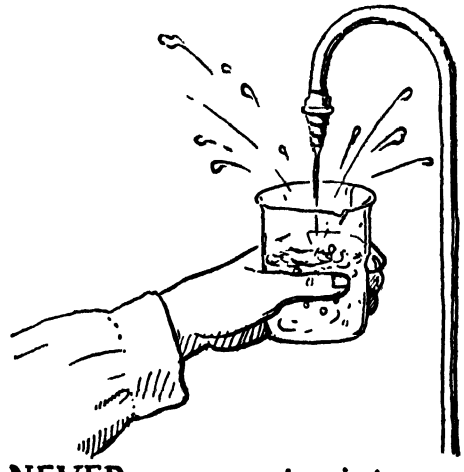
(3) Do not point your test tube at your neighbor or yourself when heating substances. A suddenly formed bubble of vapor may eject the contents violently and dangerously.

(4) When diluting sulfuric acid, *pour the acid* slowly and carefully *into the water* with constant stirring. *Never add the water to the acid.* So much heat is liberated on solution that steam may be formed with almost explosive violence.

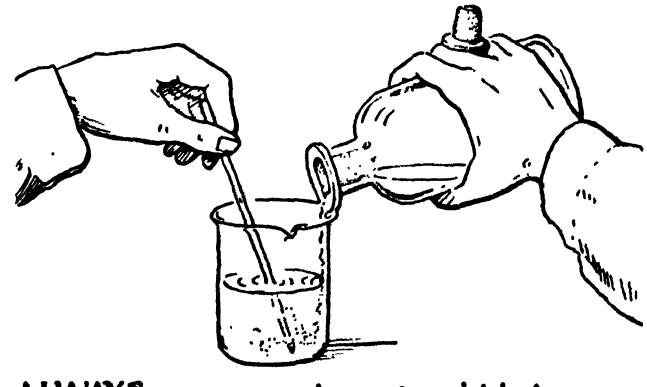
(5) Neutralize spilled acid or base as follows:

Acid on clothing—use dilute ammonium hydroxide.

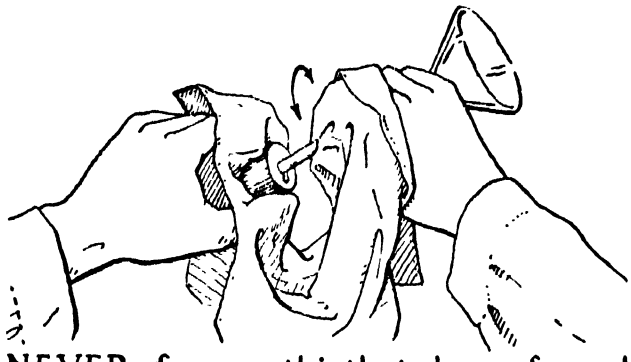
Base on clothing—use dilute acetic acid, followed by ammonium hydroxide.



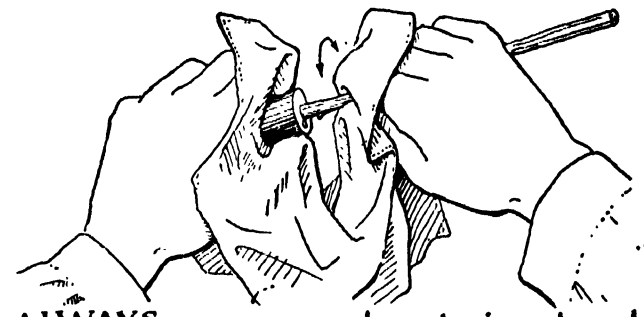
NEVER pour water into a strong acid — the heat generated may spatter the mixture or break the glass.



ALWAYS pour a strong acid into water slowly, and stir constantly.



NEVER force a thistle tube or funnel into a stopper by grasping the large end. Use the stem and twist as you push.



ALWAYS wrap your hands in a towel when putting a glass tube into a stopper. Moisten with water and insert with a twisting motion.

Acid or base on the desk top or floor—wash off with plenty of water. Solid crude sodium bicarbonate may be used to neutralize large amounts of either acid or base, and then the mixture is washed off with water.

Corrosive liquids on the skin—use plenty of water. Consult the instructor.

(6) When putting glass tubing through a rubber stopper, lubricate the tube and stopper first with water (unless moisture must be avoided in the experiment). To insert the tubing, hold it with a cloth near the end to be inserted and use a twisting motion. This applies also to the insertion of thermometers and thistle and funnel tubes. (If you hold a thistle tube by the "thistle" end, it is very likely to break when inserted in the stopper.)

(7) Never taste a chemical or solution unless directed to do so. (Poisonous substances are not always so labeled in the chemistry laboratory.) When directed to taste a solution, touch a drop of it, suspended on a stirring rod, to the tongue; then wash out the mouth with water. If any chemical is accidentally swallowed, see your instructor.

(8) When observing the odor of any liquid, do not put your face directly over the container. Sometimes a heated liquid will suddenly form, even when no longer being heated, a bubble of steam (called "bumping"). The contents might thus be discharged into your face. Fan a little of the vapor toward you by sweeping your hand over the top of the test tube or beaker.

(9) In any experiments in which poisonous or otherwise objectionable gases or vapors are discharged, perform the operations under the HOOD. This provides suction to remove any such gases or vapors.

(10) To protect your clothing from corrosive chemicals, always wear a laboratory apron when doing experimental work. (Aprons are cheaper than clothing.)



ALWAYS smell a substance by wafting its odor gently toward your face.

Laboratory Rules

(1) At the close of each laboratory period, leave your glassware clean and dry. Wash and wipe off the desk top, so it is not left spotted and dirty.

(2) Throw all solids to be discarded into the waste crocks. Wastepaper belongs in the wastebaskets. *Never throw matches, litmus paper, or any solid, insoluble chemicals into the sink.* Liquids are emptied into the sinks *and washed down with water,* because acids, and salts of copper, silver, and mercury are corrosive to plumbing, particularly if it is made of lead.

(3) The reagent bottles on the side shelves should not be carried to your desk. Clean test tubes or beakers should be used for carrying liquids, and beakers, watch glasses, or small squares of paper for carrying solids.

(4) Read the label *twice* before taking anything from a bottle.

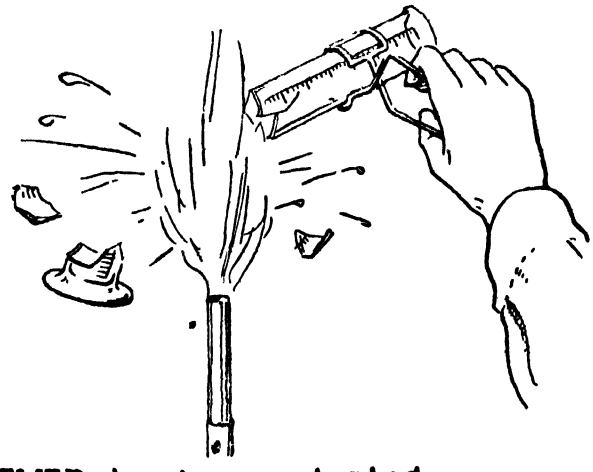
(5) Use as little reagent as is convenient to perform your experiment. Two or three milliliters are usually sufficient in test tube experiments.

(6) *Never* return unused chemicals to the stock bottles. You may make a mistake from which another student's experiments will suffer.

(7) Do not insert your own pipettes or medicine droppers into the reagent bottles. Pour out the solution instead. This will avoid any possible contamination of the stock solution.

(8) Do not lay the stopper of a bottle down, as impurities may be picked up and thus contaminate the solution when the stopper is returned. Hold the stopper as illustrated in Figure i-6 or i-7.

(9) Graduated cylinders and bottles are not to be heated, because they break too easily. (See below.) Likewise test tubes are likely to break if heated above the level of the liquid in them, and liquid is then splashed over the hot glass. Evaporating dishes and crucibles may be heated red hot if desired. Do not heat any piece of apparatus too suddenly at first, or it may break. Apply the flame intermittently at first until the vessel is hot.



NEVER heat a graduated cylinder or bottle.

Laboratory Manipulations

The following suggestions on common laboratory procedures will assist in a proper orientation to your work. Read these now, and refer to them again in succeeding experiments, as you encounter the first use of the various operations.

A. Laboratory Burners

The Bunsen burner, used for most laboratory heating, produces a cone-shaped flame, as illustrated (Fig. i-1). Ordinary beakers, crucibles, and other objects to be heated are placed just above the hottest portion of the flame which is thus allowed to spread about them. If placed down in the cold inner cone, consisting of unburned gas, the objects are not heated effectively.

The Meker burner (or the similar modern Fisher burner) is designed to give a concentrated, very hot flame (Fig. i-2). For maximum temperature, have the gas on full pressure, and with the air vents open adjust the needle valve at the base to give a short blue flame of many short cones about

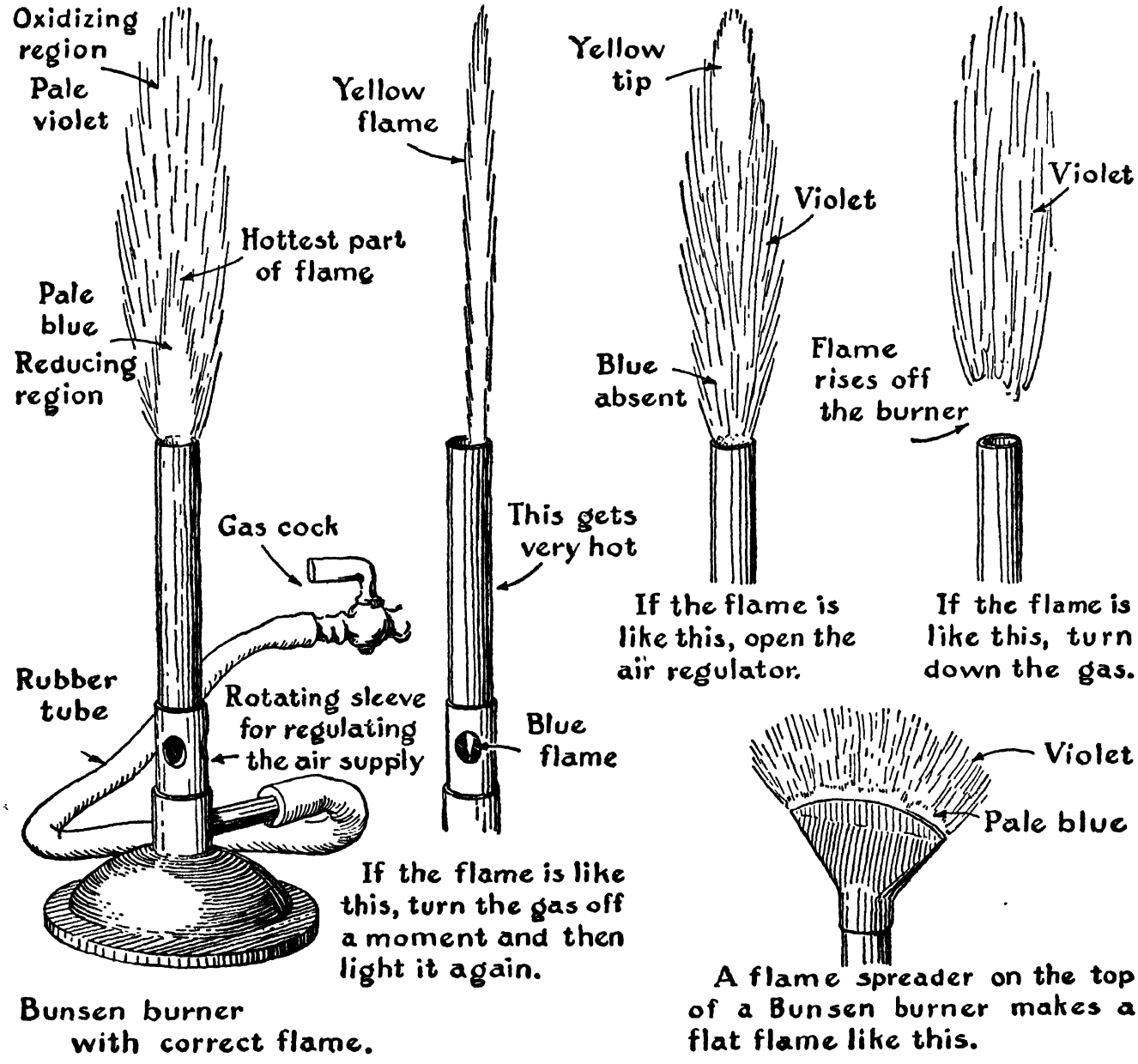


FIG. i-1. The operation of a Bunsen burner

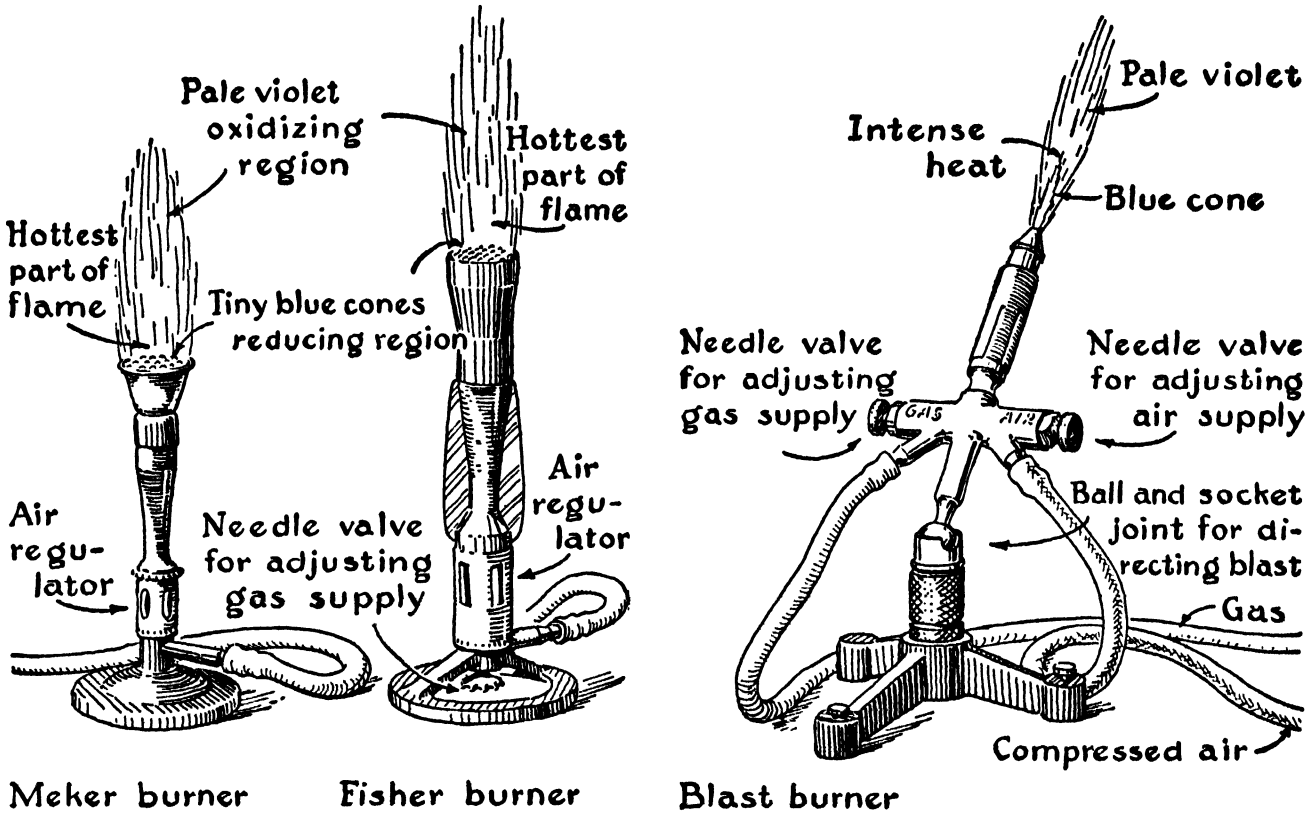


FIG. i-2. High temperature burners.

0.5 cm high. The object to be heated is placed about 1 cm above the grid.

The blast burner makes provision for mixing the gas with compressed air or oxygen gas and will give a very hot concentrated flame. It is particularly useful in glass-working operations.

B. The Manipulation of Glass Tubing

A few of the simpler and more frequently used procedures involved in the manipulation of glass tubing are presented in Figures i-3 and i-4. Study these carefully, and then construct a wash bottle as illustrated in Figure i-5.

C. The Handling of Chemicals

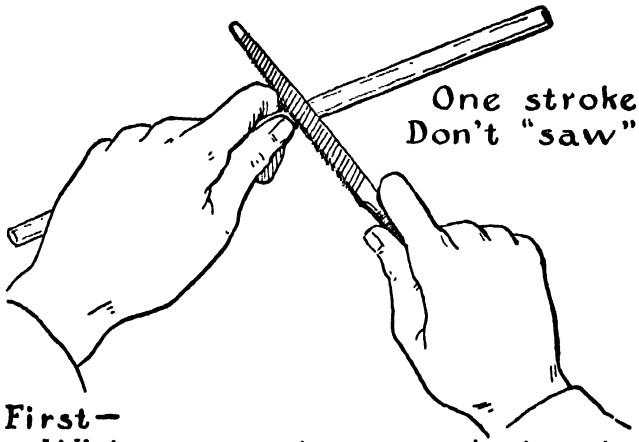
A few simple suggestions regarding the proper handling of solid and liquid chemicals are illustrated for you in Figures i-6 and i-7. We repeat: Be considerate of others by always bringing your container to the reagent shelf to obtain a chemical. Do not take the bottle to your desk. Maintain the purity of the chemicals in the reagent bottles. Do not withdraw more than you need, and never return any chemical to the bottle. Never contaminate the stopper of a bottle by laying it down; hold it as illustrated. Do not insert your own medicine dropper into a reagent bottle or the medicine dropper from a reagent bottle down into your own test tube or solutions. (Fig. i-8.)

Careful observance of these suggestions will prevent the spilling of chemicals and the contamination of the stock bottles. If you do spill any chemical, clean it up completely, at once. A dirty laboratory is not conducive to good work.

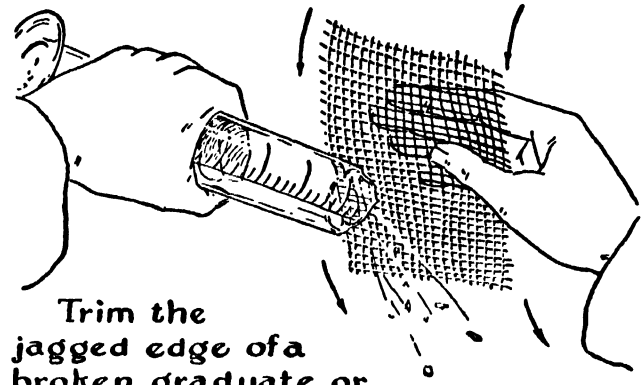
D. The Cleaning and Drying of Glassware

Most vessels can be cleaned simply by washing them first with soap solution and then with tap water, and finally rinsing them with a spray of distilled water from the wash bottle. Water wets a clean glass surface uniformly—it does not stand in droplets over the surface. By observing this, you may tell when the glass is clean. (Fig. i-9.)

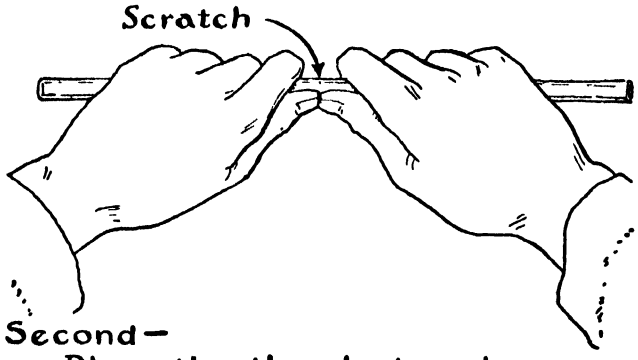
Use your test-tube brush regularly, but be sure there are no exposed sharp metal points on the brush. These will scratch the inside of the test tube and cause it to break easily when it is heated. (This is a frequent but unsuspected cause of breakage.) Films adhering to the inside of flasks and bottles may often be removed by wetting the



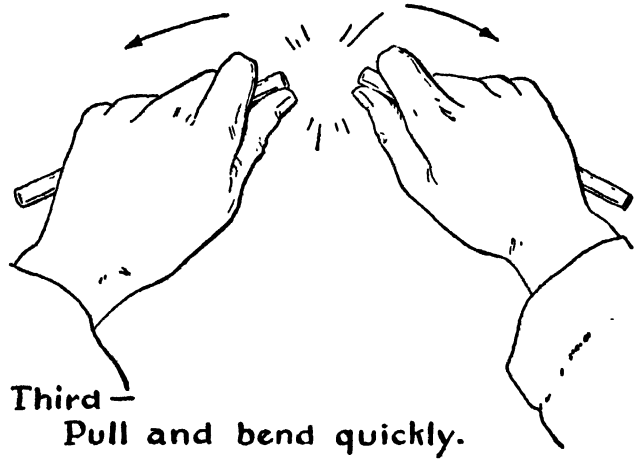
First—
With one stroke scratch the tube with the edge of a triangular file.



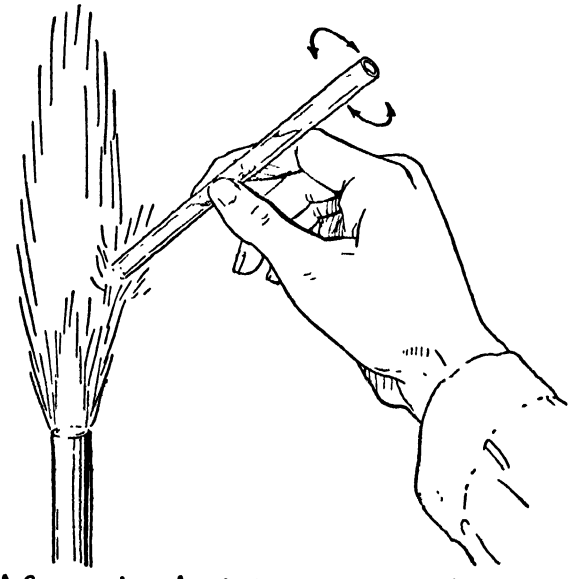
Trim the jagged edge of a broken graduate or large tube by stroking it with a piece of wire screen.



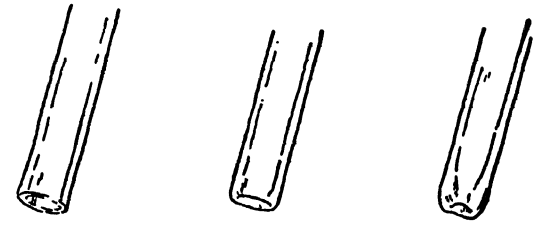
Second—
Place the thumbs together opposite the scratch.



Third—
Pull and bend quickly.



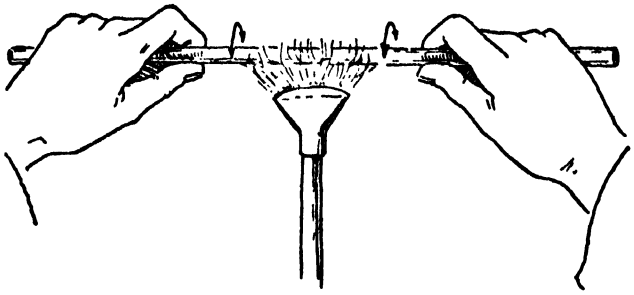
After slowly introducing the cut end into a Bunsen flame, rotate the tube back and forth until the cut edges are rounded.



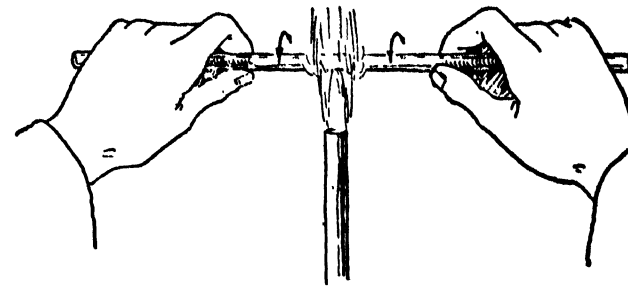
The cut end | After fire glazing | This has been heated too much.

Fire glazing the end of a tube

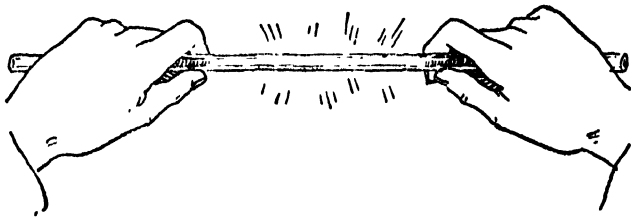
FIG. i-3. The manipulation of glass tubing.



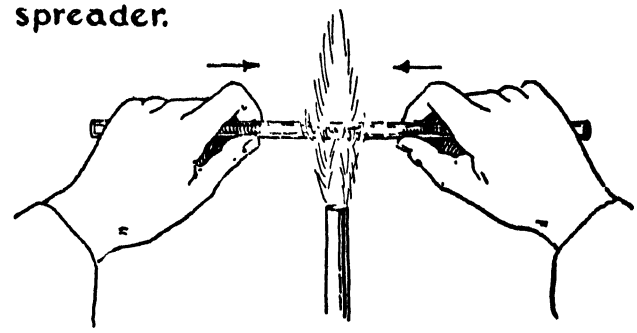
Roll the tube back and forth in a flat flame until it has become quite soft.



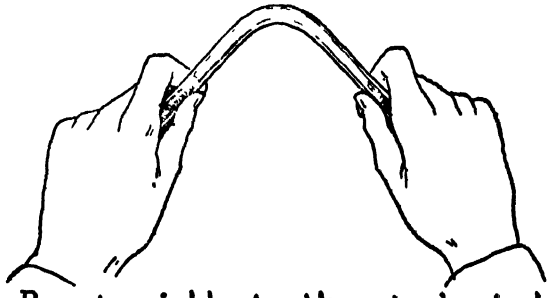
Roll the tube in a Bunsen flame until it softens. Don't use a flame spreader.



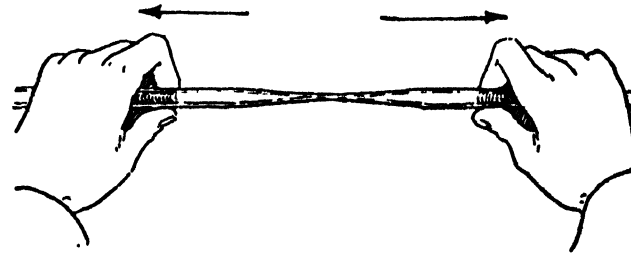
Remove from the flame and hold for a couple of seconds to let the heat become more uniform.



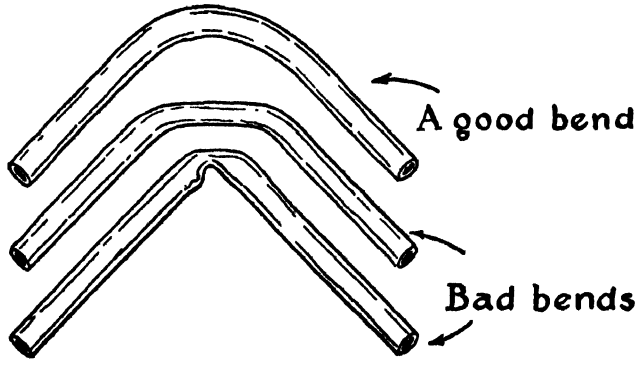
Allow the tube to become shorter as the walls thicken to about twice their original thickness.



Bend quickly to the desired shape and hold until it hardens.

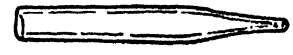


Remove from the flame and after a moment pull until the softened region is as small as desired.





Cut to length.



Fire glaze the tip.

FIG. i-4. Further manipulations with glass tubing.

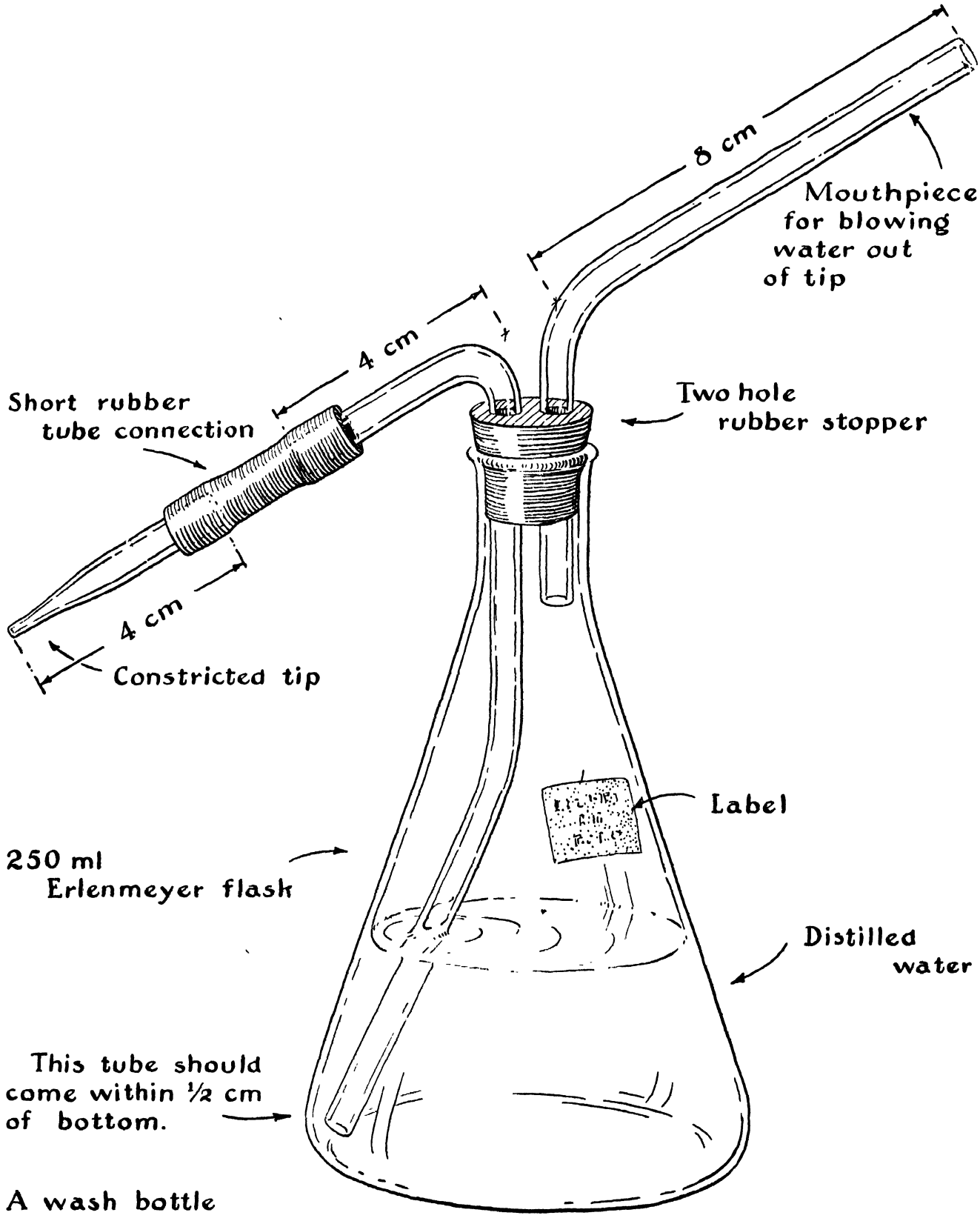
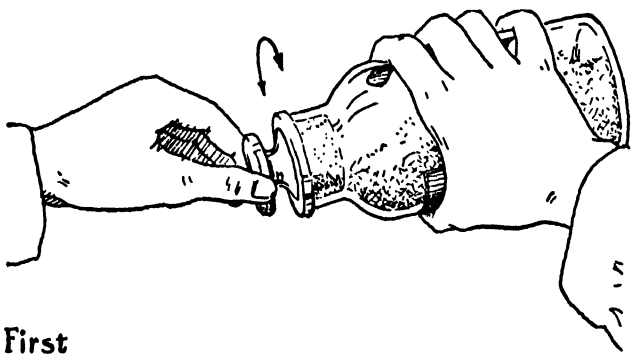
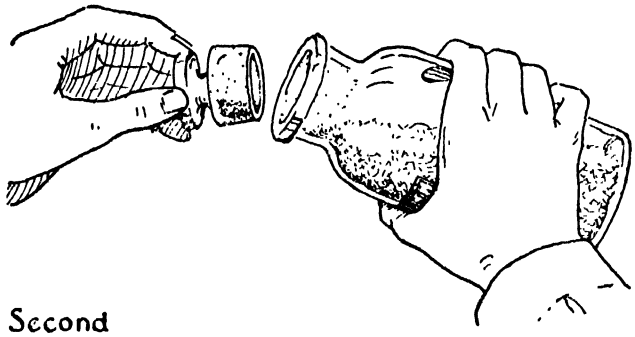


FIG. i-5. The construction of a wash bottle.



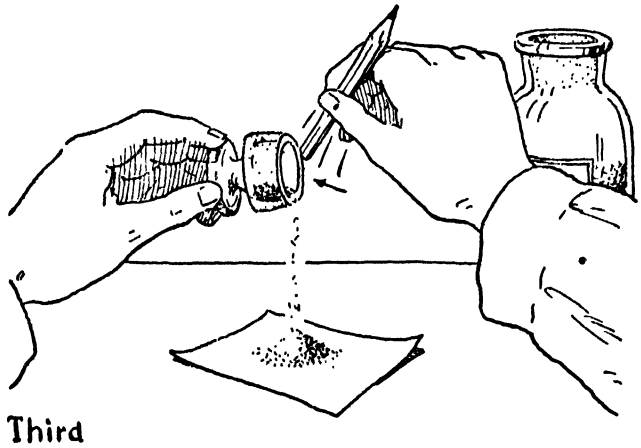
First

Roll and tilt the bottle until some of the contents enters the inside of the glass stopper.



Second

Carefully remove the stopper so that some of the contents remains in it.

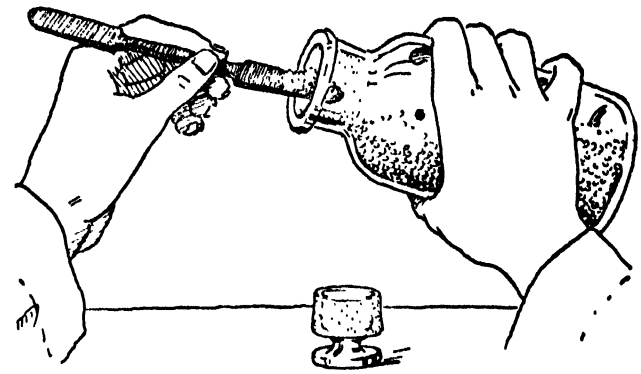


Third

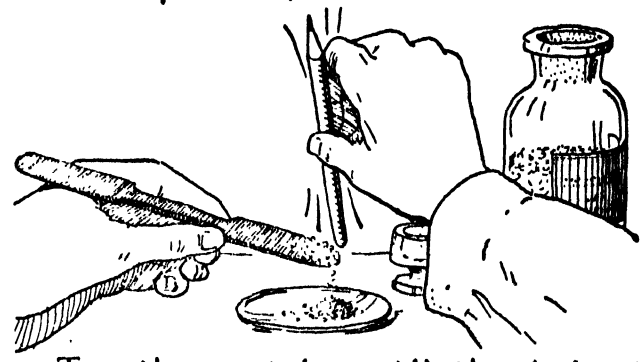
Tap the stopper with a pencil until the desired amount of material falls out.

First Method

Handling Powders and Crystals

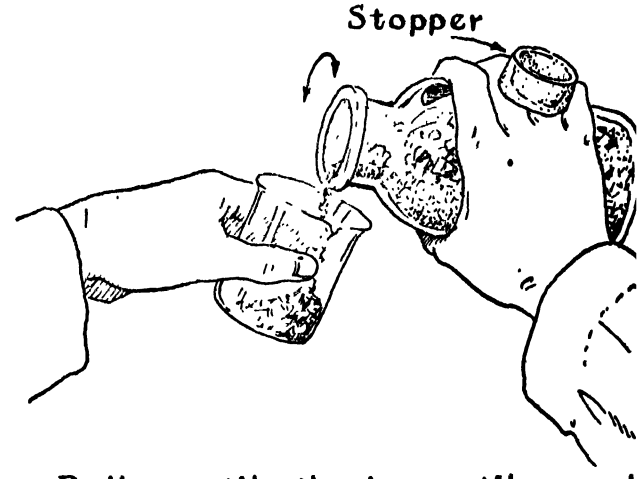


Shovel out a little of the material on the spatula provided.



Tap the spatula until the desired amount falls off.

Second Method



Roll and tilt the jar until enough of the material falls out.

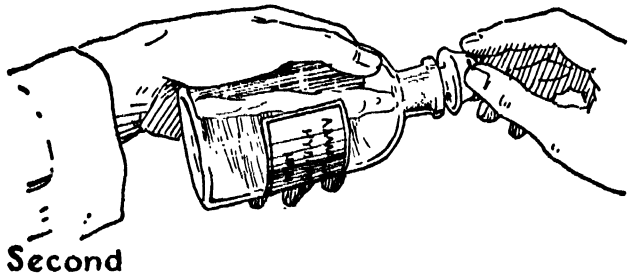
Third Method

ALWAYS replace the stopper.

FIG. i-6. Transferring powders and crystals.



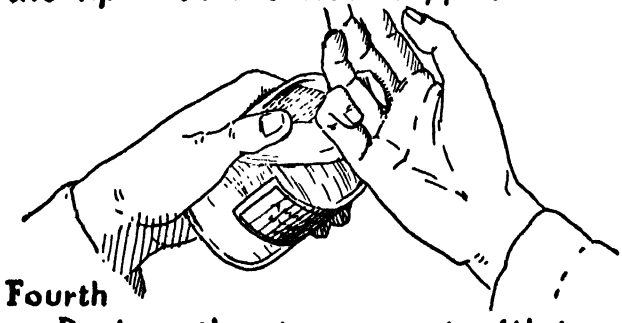
First
Read the label twice.



Second
Hold the stopper in and tilt the bottle until the contents wet the stopper.



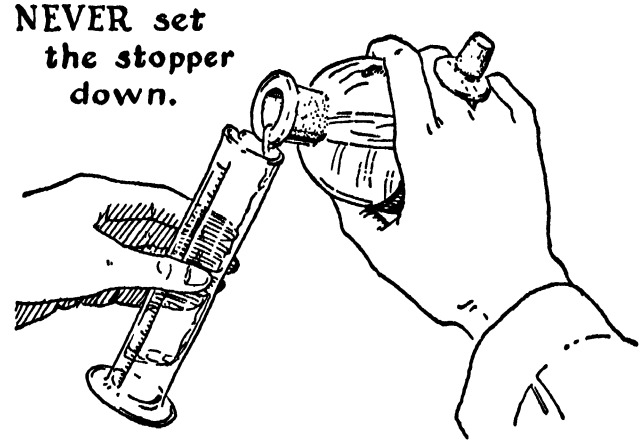
Third
Moisten the inside of the neck and the lip with the wet stopper.



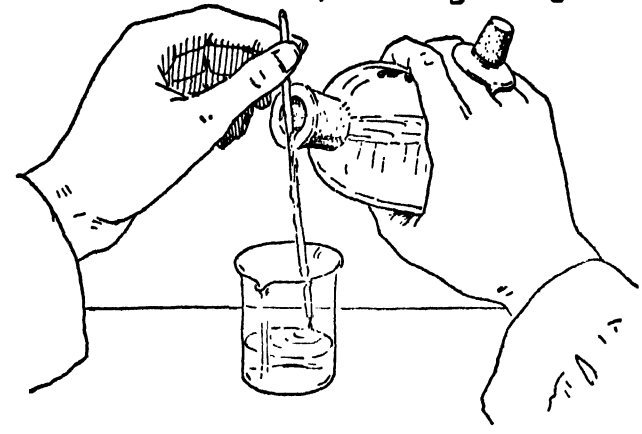
Fourth
Replace the stopper and withdraw it again with the back of the hand.

How to Remove a Stopper

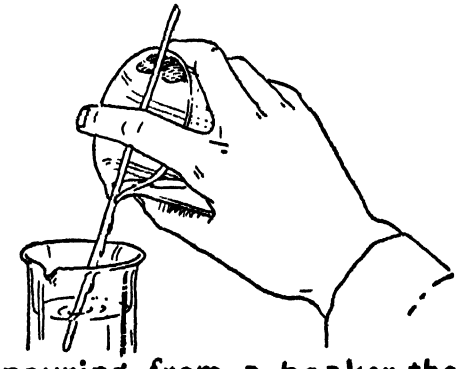
NEVER set the stopper down.



The moistened neck and lip prevent the first drops from gushing out.



Pour down a glass rod when possible.



When pouring from a beaker the stirring rod can be held in this manner.

How to Pour a Liquid

FIG. i-7. Transferring liquids.

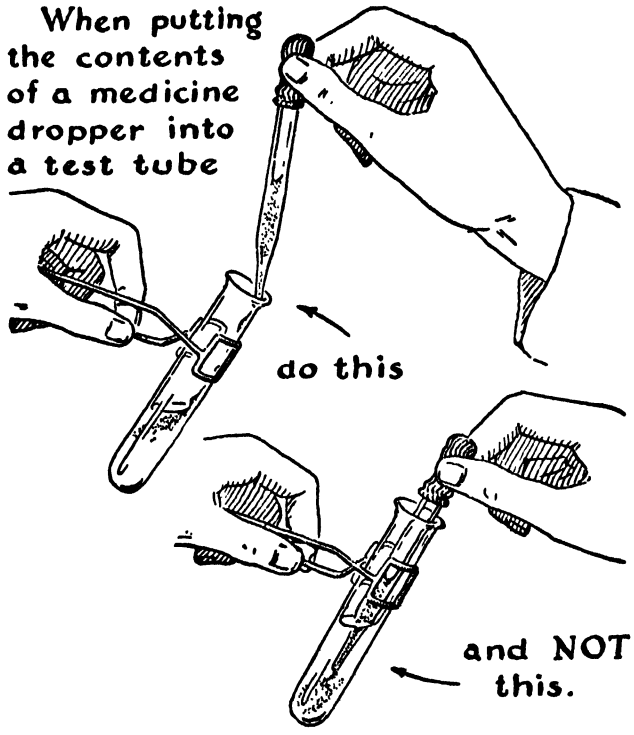


FIG. i-8. The proper use of a medicine dropper.

surface with dilute nitric acid followed by water. The use of cleaning solution (concentrated sulfuric and dichromic acids) or aqua regia (concentrated nitric and hydrochloric acids) is seldom necessary and not always effective. These acids are good oxidizing agents but not universal solvents as many freshmen imagine.

If it is necessary to dry the inside of flasks and similar vessels, they may be warmed over the Bunsen flame. A *gentle* stream of compressed air is then passed through a glass tube leading to the bottom of the vessel until it is dry. Graduated cylinders and heavy glassware such as bottles will break if heated. A warm—not hot—air jet, prepared by passing the air through a coil of copper tubing heated over a burner, is most convenient. (Fig. i-10.) All equipment should be clean and dry when returned to the stockroom.

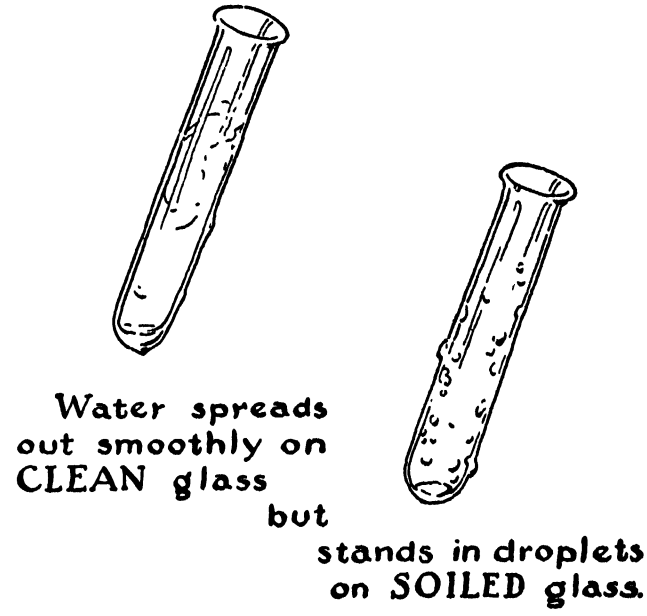


FIG. i-9. Clean and dirty glass ware.

E. The Separation of Precipitates

Precipitates which form during the course of a chemical reaction are usually separated from the

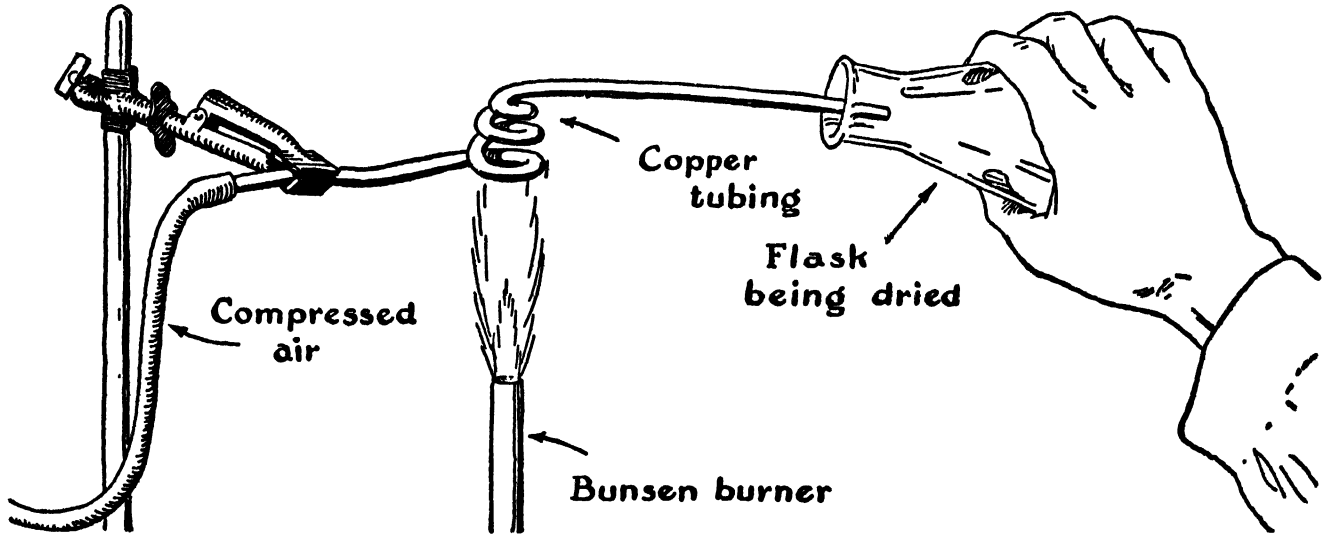


FIG. i-10. A warm air drier.

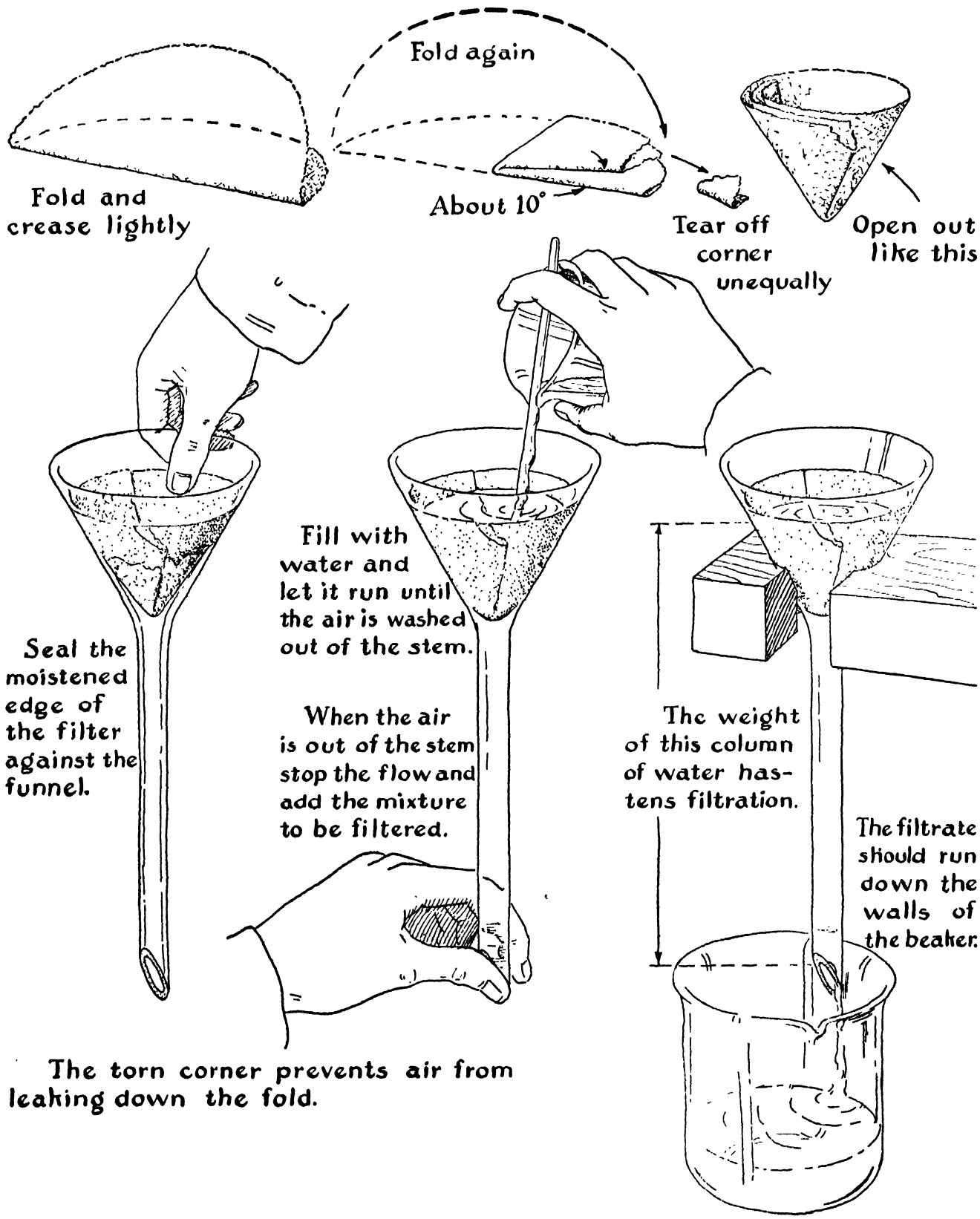


FIG. i-11. The process of filtration.

"mother liquor" in one of three ways:

(1) **Filtration.** This is simply a process of straining the precipitate through a fine sieve—the filter paper. With very fine grained precipitates, which tend to run through the filter, the separation is often aided by letting the mixture stand for some time, often with heating. This process is called *digestion.* This promotes the formation of larger crystals, with the resulting disappearance of the smaller ones, so that a clear filtrate is more easily obtained. The technique of filtration is well illustrated by Figure i-11. Study it carefully. In washing a precipitate, direct a stream of distilled water from your wash bottle around the top of the filter paper for a moment, and let all this water carrying off the impurities drain through the filter. The process may be repeated as often as necessary. Washing is more efficient when repeated with several amounts of water, than when carried out once with one larger amount.

(2) **Decantation.** If the precipitate is quite dense, the mixture may be left standing until the precipitate has settled. The clear liquid is then "decanted," or poured off, leaving the precipitate in the original container. The precipitate may be washed by adding water, letting the solid settle, and again decanting. (Fig. i-12.)

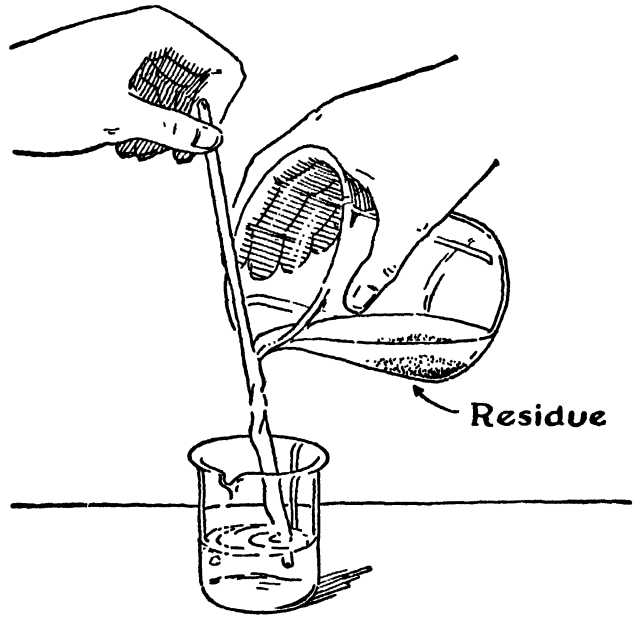


FIG. i-12. The separation of a heavy solid by decantation of the supernatant liquid.

(3) **Centrifugation.** The use of a centrifuge, which is convenient and has now become very popular, substitutes centrifugal force for the force of gravity. It thus involves the same principles of separation as simple decantation. Figure i-13 illustrates the operation of a centrifuge. The precipitate may be washed by mixing it with water and again centrifuging.

F. Laboratory Balances

A platform balance, or "Harvard trip scale," sensitive to about 0.1 gram, is used for crude weighings. An agate, knife-edge, triple-beam balance, sensitive to 0.01 gram, is used for more precise work. (Fig. i-14 (a) and (b).) For most of the

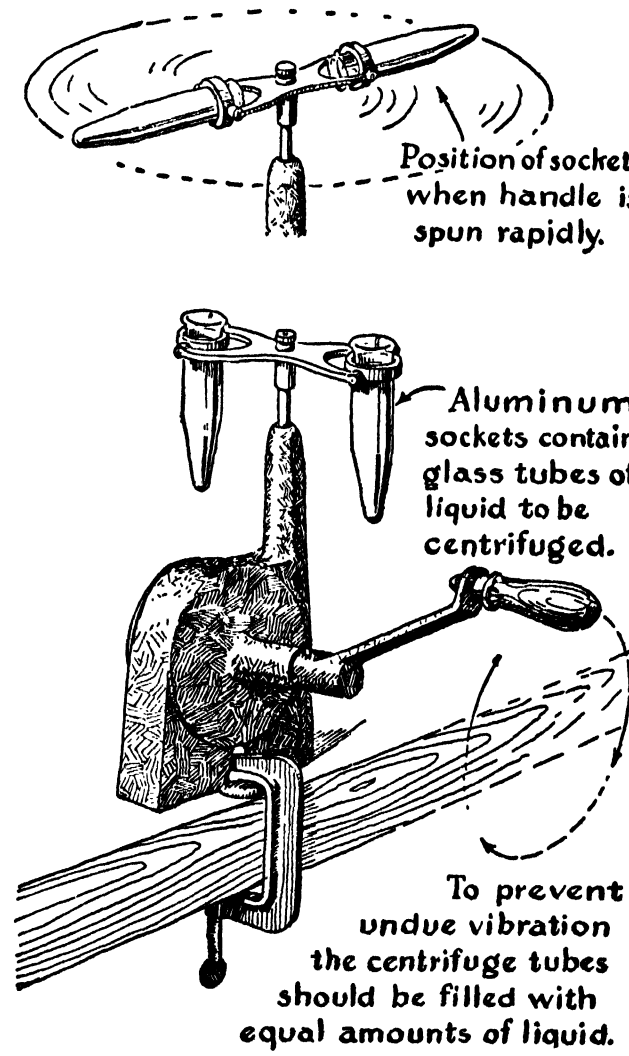


FIG. i-13. The principle of the centrifuge. The rate of settling of a precipitate is increased many fold by the application of a centrifugal force 500 to 1000 times that of gravity.

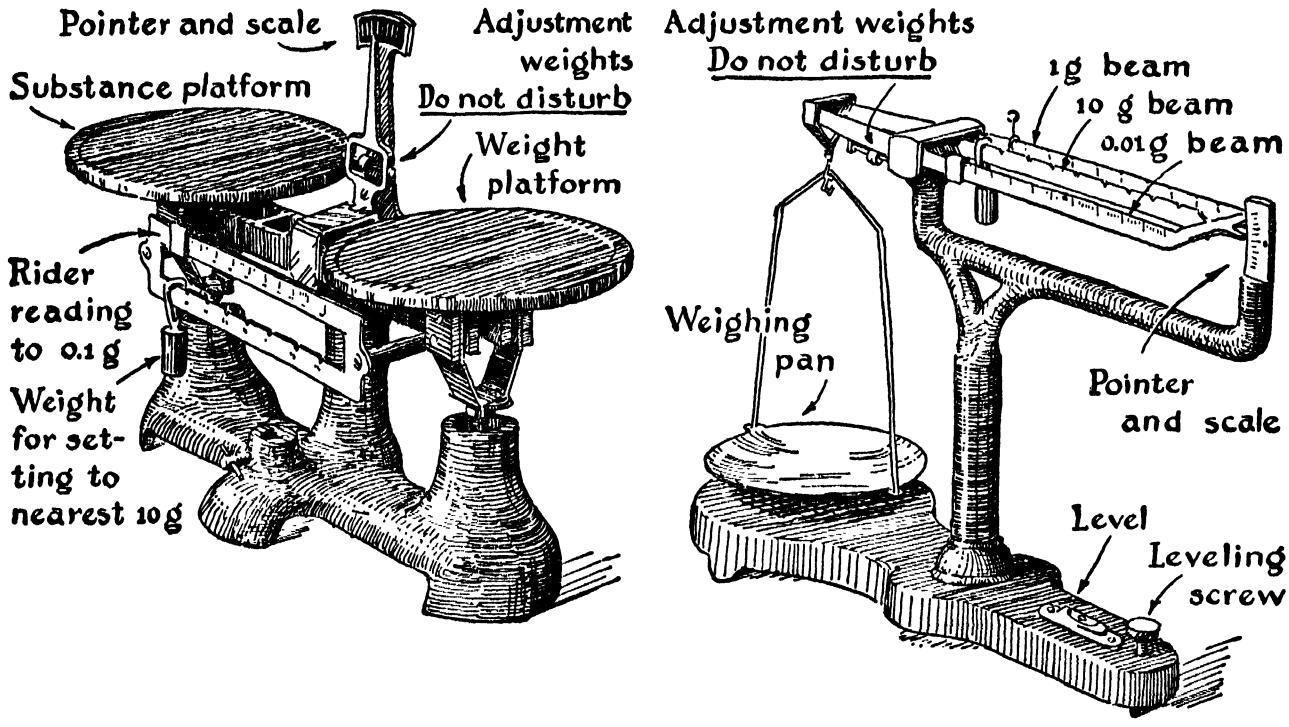


FIG. i-14. (a) A platform balance. (b) An agate knife-edge triple-beam balance.

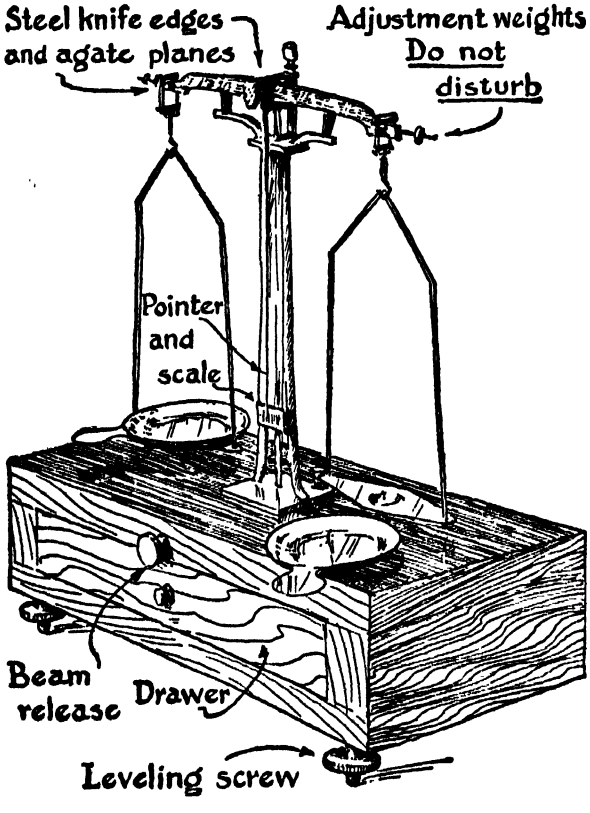


FIG. i-15. A pulp balance.

quantitative experiments, either a pulp balance (Fig. i-15), or preferably an analytical type balance (Fig. i-16), capable of weighing to the nearest milligram, should be used.

G. The Care and Use of the Balance

Precautions and Balance Rules:

(1) Handle the beam supports by using the center knob gently, so as not to jar the balance.

(2) Always have the beam supports up in place when adding or removing any objects or weights from the pan, or when adjusting the rider.

(3) Never put chemicals directly on the balance pans. Use a small beaker, or square of glazed paper.

(4) Never weigh an object while it is hot, or even warm. Convection currents of air in the balance case will render the weighing meaningless.

(5) Handle analytical weights only with the forceps provided, never with the hands. Do not borrow or lend weights. Each set is sufficient for any weighing up to 100 grams, when the largest weight in the set is 50 grams.

(6) Keep the balance case closed when taking final readings on the pointer scale, and when you are through weighing.

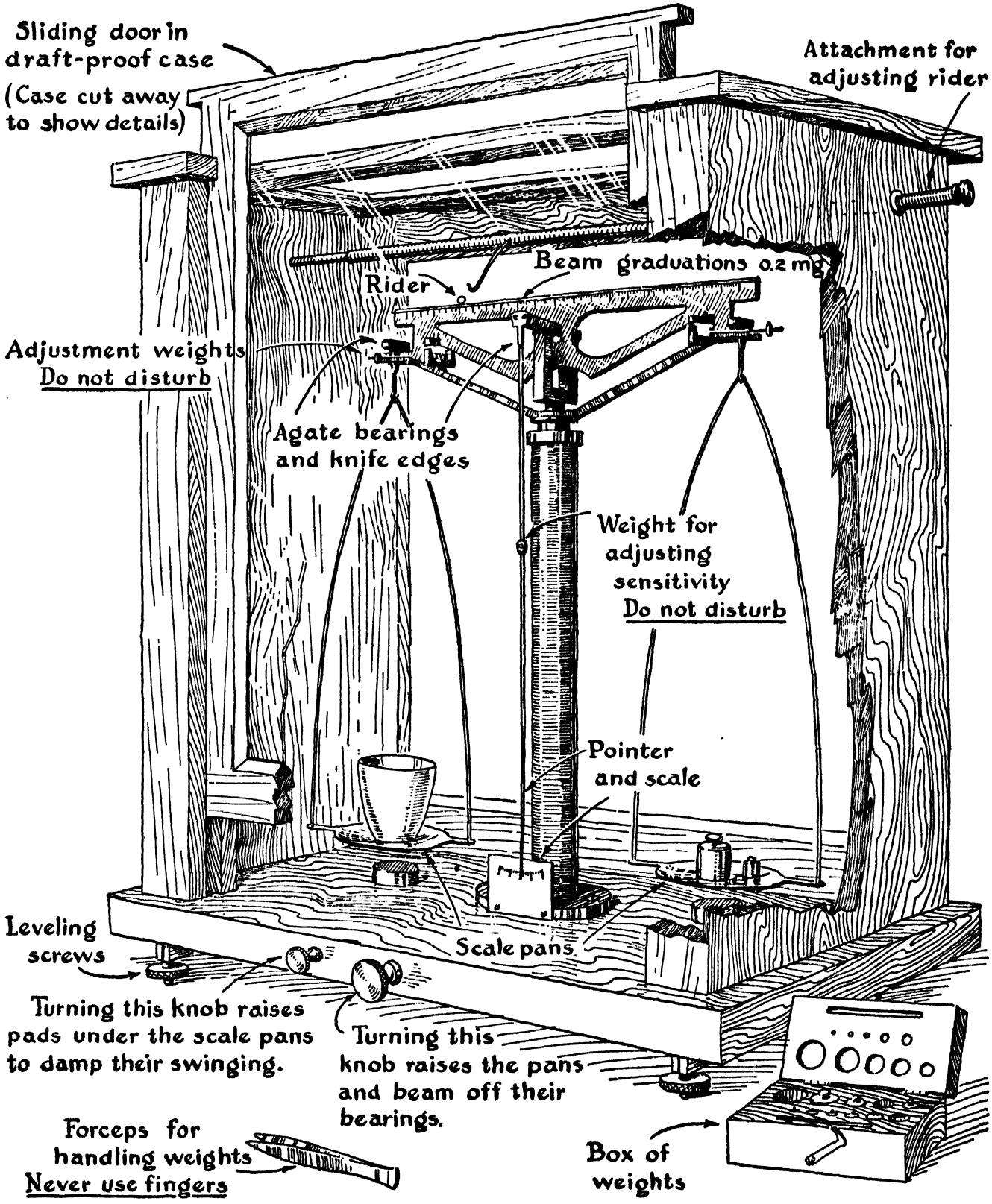


FIG. i-16. A balance for more precise weighing. Note the operation of the beam supports, and of the rider.

(7) Request the instructor to make any necessary adjustments on the balance.

Procedure in Weighing. We shall carry out weighings only to the nearest milligram (0.001 g). Your instructor will explain the exact procedure to be followed with the type of balance available in your laboratory. If an analytical balance, which is sensitive to 0.0001 g is used, it will not be necessary to take exact pointer-scale readings. In fact, unless the balance is in excellent condition, and accurately calibrated weights are used, and until you have had considerable experience in weighing, it is a waste of time to attempt closer weighing than 0.001 g.

Carry out a weighing in the following steps:

(1) *Determine the Rest Point of the Balance.* Be sure the balance pans are clean, the beam and pan supports and knife edges in proper position, with the rider off the beam, or at zero or center position. On releasing the beam and pan supports, cause the pointer to swing gently 3 to 7 scale divisions either side of the scale center, and note to the nearest half scale division, the point about which the pointer is oscillating (i.e. that point at which it would come to rest if there were no irregularity due to friction). This is the rest point, or point of reference for the succeeding weighing. (If the balance beam does not swing freely and "die down" evenly or if the rest point is over 2 or 3 scale divisions from the scale center, call an assistant to make the necessary adjustments.)

(2) *Balancing the Object and Weights on the Pans.* With the pans and beam fully supported, place the object to be weighed on the left pan. Add weights as needed to the right pan to restore the pointer fluctuations to a point almost, but not quite, to the initial rest point. In adding the weights, add first the largest denomination you think can be used, and release the beam support gently to ascertain that the weight is not too large. Add successively smaller denominations of weights until the weight has been determined within the nearest 10 milligrams (i.e. with the pointer still fluctuating about a point slightly to the right of the rest point).

(3) *Adjusting the Rider.*[1] Close the balance case so as to avoid convection currents in the air, for this final step in the weighing. The wire rider weighs 10 milligrams, hence by suitably placing this at successive 1 milligram intervals, and taking the rest point readings, adjustment may quickly be made so that the pointer swings coincide with the original rest point (within the nearest milligram).

[1] For balances which do not have a rider, follow the method as outlined in paragraph 4 for the final adjustment.

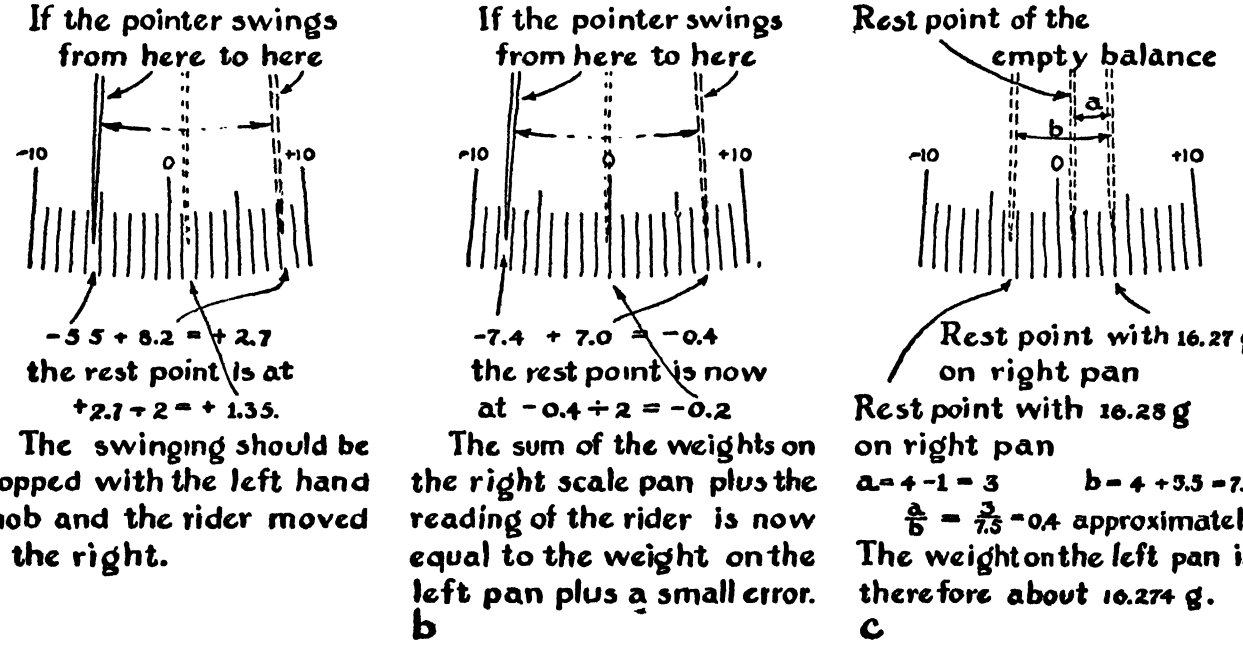


FIG. i-17. (a) and (b). The use of pointer scale readings to determine the rest point. (c) The determination of the weight to 0.001 g when the smallest weight used is 10 mg and the balance has no rider.

(Note that if a 10-mg rider is used on a balance with a rider scale of only 5 scale divisions, each division equals 2 mg. See Fig. i-17ab.)

(4) *Using the Method of Pointer Scale Readings.* For balances without a rider, the weight to the nearest milligram may be obtained as follows. Suppose the rest point as found in section (1) above is 1 scale division to the right of the scale 0 (+1, see Fig. i-17c). Suppose also that, when weighing the object, the scale reading with 16.270 g on the pan (totaling within 10 mg of the true weight), is +4 scale divisions. Now add a 10-mg weight to the right pan, and again take the scale reading. Suppose it now reads −3.5 scale divisions. Note that adding 10 mg moved the scale-reading 7.5 scale divisions, while we only want to move it 3 scale divisions, (to +1). We therefore want to add 3/7.5 × 10 mg, or 4 mg. The final weight is then 16.274 g.

(5) *Counting the Weights.* More errors are made in counting weights than in making the weighing adjustments. First count the weights on the pan and check by noting the empty places in the weight box. Make a record of each weight denomination you use, so that you can recheck the counting of the weights, if the results of the experiment indicate such an error may have been made. Keep and label this record. Total the result as illustrated, then enter the weight at once on your experiment report sheet. (Be sure that you record a 50-mg weight, for example, as 0.050 g, and not as 0.500 g, when computing the total weight.)

Example of totaling weights:

		10.000 g
		5.000
		1.000
200 mg	=	0.200
50 mg	=	0.050
20 mg	=	0.020
4 (rider)	=	0.004
		16,274 g

The weight of the object then, was 16.274 grams. Note that the milligram weights are finally expressed as fractions of a gram, in the column to be added.

H. Volumetric Measurements

Approximate Volumes. The volume stamped with the trademark on beakers and flasks is only approximately correct. It can be used only where crude estimates of capacity will suffice. Frequently you are asked to add a small volume of from 1 to 3 ml of a reagent. This can often be accomplished with sufficient precision by estimating the amount in a 10-cm test tube, which has a total capacity when filled of 8 to 10 ml. Likewise, you should know that a 15-cm × 2-cm test tube has a capacity of about 30-ml. Use your graduated cylinders only when more precise measurements are necessary. It is not good practice to carry out chemical test reactions in graduated cylinders, as they cannot be heated, and are more difficult ot clean. Use test tubes for all such tests.

Reading a Meniscus. The meniscus is illustrated in Figure i-18. In all graduated ware, such as burettes, graduated cylinders, and volumetric flasks, always read the bottom of the meniscus. Be

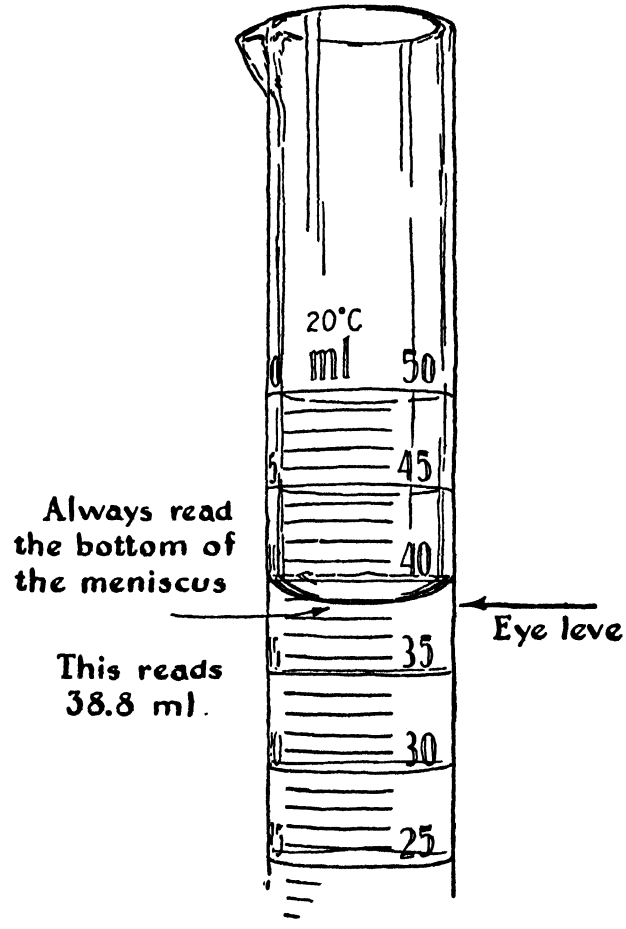


FIG. i-18. The proper method of reading a meniscus (curved surface of a liquid) in order to measure the volume of the liquid.

sure the eye is on a horizontal with the level of the liquid, so as to avoid the error of parallax. Good and reproducible—though not too bright—lighting is essential for precise measurements, so that the meniscus is viewed under the same conditions in successive readings. Arrange the graduated cylinder, or other vessel, so that you will look toward the light. White opaque paper back of the vessel sometimes helps, and a dark surface on the paper just a little below the level of the meniscus, or your finger held back of the vessel just below the meniscus, helps to give a sharp definition.

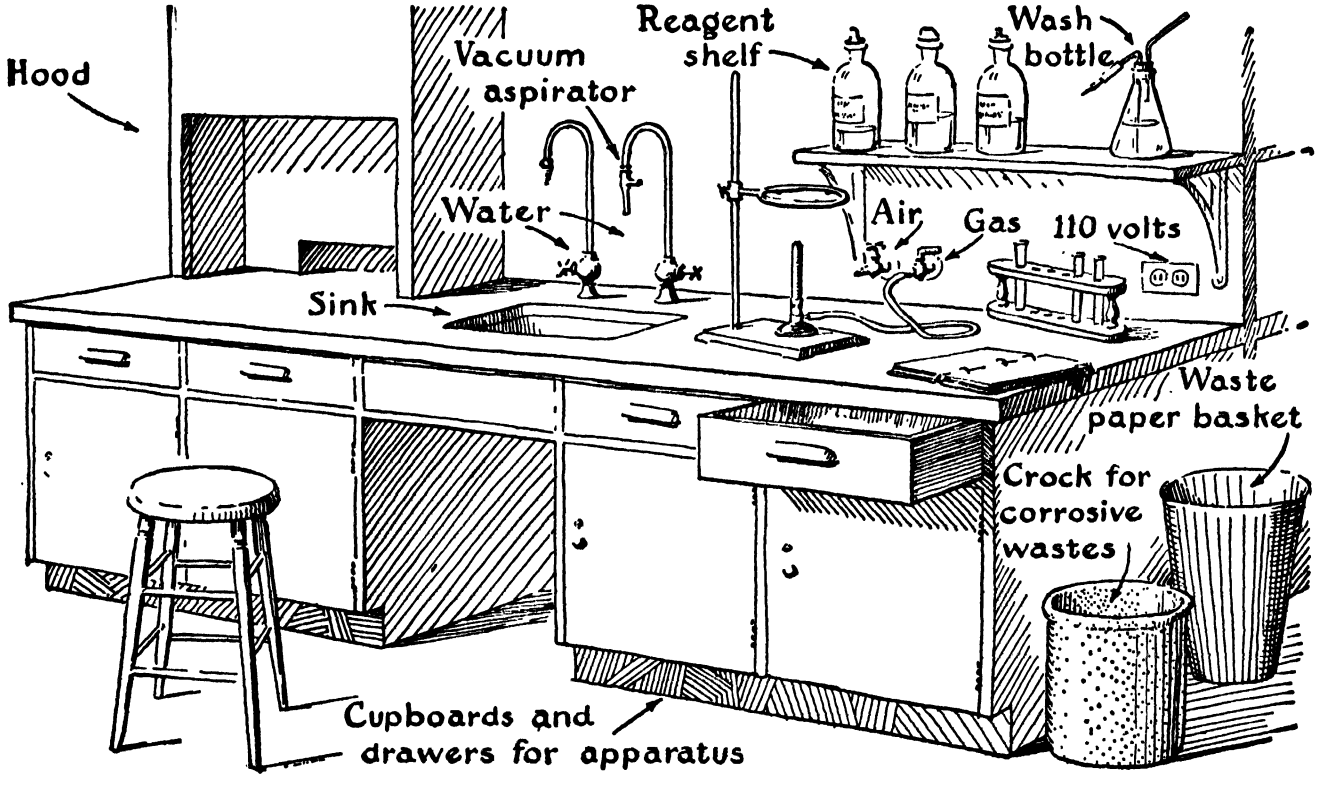


FIG. i-19. A typical laboratory table arrangement.

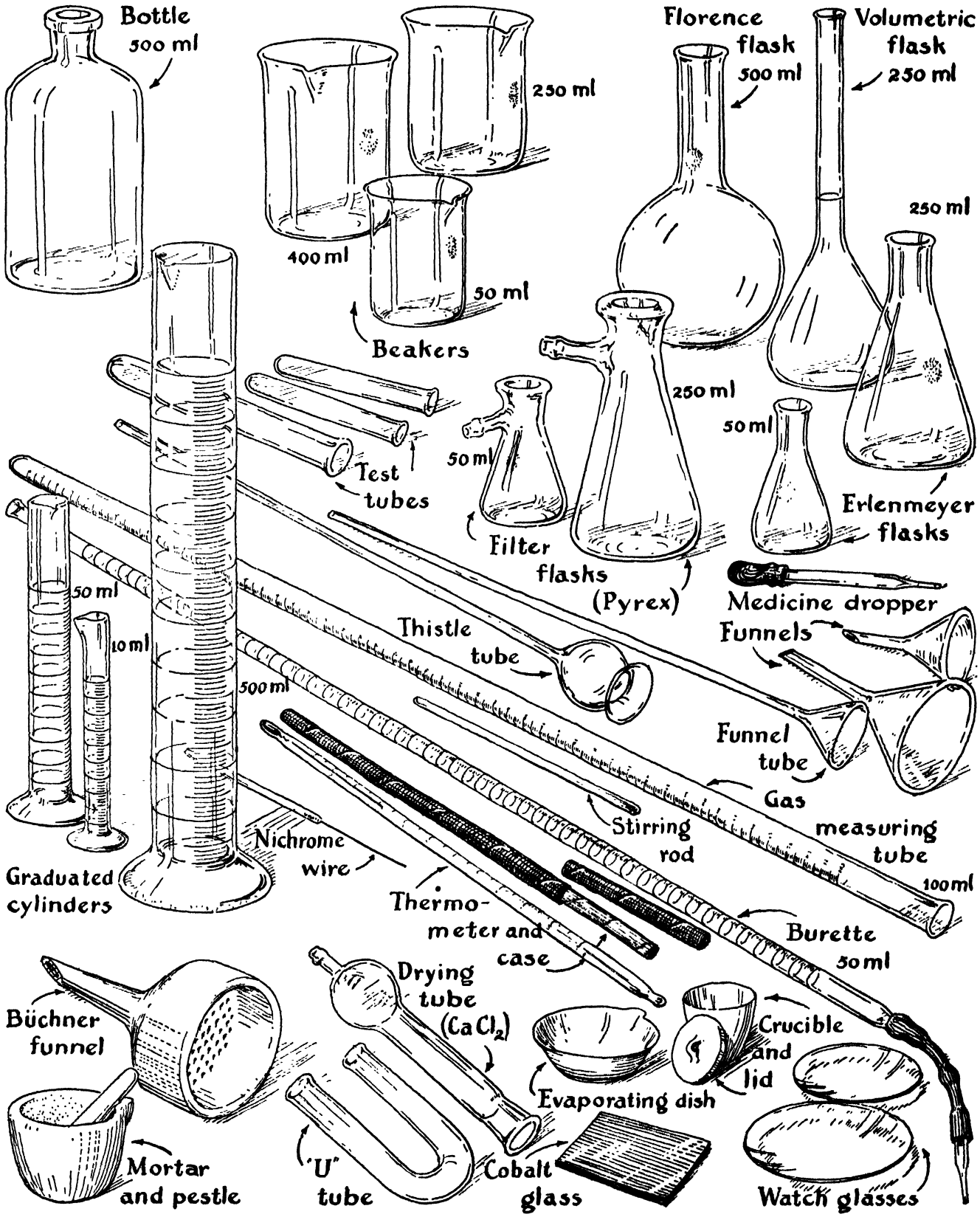


FIG. i-20. Chemical laboratory apparatus—glass and porcelain.

Professional workers in every field keep their tools and equipment in the best possible working condition. Keep your equipment clean and conveniently arranged in your locker, so that it is ready for use.

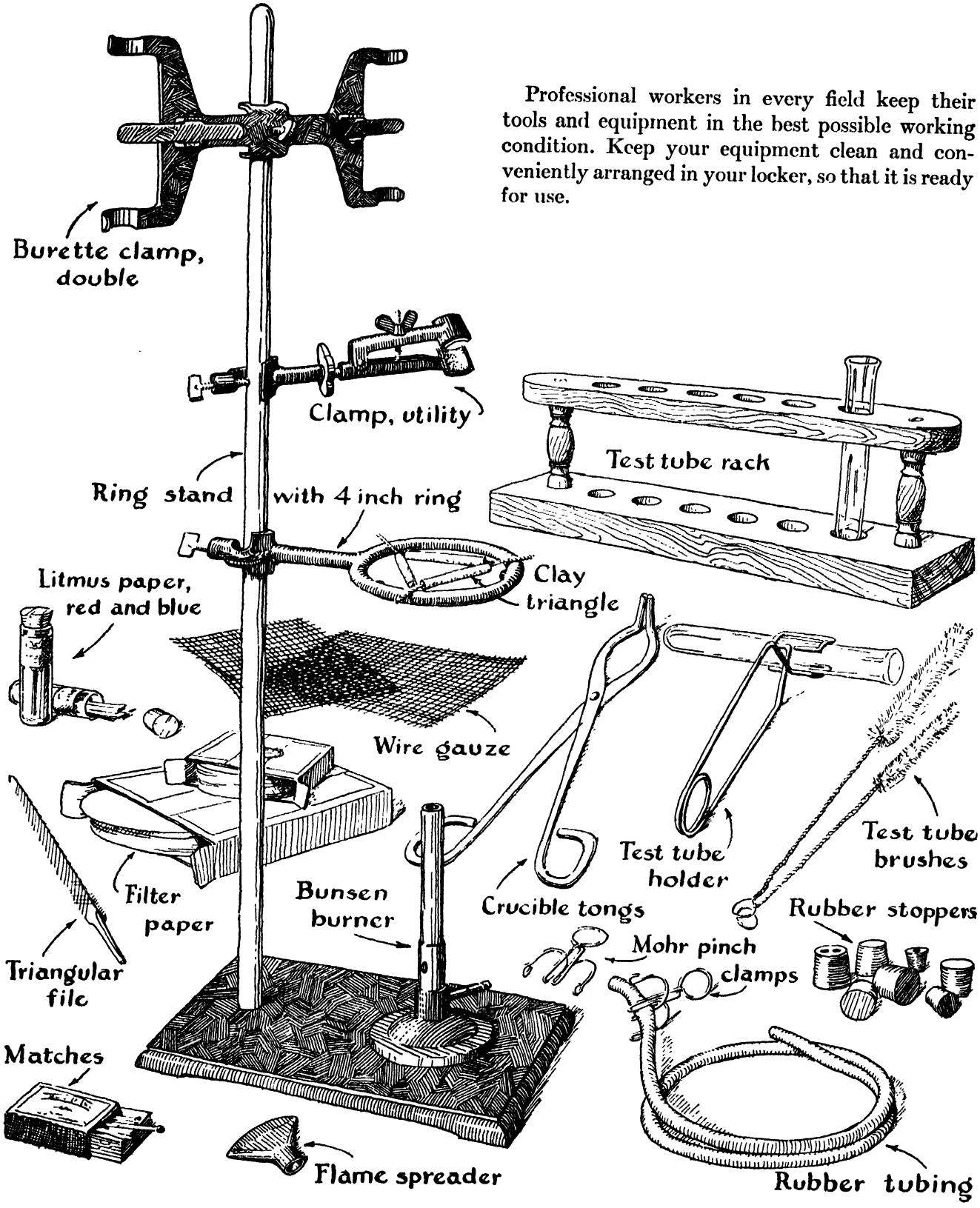


FIG. i-21. Chemical laboratory apparatus—accessories and implements.

Introductory Laboratory Techniques 1

Experimental Procedure

When beginning work in the chemistry laboratory you should do these four things:

(1) Check the laboratory equipment in the locker assigned you. Refer to the drawings in Figures i-20 and i-21 on the preceding pages for the identification of any item with which you are not familiar. Ascertain that all items are present and examine them carefully to be sure they are in an acceptable condition. Hereafter, you will be responsible for this equipment and will be charged for any breakage or shortage at the conclusion of the course.

(2) Familiarize yourself with the "Safety Precautions," "Laboratory Rules," and "Laboratory Manipulations" as given on Pages vii to xxiv.

(3)[1] Learn the elements of glass working, as directed and illustrated by the instructor, in accordance with the suggestions on the manipulation of glass tubing, paragraph B, in the preceding section. Practice the fundamental operations, as shown in Figures i-3 and i-4, until you have attained a satisfactory proficiency, and then prepare a wash bottle in accordance with Figure i-5. Use a 250-ml Erlenmeyer or Florence flask for this purpose. An acceptable wash bottle will have the upper sections of the glass bends aligned in a straight line, cut to the designated lengths, and properly fire polished. Your instructor will indicate his approval by initialing your report sheet in the space provided.

(4) Learn the metric system of measurements if you are not already familiar with it. See Table II, "The Metric System of Units," in Appendix II. Carry out the suggestions as given in the report sheet for this experiment for the measurement in metric units of the length, volume, or weight of various laboratory items, using the appropriate measuring device—a meter stick, a graduated cylinder, or a suitable balance which is sensitive to 0.1 g. You will thus gain a visual appreciation of metric dimensions. Further experience may be gained by measurements of the density of various substances, as outlined in the next paragraph.

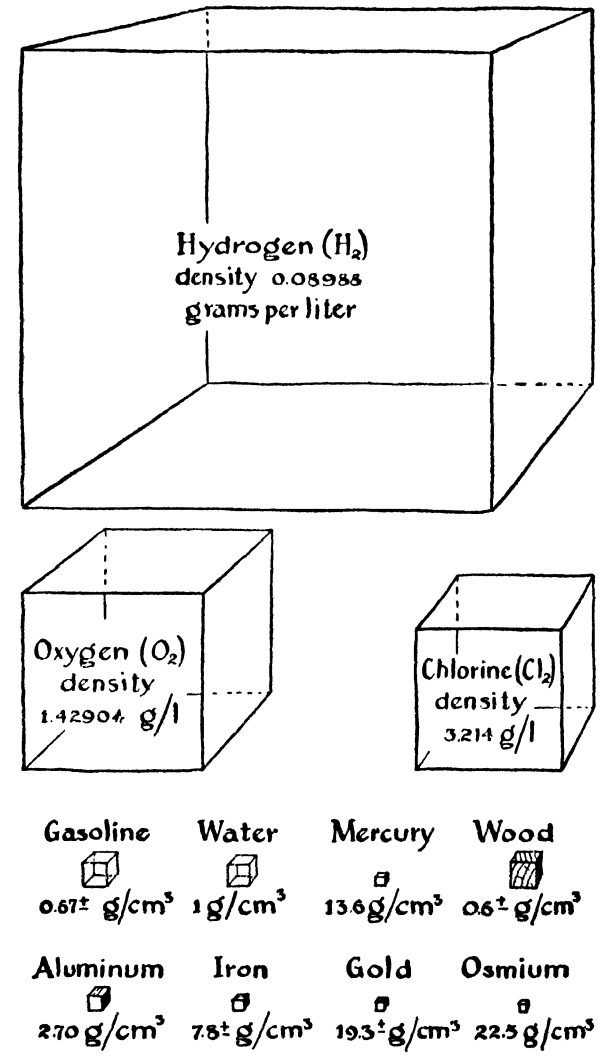


FIG. 1-1. To illustrate the relationship of density to volume. The different size cubes represent the relative volumes of equal weights (about 0.03 g) of various materials, at 0°C.

Density. The determination of this important physical property requires measurements of two

[1] In order to avoid congestion at the balances, half the class may be designated to do (4) on metric measurements, while the other learns glass working.

quantities: the mass, M, and the volume, V, of a given quantity of a substance.[1] The ratio of these two, or the mass per unit volume, is the density, that is, D = M/V. In the metric system, the result is expressed as grams per cubic centimeter, g/cm³. See also Figure 1-1.

(a) *Density of Liquids.* After receiving instructions on the method of weighing with the type of balance you are to use (also read paragraphs F, P. xix, and G, P. xx), weigh a clean, dry, 150-ml beaker to the nearest 0.1 g. (Enter this and all other data *as you obtain it* directly in the report sheet.) Place between 40 and 50 ml of the liquid to be used (water, carbon tetrachloride, or an unknown[2] provided by the instructor) in your graduated cylinder. Read the volume to 0.1 ml (note the precautions in reading a meniscus, paragraph H, P. xxiii), and carefully transfer this liquid as completely as possible to the beaker. Re-weigh the beaker and contents. From these data, calculate the density of the liquid.

(b) *Density of Solids.* As an example of the technique to use with an irregularly shaped solid, determine the density of roll sulfur. Select about 20 to 30 g of pieces of roll sulfur which have been crushed small enough to be placed in your 50- or 100-ml graduated cylinder, but avoid unduly small pieces and *any* powder. Weigh the sulfur in a beaker, or evaporating dish, which has been previously weighed. Place about 30 ml of water in the graduated cylinder and read the volume to 0.1 ml. Carefully add the pieces of sulfur, tilting the cylinder and sliding them in so as to avoid any loss of water by splashing. Tap the sides to dislodge air bubbles, and again read the volume. The increase will be the volume of the sulfur. See Figure 1-2.

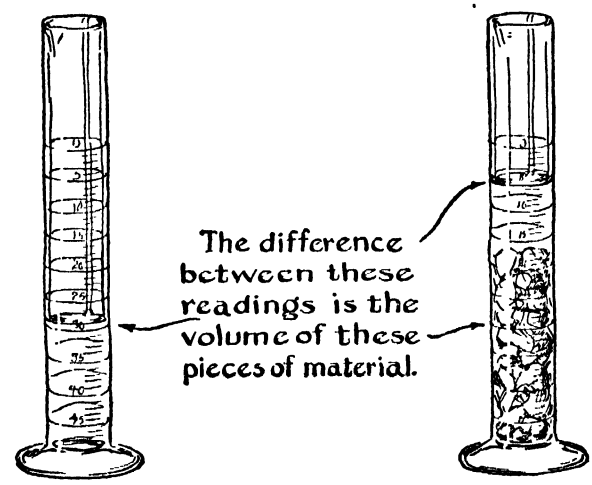


FIG. 1-2. Illustrating a method of measuring the volume of an irregularly shaped solid.

Calculate the density. Other materials, as suitably shaped pieces of metal or metal shot, marble chips, etc., may be similarly used.

If it is desired to determine the density of a regular shaped solid, as a rectangular block or a cylinder, the volume may be calculated from measurements of the length, breadth, and thickness, or the length and diameter, respectively. The weight may be obtained directly on the balance, and the density calculated.

[1] It is important when making measurements of physical quantities, such as weight, length, or volume, that the measuring devices you use be consistent with the *precision of measurement* desired. Thus a precision of 1% in the weighing of a 50-gram sample requires a balance which is accurate to only 0.5 gram (1% × 50 g = 0.5 g); for the same precision with a 1-gram sample you need a balance which is accurate to 0.01 gram. In this experiment, platform balances which read to 0.1 gram and graduated cylinders which can be read to about 0.2 ml should not cause errors in the calculated density greater than about 1%.

The *percentage error* in an experiment is calculated by dividing the actual error by the accepted value, and then multiplying the result by 100 to express it as percent, i.e. parts per hundred.

See Appendix I for a more complete discussion of The Measurement of Physical Quantities.

[2] Suitable solutions of unknown density may be prepared by the instructor by dissolving inexpensive soluble salts such as $CaCl_2$, NaCl, etc. in water.

REPORT: Exp. 1

Introductory Laboratory Techniques

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Glass Working

Instructor's approval of wash bottle . . . . . _____

2. Metric Measurement of Length

Learn to recognize approximate dimensions at a glance. Practice by measuring numerous objects about the laboratory. Record the dimensions of the following, to 0.1 cm or 1 mm.

Large test tube: Length_____ Diameter_____

Small test tube: Length_____ Diameter_____

Large graduated cylinder: Length_____ Diameter_____

Diameter of: Evaporating Dish_____ Crucible_____

Conversion factor. In order to determine the number of centimeters in an inch, measure the length of this page, in centimeters, and in inches. Express any fractional part of an inch (measured to the nearest sixteenth) as a decimal.

Width of this page_____ cm _____ in.

Calculation of conversion factor (ratio of centimeters to inches):

Your value . . . . . _____

Ratio, from Appendix Table II_____

3. Metric Measurement of Volume

Learn to recognize approximate volumes at a glance. Practice by measuring various vessels in your desk equipment. In particular, learn to estimate the height of water in your small and large test tubes which corresponds to 1 ml, 2 ml, 5 ml, and 10 ml volume. You will frequently estimate small volumes in this manner. Likewise, to dispel any false illusions you may have as to the precise volumes of beakers, flasks, etc., as indicated by the trademark, fill several of these level full with water, and determine the actual volume by repeated fillings into your graduated cylinder.

Capacity of test tubes: small_____ large_____

Evaporating dish_____ Crucible_____

Beakers: "150" ml_____ "400" ml_____ "250" ml flask_____

4. Density of a Liquid (See directions in "Experimental Procedure")

Liquid used		
Weight, beaker + liquid		
Weight, beaker		
Weight, liquid		
Volume of liquid		
Density, calculated[1]		
Density, from literature		
Percentage error[1]		

[1] Show method of calculation here:

5. Density of a Solid

Solid used	*Sulfur*	
Weight of solid		
Final volume		
Initial volume		
Volume of solid		
Density, calculated[1]		
Density, from literature		
Percentage error[1]		

[1] Show method of calculation here:

6. Questions

(a) How would you modify the procedure as outlined, if you wished to determine the density of a solid which is soluble in water, for example, rock salt, or sugar?

(b) Would your density determinations be more precise if you weighed your samples to 0.01 or 0.001 g, instead of only to 0.1 g, while other measurements were carried out as before? Explain.

(c) If 20 g of sulfur is used in the above determination, what is the limiting precision of measurement when the weight is determined to a precision of 0.1 g.

_____%

A Review of Fundamental Mathematical Operations — A

A Study Assignment

If you are a typical beginning student of chemistry, you are probably concerned about the rumors you have heard that chemistry requires a good background in mathematics. You should recognize very early that chemistry is one of the *exact* sciences, and it is indeed fortunate that we are able to express many of its precise concepts, laws, and principles in the form of mathematical relationships. Once these relationships have been set up properly, however, you should be relieved to know that the mathematical operations required to simplify and solve the equations are mainly the arithmetical operations of multiplication, division, addition, subtraction, and handling fractions, and the simple algebraic operations required to solve first-degree and, occasionally, second-degree equations.

The difficulties which students encounter with chemical problems are very rarely due to the inability to perform the mathematical operations; they stem, rather, from an incomplete understanding of the chemical laws or principles which form the basis of the mathematical set-up. In many cases the difficulty is simply due to the fact that the terms used in chemistry are new. For example, whereas a student would give a ready answer for a problem which asks how many eggs, at 72 cents per dozen, one could purchase for $1.56, he may be bewildered by an exactly analogous problem which asks how many milliliters of concentrated sulfuric acid, with density of 1.84 g/ml, should be used to provide 265 g of this substance for an experiment. Consequently, you should strive to obtain a thorough understanding of, and familiarity with, all the terms and principles, so that you can reason out the proper set-up for the problem. You should always avoid solving problems by substituting blindly in some formula which you have merely memorized and may not understand.

A. How to Set Up Chemical Problems

Although it is impossible to outline a general method for solving problems that is suitable to everyone, the following analysis of what is involved in problem-solving may be useful.

1. Read the problem carefully. Be sure to find out the meaning of every term or concept involved.

2. Pick out the law(s), principle(s), or definition(s) which may apply to the problem. Review these if necessary.

3. Reason out the proper relationships between the numerical terms to obtain the mathematical set-up.

4. As a check on your reasoning in the previous step, it is well to label each term with its dimensional unit(s). Factor out these units wherever possible to determine if the indicated calculations in the set-up will give the units desired in the answer. Units are multiplied or divided just as if they were numerical terms in this *factor-the-units* check.

5. The final step then involves carrying out the mathematical operations either by manual methods or, preferably, with the aid of logarithms or a slide rule. Some suggestions on the use of these time-saving devices are given in the review which follows.

To illustrate the application of the above analysis, let us consider some problems dealing with an important physical property, the density of a substance.

Illustrative Problem 1. A rectangular bar of iron has the dimensions 1.10 cm by 2.17 cm by 6.41 cm. It weighs 121.7 g. What is the density of iron?

1. Density is defined as the ratio of the mass of a specimen to its volume. It should also be recognized that the volume of a rectangular bar may be found by multiplying its length by its width by its height.

2. The definition of density may be expressed mathematically as

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

3. The data of the problem are then analyzed

and the mass of the bar placed in the numerator and the volume expression in the denominator:

$$\text{density} = \frac{121.7\ \text{g}}{1.10\ \text{cm} \times 2.17\ \text{cm} \times 6.41\ \text{cm}}.$$

4. Before carrying out the mathematical operations, check the units in the set-up to be sure the units of density, g/cm³, will be obtained.

5. When the arithmetic operations are carried out, the result is:

$$\text{density} = \frac{121.7\ \text{g}}{15.5\ \text{cm}^3} = 7.85\ \text{g/cm}^3.$$

Illustrative Problem 2. An experiment calls for 204 grams of mercury. What volume of liquid mercury should be measured out in a graduated cylinder to obtain the desired weight? The density of mercury at room temperature is 13.6 g/cm³.

This time let us proceed by the "Monte Carlo" or "Las Vegas" method instead of the systematic analysis. As you see in Figure A-1, there are four possible ways of setting up the data given in this problem, and the student, Mr. M. I. Lucky, has one chance out of four to pick the right one.



FIG. A-1. One chance out of four.

The alternative to this method of chance is, o course, to reason out a solution based on an under standing of the terms and concepts involved, followed by a *factor-the-units* check. Since density is the weight of one cubic centimeter, you should reason that by dividing the weight of mercury desired by its density you should obtain the number of cubic centimeters required:

$$\text{volume} = \frac{204\ \text{g}}{13.6\ \text{g/cm}^3}.$$

A check of the units shows that carrying out this operation as indicated, g ÷ g/cm³ = g × cm³/g = cm³, gives the units of volume desired in the answer. Now the numerical answer may be safely obtained by dividing 204 by 13.6, which gives 15.0 cm³ as the volume of liquid mercury. In Figure A-2, another student, Mr. I. M. Shoor, has checked all the possible set-ups in Figure A-1 by the *factor-the-units* method and has identified the proper one.

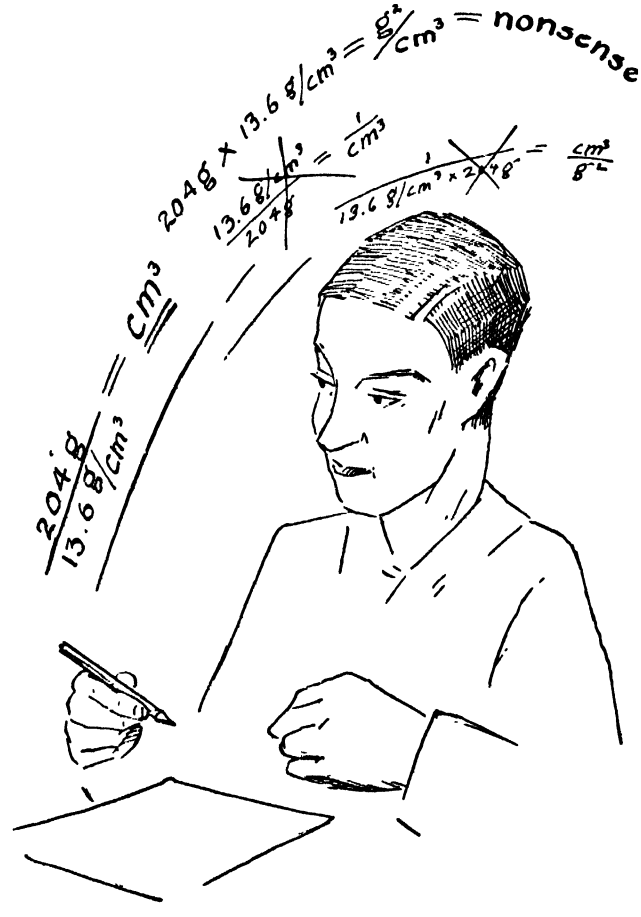


FIG. A-2. Factor-the-units check.

In summary, remember that the purpose of problem-solving in chemistry is to help you get a better working knowledge of the important laws, principles, and relationships which unify the many facts of the science. The crucial part of any problem is the determination of the proper set-up or mathematical relationship. Your ability to do this will be limited only by lack of understanding of the meaning of the terms, concepts, laws, and principles involved. The mathematical operations necessary to solve the set-ups are usually quite simple, but in case you need a refresher the following review and exercises are included.

B. How to Solve Algebraic Equations

1. The same quantity may be added to or subtracted from each side of an equation without changing the equality.

2. Each side of an equation may be multiplied or divided by the same quantity without changing the equality.

3. *First-degree equations*, in which the exponent of the unknown quantity does not exceed one, may be solved by applying the above axioms.

Example 1. $6x - 4 = 2x + 16$ Solve for x.

Add 4 to each side: $6x = 2x + 20$

Subtract 2x from each side: $4x = 20$

Divide each side by 4: $x = 5$

Example 2. $\frac{y}{x} = \frac{2a}{3b}$ Solve for x.

Multiply each side by 3b: $\frac{3by}{x} = 2a$

Multiply each side by x: $3by = 2ax$

Divide each side by 2a: $\frac{3by}{2a} = x.$

4. *Quadratic equations*, in which the exponent of the unknown quantity does not exceed two, may be solved as follows:

Example 1. $4x^2 - 9 = 0$ Solve for x.

Add 9 to each side and divide each side by 4, to obtain:

$$x^2 = \frac{9}{4}.$$

Take the square root of each side: $x = \pm \frac{3}{2}$.

If a quantity x is a mass or volume or some other quantity which can have only a positive value, then the correct value would be $+\frac{3}{2}$, and the root $-\frac{3}{2}$ would be ignored.

Example 2. $4x^2 + 4x = 3$ Solve for x.

This equation is similar to the general quadratic equation

$$ax^2 + bx + c = 0$$

which may be solved by the method of completing the square to give the formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}.$$

To solve our example, we subtract 3 from each side:

$$4x^2 + 4x - 3 = 0.$$

Then substitute the coefficients in the above formula:

$$x = \frac{-4 \pm \sqrt{4^2 - 4(4)(-3)}}{2(4)}$$

$$= \frac{-4 \pm 8}{8} = \frac{1}{2} \text{ or } -\frac{3}{2}.$$

C. Proportion and Graphical Relations

A fraction expresses a division, that is, a ratio between the numerator and the denominator. Two such ratios (or fractions) which are equal to one another constitute *a proportion.*

Example 1. Direct Proportion. The corresponding volumes and absolute temperatures of a given quantity of gas have a constant ratio, i.e. are directly proportional. This is Charles' Law. This fact may be expressed by the equations

$$V = kT, \text{ or } \frac{V}{T} = k.$$

Since any two corresponding values of V/T are equal to k, we may write the proportion

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ or by transposing, } \frac{V_1}{V_2} = \frac{T_1}{T_2}.$$

If the temperature of 45 ml of hydrogen gas is decreased from 20° C (293° K) to −100° C (173° K), the decreased volume, V_1, is given by

$$\frac{V_1}{45 \text{ ml}} = \frac{173°}{293°}.$$

Multiplying both sides of this equation by 45 ml, we have

$$V_1 = \frac{173°}{293°} \times 45 \text{ ml} = 26.6 \text{ ml } H_2.$$

Calculate the volume at 100° C. (*Answer*, 57.3 ml.)

Example 2. Inverse Proportion. The corresponding volumes and pressures of a given quantity of gas bear an inverse proportional relationship to one another. This fact is known as Boyle's Law, and may be expressed by the equations

$$V = \frac{k}{P}, \text{ or } PV = k.$$

Since any two corresponding values of PV are equal to k, we may write the proportion

$$P_1V_1 = P_2V_2, \text{ or transposing, } \frac{V_1}{V_2} = \frac{P_2}{P_1}.$$

If the pressure of 45 ml of oxygen gas is increased from 1.0 atmosphere to 3.0 atmospheres, the decreased volume, V_1, is given by

$$\frac{V_1}{45 \text{ ml}} = \frac{1.0 \text{ atm}}{3.0 \text{ atm}}$$

or
$$V_1 = \frac{1.0 \text{ atm}}{3.0 \text{ atm}} \times 45 \text{ ml} = 15 \text{ ml } O_2.$$

You may verify other corresponding values as follows: When $P_5 = 5.0$ atm, $V_5 = 9.0$ ml O_2, and when $P_1 = 0.50$ atm, $V_1 = 90$ ml O_2.

Scientists very frequently make *a graph* of their experimental data as a means of discovering fundamental relationships, or of comparing their data with some known law. The extent to which their experimental values lie on a smooth curve is an indication of the precision of their measurements.

The graph (Fig. A-3) for the data of Example 1, above, shows that *a direct proportion plots as a straight line.* Only two points are needed to fix the line, from which any other values then may be read. If the line were extrapolated to a volume of zero, it would cross the temperature axis at −273° C. Of course, hydrogen would behave less like a perfect gas as the temperature is decreased, and would change to the liquid, and finally to the solid, state. By plotting precise experimental data for the volumes and temperatures, or pressures and temperatures, of a sample of hydrogen, the value of absolute zero can be determined.

The graph (Fig. A-4) for the data of Example 2, above, shows that *an inverse proportion plots as a hyperbola.* A number of points are necessary to fix the curve.

Figure A-5 shows a characteristic curve for the change in solubility of a salt with temperature. This is not a first order, or linear curve, and would have to be expressed by an equation in higher powers of x, where x represents the temperature. Usually a quadratic equation will give a close approximation to the data.

D. Exponents

Very Large and Very Small Numbers. The student of chemistry finds that he uses many extremely large numbers, such as Avogadro's Number: 602,300,000,000,000,000,000,000; and many extremely small numbers, such as a sulfide ion concentration of 0.00000000000000031 *M*. The reason obviously is the minute sizes of atoms and molecules, and the correspondingly enormous numbers of them which can exist even in a small space.

Since such numbers are awkward to handle, they are often expressed more conveniently by writing them as some simple number times ten

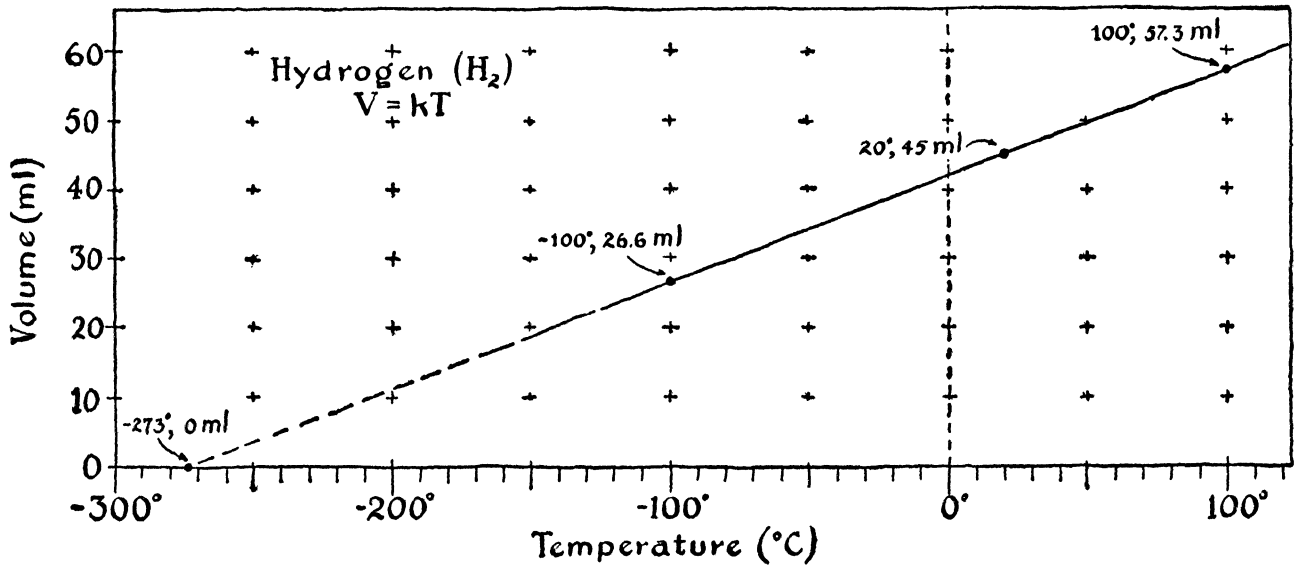


FIG. A-3. The relation between the temperature and corresponding volume of a sample of a gas, such as hydrogen. *A direct proportion,* as represented by Charles' law, V = kT, plots as a straight line.

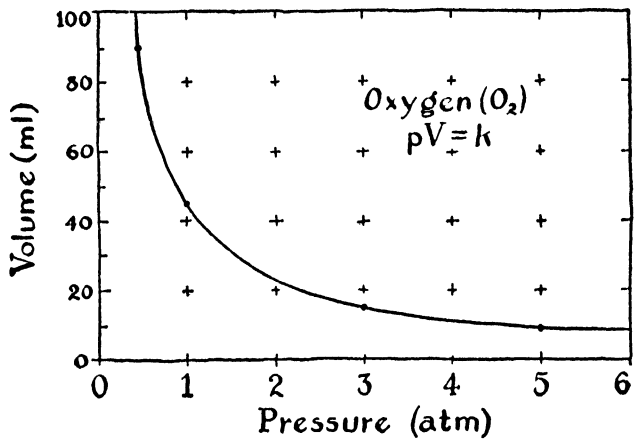


FIG. A-4. The relation between the pressure and corresponding volume of a sample of a gas, such as oxygen. The graph of *an inverse proportion*, as represented by Boyle's law, pv = k, is an hyperbola.

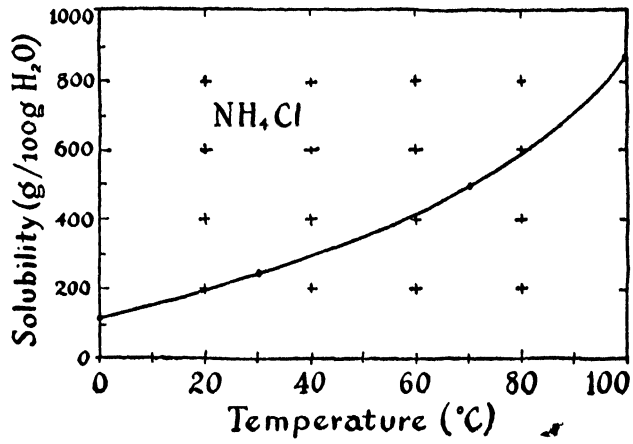


FIG. A-5. The change in solubility of ammonium chloride with temperature. Such a solubility graph is seldom linear, but can often be expressed by an equation of the binomial type: $y = a + bx + cx^2 + \ldots$

raised to a power (the power is indicated by an *exponent*). Thus, Avogadro's Number may be written 0.6023×10^{24}, or 6.023×10^{23}. The exponent 23 means that 10 is raised to the 23rd power. The number 6.023×10^{23} means that when the decimal point in 6.023 is moved 23 places to the right, the indicated number is obtained. Any number such as 129,000 may be written in various forms, as, for example: 129×10^3, 1.29×10^5, or 0.129×10^6.

The number 0.00000000000000031 may be written as 3.1×10^{-16}, meaning that to obtain the number the decimal point in 3.1 must be moved 16 places to the left. Likewise, any number such as 0.000736 may be written in a number of equivalent forms, as, for example: 7.36×10^{-4}, 736×10^{-6}, or 0.0736×10^{-2}.

The Meaning of a Negative Exponent. In handling negative exponents, the student should note that $10^{-4} = \frac{1}{10^4} = \frac{1}{10{,}000} = 0.0001$. Likewise, $10^3 = \frac{1}{10^{-3}}$, and so forth. In other words a number expressed as a negative power of ten is equal to the reciprocal of ten raised to the corresponding positive power, and vice versa.

Multiplication and Division of Exponential Numbers. For numbers written in exponential notation, *to multiply* the numbers, *add* the exponents, and *to divide* the numbers, *subtract* the exponents. Other factors in the indicated product or quotient are to be multiplied or divided as usual.

Examples of Multiplication:

$2^2 \times 2^3 \times 2^7 = 2^{2+3+7} = 2^{12}$,
$10^5 \times 10^{-2} = 10^3$, (Note that $5 + (-2) = 3$.)
$(2 \times 10^3)(4 \times 10^2) = 8 \times 10^5$.

Examples of Division:

$10^7/10^3 = 10^{7-3} = 10^4$,
$10^2/10^{-5} = 10^7$, (Note that $2 - (-5) = 2 + 5 = 7$.)
$(6 \times 10^2)/(2 \times 10^3) = 3 \times 10^{-1} = 0.3$.

Powers of Exponential Numbers. The exponent is multiplied by the power desired.

Examples:

$(10^2)^3 = 10^2 \times 10^2 \times 10^2 = 10^6$,
$(2 \times 10^3)^4 = 16 \times 10^{12}$.

Roots of Exponential Numbers. The exponent is divided by the root desired. In case the exponent cannot be divided evenly, the number must be changed to a form so that this can be done.

Examples:

The square root of $5^6 = (5^6)^{1/2} = 5^{6/2} = 5^3$,
The cubic root of $8 \times 10^{12} = (8 \times 10^{12})^{1/3} = 2 \times 10^4$,
The square root of $5 \times 10^{-7} = (5 \times 10^{-7})^{1/2} = (50 \times 10^{-8})^{1/2} = 7.1 \times 10^{-4}$.

Addition and Subtraction of Exponential Numbers. The numbers first must be changed to a nonexponential form, or to the same power of ten.

Examples:

$10^2 + 10^3 = 100 + 1000 = 1100 = 1.1 \times 10^3$,
$(6 \times 10^{-2}) - (2 \times 10^{-3}) = (6 \times 10^{-2}) - (0.2 \times 10^{-2}) = 5.8 \times 10^{-2} = 0.058$.

E. Logarithms

The common logarithm of a number is the power to which 10 must be raised to obtain the number; that is, a logarithm is an exponent and the preceding rules for exponents are applicable. The logarithms of all numbers which are integral powers of 10 are whole numbers:

Log of: 100, or $10^2 = 2$	Log of: 0.1, or $10^{-1} = -1$
10, or $10^1 = 1$	0.01, or $10^{-2} = -2$
1, or $10^0 = 0$	and so on.

The logarithms of all intervening numbers, which are not integral powers of 10, are made up of two parts: a whole number, called the *characteristic*, and a decimal fraction, called the *mantissa*. A table of logarithms gives only the mantissas.

The use of logarithms in the solution of problems shortens the labor of calculation, particularly in a series of multiplications and divisions.

Example: Using a table of logarithms, find the logarithm of 174.5.

The mantissa depends on the series of digits, without regard to the decimal point. Mantissas are given as positive numbers in logarithm tables.

Find the number opposite 17, in column 4.. 2405
Find the number in proportional parts 5, row 17..... 12
The sum, with a decimal point prefixed, is the mantissa..... .2417

The characteristic depends only on the decimal point in the number. For numbers greater than 1, it is a *positive integer* which is one less than the number of digits to the left of the decimal point. For numbers less than 1, it is a *negative integer* which is one more than the number of zeros immediately following the decimal point. In this example, the characteristic is 2.

The log of 174.5 is therefore 2.2417.

The log of 0.001745 is $\bar{3}.2417$. This means $-3 + 0.2417$, or written as one negative number, it means -2.7583.

Example: Find the number corresponding to the logarithm 1.5280.

In the table, the mantissa next lower than 5280 is 5276, which is 4 units too small, and which corresponds to the digits 337. In the proportional parts columns of the same row 33, find 4, which is in proportional parts column 3. This is the fourth digit in the number. The sequence of digits is 3373. Since the characteristic is 1, there are two digits to the left of the decimal point, and the number is 33.73.[1]

To multiply numbers, add their logarithms and find the antilogarithm (number corresponding to a logarithm) of this sum. **To divide numbers,** subtract their logarithms and find the antilogarithm of this difference. In a series of consecutive multiplications and divisions, it is convenient to add the cologarithms of the divisors, instead of subtracting their logarithms. The **cologarithm** of a number is found by subtracting its logarithm from 10, and then appending -10. For example, the logarithm of 174.5 is 2.2417. The cologarithm is $7.7583 - 10$.

Example: Find the volume at standard conditions of 253 ml of oxygen measured at 25° C (298° K) and 742 mm mercury pressure.

$$\text{Volume at 0° C and 760 mm Hg} = 253 \text{ ml} \times \frac{273°}{298°} \times \frac{742 \text{ mm}}{760 \text{ mm}} = ?$$

$\log 253 = 2.4031$
$\log 273 = 2.4362$
$\log 742 = 2.8704$
$\log 298 = 2.4742$, $\operatorname{colog} 298 = 7.5258 - 10$
$\log 760 = 2.8808$, $\operatorname{colog} 760 = 7.1192 - 10$
$22.3547 - 20 = 2.3547$

Antilog of 2.3547 = 226.3, or 226 ml volume at standard conditions.

To find a given power of a number, multiply its logarithm by the power desired, and find the antilogarithm of this product.

Example: Find the fifth power of 15, i.e., find 15^5.

The log of 15 is 1.1761. Multiplying by 5, we have 5.8805
Antilog of 5.8805 = 759500, or $7.6 \times 10^5 = 15^5$.

To find a given root of a number, divide its logarithm by the root desired, and find the antilogarithm of this quotient. Note that if the characteristic is negative, the entire logarithm must be changed to a negative number before dividing by the root.

---

[1] It is possible, by interpolation in the proportional parts columns, to determine the logarithm of 5-digit numbers, and vice versa. However, most experimental work in this course is significant to three figures only, so that it is not even necessary to use the proportional parts columns at all.

uple: Find the cube root of 0.00248.

Log 0.00248 = $\bar{3}.3945 = -3 + 0.3945 = -2.6055$
$\frac{1}{3}$ log $-2.6055 = -0.8685 = \bar{1}.1315$
Antilog $\bar{1}.1315 = 0.1354$, which is the cube root of 0.00248.

(An alternate and perhaps simpler procedure is to transform the number 0.00248 to 2.48×10^{-3}, and then take the cube root of each of these factors separately.)

F. The Slide Rule

The slide rule scales which are used for multiplication and division are graduated in lengths proportional to the logarithms of the digits from 1 to 10, but the digits are placed on the scale, rather than the logarithms. Hence, to multiply numbers add the lengths, and to divide numbers subtract the lengths, by sliding the movable scale so that the lengths can be added or subtracted mechanically. The details of operation, which are quite easily mastered, are given in the manual accompanying the instrument.

Since a course in chemistry necessitates a considerable amount of calculation, you are encouraged to obtain and use a slide rule. An inexpensive 10-inch rule is satisfactory. It may be read to about three significant figures, which is sufficiently precise for most calculations in this course.

Drill Problems

(You may refer to the answers to some of these problems, on P. 341, *after* solving them by yourself.)

1. Express in the exponential form:

(a) 1000
(b) 200
(c) 5,500
(d) 0.1
(e) 0.001
(f) 0.004
(g) 0.000000000003
(h) 750,000,000,000
(i) 2,006,000
(j) 0.00204

2. Change the decimal point in these expressions, without changing the value of the number, so that there is one digit to the left of the decimal point.

(a) 42.6×10^3
(b) 41075×10^{-5}
(c) 0.375×10^{-4}
(d) 0.07287×10^2
(e) 0.000465×10^3
(f) $6{,}023 \times 10^{20}$
(g) 30103
(h) 0.625×10^4

3. Simplify these expressions as indicated, by multiplying, dividing, taking a power, extracting a root, adding, or subtracting.

(a) $10^2 \times 10^4$
(b) $10^3 \times 10^5 \times 10^{-2}$
(c) $(4.6 \times 10^4) - (3 \times 10^3)$
(d) $(5.42 \times 10^{-1}) + (1.3 \times 10^2)$
(e) $(10^3)^2(10^2)(10^{-5})$
(f) $10^6/10^4$
(g) $(10^2)(10^{-3})/(10^{-2})$
(h) $(2 \times 10^5)(4 \times 10^6)$
(i) $(2.5 \times 10^3)^2$
(j) $(25 \times 10^6)^{1/2}$
(k) $\dfrac{(10^3)(16 \times 10^6)^{1/2}}{10^4}$
(l) $\sqrt{3.6 \times 10^5}$
(m) $\dfrac{(4.6 \times 10^4)(2.1 \times 10^{-2})}{(3 \times 10^2)(2.3 \times 10^{-4})}$
(n) $\dfrac{(x^2)(y^3)(2x^3)}{(x^4)^{1/2}(y^{-2})(z^{-1})}$

4. Express the following scientific laws as mathematical equations:

(a) The pressure (P) of a gas, at constant volume (V), is directly proportional to its absolute temperature (T). (*Solution:* Stated as a direct proportion, we have: $P \propto T$. Now by replacing the proportionality sign by an equal sign and a proportionality constant, we have the equation: $P = kT$.)

(b) The kinetic energy of a particle in motion is equal to one half the product of its mass times the square of its velocity.

(c) The atomic number (Z) of an element is inversely proportional to the square root of the wave length (λ) of its characteristic X-ray spectra.

(d) Two electrically charged particles (ions) of opposite charge will attract one another with a force which is directly proportional to the product of their charges (e_1 and e_2), and inversely proportional to the square of the distance (d) between them.

(e) At constant pressure, the volume of a gas changes by 1/273 of its volume at 0° C, for each degree of temperature change.

5(a) At constant temperature, the masses (m_1 and m_2) and the squares of the average velocities (v_1 and v_2) of the molecules of two gases are inversely proportional to one another. State as an equation, then use to solve the following problem.

(b) If the average velocity of methane molecules (CH_4) is 4×10^5 cm/sec at a given temperature, what will be the average velocity of sulfur dioxide molecules at this same temperature?

6. Look up the logarithm of each

(a) 146.8
(b) 7.408
(c) 0.003682
(d) 50
(e) 0.6023×10^{24}
(f) 1.8×10^{-5}

7. Find the antilogarithms of which the following are the logarithms:

(a) 2.4829
(b) 1.0654
(c) 4.5542
(d) 9.8451 − 10
(e) 6.7410 − 10
(f) 18.6275 − 20

8. Solve the following by logarithms, and then check your answers by the slide rule:

(a) The volume of a sample of gas at standard conditions:

$$267 \text{ ml} \times \frac{273^\circ \text{ K}}{305^\circ \text{ K}} \times \frac{734 \text{ mm Hg}}{760 \text{ mm Hg}} =$$

(b) The number of molecules in a drop of water:

$$\frac{0.050 \text{ g}}{18 \text{ g/mole}} \times 0.6023 \times 10^{24} \text{ molecules/mole} =$$

9. Use the simplest procedure practical to solve the following:

(a) $(6.5 \times 10^{-1})^2$
(b) $(3.75 \times 10^2)^3$
(c) $(4.025)^2(1.234)^3$
(d) $(3125)^{1/5}$
(e) $(3.1 \times 10^2)^3(1.4 \times 10^{-3})^2$
(f) $(0.02478)^{1/2}$
(g) $(8.1 \times 10^{11})^{1/2}$
(h) $(4.9 \times 10^{-3})^{1/2}(3.0 \times 10^4)$

10. Find the value of x in the following binomial expressions:

(a) $x^2 + 6x - 12 = 0$
(b) $2x^2 + 7x - 14 = 0$
(c) $x^2 + (1.7 \times 10^{-5})x - (1.7 \times 10^{-5}) = 0$
(d) $x(x + 0.01) = 3 \times 10^{-3}$

Self-Test

The following is a 10-minute multiple-choice test which may be used to check your ability to handle some fundamental mathematical operations. Score each correct answer on part A as one point and on part B as two points. Select the one best answer by encircling one of the numbers at the right.

Part A. Mathematical Operations

1. $d = \frac{m}{v}$ · What does m equal? 1 2 3 4 5
(1) d/v, (2) vd, (3) v/d, (4) d − v, (5) $\frac{dv}{m}$

2. $x - 2 = 4 + 4y$. What does x equal? 1 2 3 4 5
(1) 4y − 2, (2) 2y − 6, (3) 4y + 6, (4) 2y + 2, (5) 2 − 2y

3. $\frac{2}{x} - \frac{1}{y}$ · Reduce to a common denominator. 1 2 3 4 5
(1) $\frac{2y - x}{x - y}$, (2) $\frac{1}{x - y}$, (3) $\frac{1}{xy}$, (4) $\frac{2y - x}{xy}$, (5) 2y − x

4. y − (y − b + a). Simplify. 1 2 3 4 5
(1) 2y + b − a, (2) a − b, (3) 2y − b + a, (4) b − a, (5) b + a

5. $x^2 - 9 = 16$. What does x equal? 1 2 3 4 5
(1) 1, (2) 13, (3) $\sqrt{7}$, (4) 7, (5) 5

6. $y = \frac{4 \times 10^4 \times 6 \times 10^{-1}}{3 \times 10^2}$ · What does y equal? 1 2 3 4 5
(1) 0.8, (2) 8, (3) 80, (4) 800, (5) 800,000

7. What is the square root of 16,900? 1 2 3 4 5
(1) 13, (2) 43, (3) 130, (4) 430, (5) 1300

8. What is 0.0096 divided by 0.06? 1 2 3 4 5
(1) 16, (2) 1.6, (3) 0.16, (4) 0.016, (5) 0.0016

9. What is 8% of 12? 1 2 3 4 5
(1) 0.96, (2) 1.5, (3) 9.6, (4) 0.015, (5) 0.066

10. 7 is 5% of what number? 1 2 3 4 5
(1) 0.35, (2) 0.00714, (3) 14, (4) 35, (5) 140

Part B. Setting Up Mathematical Relationships

11. A table is half as wide as it is long. What is its area if x represents the width of the table? 1 2 3 4 5
(1) 3x, (2) x^2, (3) 6x, (4) $2x^2$, (5) $4x^2$

12. If six-tenths of a ton of coal costs $8.40, what would a five-ton load of coal cost? Choose the proper set-up. 1 2 3 4 5
(1) $\$8.40 \times 5 \times 0.6$, (2) $\frac{\$8.40 \times 0.6}{5}$, (3) $\frac{5 \times 0.6}{\$8.40}$, (4) $\frac{\$8.40 \times 5}{0.6}$, (5) $\frac{\$8.40}{5 \times 0.6}$

13. The density of mercury is 13.6 g/cm³. How much would 18 cubic centimeters of mercury weigh? 1 2 3 4 5
(1) $\frac{18}{13.6}$, (2) $\frac{13.6}{18}$, (3) 13.6×18, (4) $\frac{1}{13.6 \times 8}$, (5) none of the above.

14. The pressure of a gas in an automobile tire increases as the absolute temperature is increased. The mathematical statement of this is: 1 2 3 4 5
(1) $P = \frac{k}{T}$, (2) $P = kT$, (3) $T = \frac{k}{P}$, (4) $PT = k$, (5) $\frac{1}{P} = kT$

15. An automobile traveling at a velocity of y miles per hour consumes gasoline at the rate of x miles per gallon. How much gasoline is required to travel a distance of z miles at this rate of speed? 1 2 3 4 5
(1) $\frac{z}{x}$, (2) $\frac{x}{z}$, (3) xyz, (4) $\frac{xz}{y}$, (5) $\frac{zy}{x}$

Physical Properties of Substances 2

College Chemistry, Chapters 1, 2

Review of Fundamental Concepts

The Kinds of Matter

Carefully study Figure 2-1, Page 14, and also review the definitions as stated in your text, as to the exact meanings of the following terms which classify and describe the kinds of matter:

A *substance*—all samples of which are identical in composition, as water, baking soda, and common salt. A *mixture*—made up of more than one substance. If the mixture is so intimate and homogeneous that the several components are present as one phase, without separate boundaries, we speak of it as a *solution.*

Properties—the qualities or characteristics which distinguish one substance from another. *Physical properties*—those which can be observed without changing the identity of the substance, as color, odor, density, melting and boiling points, crystalline form, hardness, malleability, ductility, and thermal and electrical conductivities. *Chemical properties*—those which describe the changes occurring when a substance is being transformed into one or more different substances. *A test for a substance*—a property sufficiently specific to identify it, particularly if interfering substances have been removed.

In this experiment we shall observe some of the physical properties which characterize the several types of substances, while Experiment 3 will introduce some of their chemical properties. The representative substances studied will include two metallic elements (copper and zinc), two nonmetallic elements (sulfur and iodine), an acid (hydrochloric acid), a base (calcium hydroxide), and several salts (cupric carbonate, cupric nitrate, potassium chlorate, and others).

Experimental Procedure

Chemicals: Cu (turnings), Zn (mossy), S (roll), I_2, HCl, $Ca(OH)_2$ (solid), $CuCO_3$, $Cu(NO_3)_2$, $KClO_3$, and other salts for crystallization, as NaCl, $NaNO_3$, KNO_3, CS_2.

Reread the laboratory rules on Page ix. Note again in Figures i-6 and i-7 the suggestions on handling and removing chemicals from the reagent bottles so as to avoid spilling them. Do not waste chemicals by removing from the bottle more than you need. Do not attempt experiments not called for without consulting the instructor (Safety Precaution No. 1).

For each of the reactions which follow, fill in the table in the report sheet as you obtain the data. The chemical formula may be learned from the label on the bottle, or from your text. (Although you may not yet know the significance of these formulas, learn now to associate the appearance of the substance, its name, and correct formula.)

Follow the suggestions below in observing each characteristic property for each substance in the table.

1. Color and Physical State. Record accurately and concisely the color and general physical form and appearance of each substance.

2. Odor and Taste. Smell cautiously by fanning the vapors toward the nose (Safety Precaution No. 8). Never taste chemicals except when directed to do so, and then only by touching the substance to the tongue. Do not taste copper salts as they are somewhat poisonous. The other substances used in this experiment may be tasted, but first dilute the hydrochloric acid very much—a few drops of acid in 5 ml of water. If the sour taste is insufficient to observe, add a little more acid.

3. Density and Melting Point. The density of sulfur was determined in Experiment 1. No further experimental work is provided here. Note and compare the values of the densities, and also of the melting points, which are given for your information in the report sheet. Note that some of the compounds decompose into simpler substances, rather than have a melting point of their own. A number of problems on density are included in the report sheet.

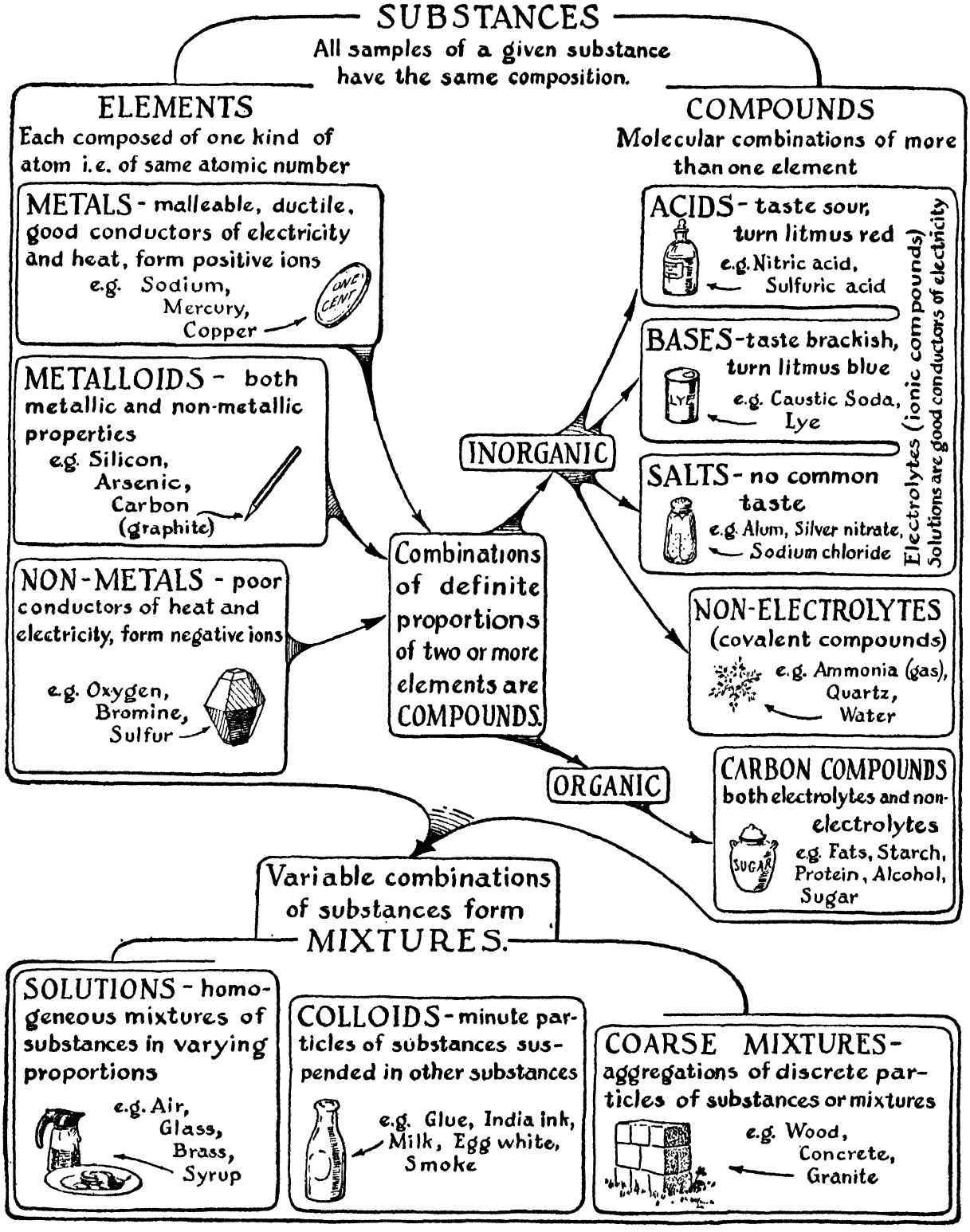


FIG. 2-1. The kinds of matter.

4. Solubility in Water. Determine the relative solubility (designate only as soluble, fairly or slightly soluble, or insoluble) of each substance with which you are not previously familiar by shaking an amount equal to the size of a pea with about 5 ml of distilled water in a clean 15-ml test tube for about 3 to 5 minutes. Do not waste distilled water by withdrawing more than you need. It is an expensive chemical. If unable to tell, by the disappearance of the solid or the color of the solution, whether much or any of the substance has dissolved, proceed as follows: Filter the mixture (see instructions on filtration, Fig. i-11) into a clean evaporating dish or watch glass, and evaporate a few drops of it to dryness. A watch glass can only be used high above a small flame, or it may break. See Figure 2-2. The amount of residue indicates the relative solubility.

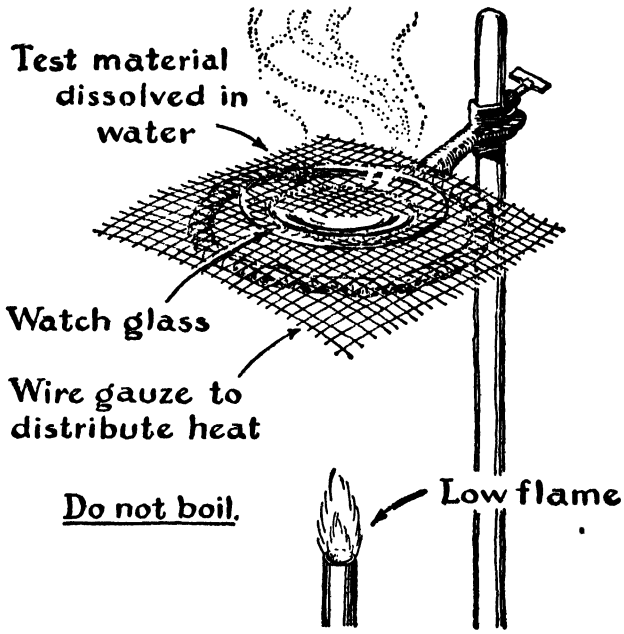


FIG. 2-2. The evaporation of a small amount of liquid in a watch glass to test for the presence of dissolved salts.

5. Crystalline Form. Prepare crystals of as many of the substances below as your instructor directs. Observe, with a low-power magnifying glass, the characteristic habit of crystallization of each type of crystal (you may also observe crystals of different substances prepared by your classmates), and describe each in your report sheet. If practical, include a sketch of the crystals. While observing the various crystals, be thinking of any supporting evidence of the atomic theory which the formation and growth of crystals suggests.

(a) *Rhombic Sulfur.* Place about 2 g of crushed, roll sulfur[1] and about 5 ml of carbon disulfide in a 15-ml test tube. (**Caution:** *Do not handle carbon disulfide within five feet of any flame; its vapor, mixed with air, is very explosive.*) Mix gently for about 5 minutes to promote solution. Fold a filter paper in the usual manner and hold this (without a funnel) directly over a watch glass to filter the mixture. Set the watch glass aside in a safe, quiet place, until the liquid has evaporated. Observe the crystals.

(b) *Monoclinic Sulfur.* Sulfur also crystallizes, at an elevated temperature from the molten material, as monoclinic crystals. The equilibrium temperature of the two *allotropic forms* is 95.5° C. Such a *transition temperature* is a definite physical property of a substance, analogous to the melting point, or boiling point.

Prepare a cone of filter paper, and support it either in a funnel or a small beaker. Heat a 15-cm test tube, which has been filled two-thirds full of sulfur, slowly and uniformly *so as not to superheat any portion of it.* The sulfur will darken in color if it is superheated. This can be avoided by moving the test tube, held in a test tube clamp, in and out of the flame. When the sulfur is just melted it should be a light yellow, straw colored liquid. Now pour this into the filter cone previously prepared, and with a match stick in hand, watch it, while cooling, for the formation of long needle-shaped crystals. Just as the surface begins to solidify, break it open with the match stick, and quickly pour the remaining molten sulfur into a beaker of water. Let the filter cone cool, break it open, and observe the crystals.

(c) *Iodine.* Iodine has a very appreciable vapor pressure at temperatures considerably below its melting point, so it may be easily *sublimed* (caused to crystallize directly from the vapor without first liquefying) from a warm surface to a cooler one. (Due to the higher cost of iodine, the instructor may designate a limited number of students to demonstrate this.)

Put about 1 g of iodine in an evaporating dish, placed on a wire gauze and ring support. Over the

[1] Flowers of sulfur is not satisfactory for this purpose.

evaporating dish, place a watch glass which is partially filled with water to act as a cool, condensing surface. See Figure 2-3. Now, very gently

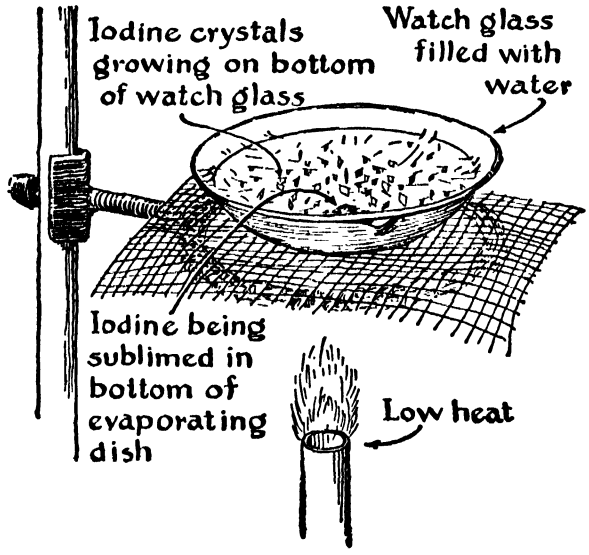


FIG. 2-3. Apparatus for the recrystallization of iodine by sublimation.

and with a small flame, warm the evaporating dish. Do not rush the process, as the growth of larger crystals is favored by slow growth with no disturbance of the vessel. When a sufficient time has elapsed, cool the vessel and observe the crystals.

(d) *Various Salts.* Prepare a small amount of a concentrated solution by shaking about 3 g of the salt (sodium chloride, potassium chlorate, potassium nitrate, sodium nitrate, etc.) with about 5 ml of water in a test tube for about 5 minutes. Let any undissolved salt settle, and decant (Fig. i-12) the clear liquid on to a clean watch glass. Set aside in a quiet place overnight or until the next laboratory period, to permit the water to evaporate. Observe the crystals. (Ordinary table salt frequently contains well developed crystals which may be observed under low magnification. Rock salt, also, may contain excellent crystals. *Optional:* Some student may try crystallizing sodium chloride from a small amount of a 30% urea solution, instead of from water, to see if he can obtain the octahedral facial development of salt crystals.)

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

REPORT: Exp. 2

Physical Properties of Substances

Substance	*Formula*	*Color and State*	*Odor and Taste*	*Density g/cm³*	*Melting Point °C*	*Solubility*
Copper (metal)				8.93	1083	
Zinc (metal)				7.14	419	
Sulfur (non-metal)				2.07	113	
Iodine (non-metal)				4.93	113	
Hydrochloric acid[1]				1.10	(No entry)	(No entry)
Calcium hydroxide (base)				2.34	dec. 580 $-H_2O$	
Cupric carbonate (salt)				3.9	dec. 200	
Cupric nitrate (salt)				2.05	dec. 170 $-HNO_3$	
Potassium chlorate (salt)				2.32	368	

[1] Hydrochloric acid is a solution of the gas hydrogen chloride, in water. The "dilute" laboratory reagent contains 21.9 g/100 ml of solution.

Crystalline Form. Characterize and sketch the various crystals which you have observed.

What supporting evidence of the atomic theory does the formation and growth of crystals suggest to you?

Problems on Density

Introductory note on the solution of problems. See Appendix I on the "Use of Dimensions" in the solution of problems, also for examples of the solution of density problems.

In each problem label each quantity with its appropriate unit; set up the problem to indicate all mathematical operations, but omit the actual multiplication and division. The formula to be used in the solution is not sufficient. Actual quantities must be substituted for each symbol, as in the examples cited. The entire problem should be neat and legible. Record the answer in the space at the right. *Good form is essential in your work.*

Answers

1. What is the density of a brass sample if 50 g of the coarse turnings, when placed in a graduated cylinder containing 10.3 ml of water, raise the level of the meniscus to a reading of 16.2 ml? (Consider that 1 ml = 1 cm^3.)

1 _____ g/cm^3

2. What is the weight in pounds of a cubic foot of mercury, whose density is 13.6 g/cm^3? (See Appendix II, Tables II and III, for any needed conversion factors.

2 _____ lb

3. An experiment calls for 50 g of concentrated sulfuric acid, density 1.84 g/cm^3. Suppose no balance is available and you decide to use a graduated cylinder. What volume should you use?

3 _____ ml

4. The dilute nitric acid on the desk has a density of 1.19 g/cm^3 and is 32%[1] nitric acid, the remainder being water.
   (a) How many grams does 8.0 ml of this acid weigh?

4 (a) _____ g

   (b) What is the weight of pure nitric acid in this 8.0 ml?

(b) _____ g

5. What volume of magnesium, density 1.74 g/cm^3, would be equal in weight to 100 cm^3 of lead, density 11.4 g/cm^3?

5 _____ cm^3

[1] The percent composition of solids and liquids is given as percent by weight unless percent by volume is specifically stated. The composition of gases is usually expressed as percent by volume, however.

Some Elementary Chemical Properties of Substances — 3

College Chemistry, Chapters 3, 4

Review of Fundamental Concepts

This experiment continues the study of properties of the same list of substances used in Experiment 2, this time from the standpoint of typical modes of *chemical* behavior, resulting in the formation of new substances.

Physical and Chemical Changes Taking Place on Heating

When a substance is heated in the air, it may:

(1) Change its physical state—from solid to liquid, liquid to gas, or directly from solid to gas.

(2) React chemically with a constituent of the air (usually oxygen) to produce one or more new substances.

(3) Decompose to produce simpler substances. Elements, of course, ordinarily cannot decompose.[1] The products of a decomposition must contain all the elements originally present. None can be destroyed, and no additional elements can be present save possibly some constituent of the air with which there has been a reaction.

The physical changes which accompany a given chemical change often serve to identify it. Thus, mercuric oxide (a red powder) decomposes to form mercury (a silvery metallic liquid) and oxygen (a colorless gas). On heating calcium carbonate (limestone), two simpler compounds result, calcium oxide (quicklime) and carbon dioxide (a colorless gas). Carbon (e.g., coke), heated in air, forms carbon dioxide, the oxygen coming from the air.

Properties of and Tests for Some Common Gases

Use the descriptions below to help you identify any gaseous products formed during the course of the experimental procedure that will follow these descriptions.

(1) *Oxygen*, O_2: Colorless and odorless. Causes the glowing end of a wood splint to increase greatly in brightness or even burst into flame. This test may be made by thrusting the glowing end of a splint into the gas being tested. Only one other common gas, nitrous oxide, N_2O, has similar properties.

(2) *Hydrogen*, H_2: Colorless and odorless. One of a number of gases which burn when ignited in the presence of air or explode when a mixture of the gas and air is ignited. With a lighted match held near the mouth of the tube, one can detect the presence of hydrogen.

(3) *Carbon dioxide*, CO_2: Colorless, odorless, with a slight acid or sour taste if in solution. Recognized by the milky precipitate of calcium carbonate it forms when exposed to calcium hydroxide solution (limewater). This may be observed by suspending

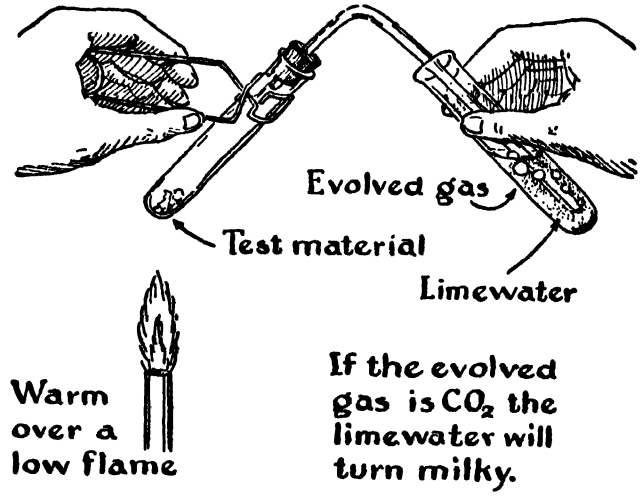


FIG. 3-1. The limewater test for carbon dioxide.

a drop of limewater from a glass tube or rod held in the mouth of the test tube containing the substance being tested, and noting whether it turns milky. (Touch the glass rod to some limewater in a test tube. Never put a rod, medicine dropper, etc. directly in a reagent bottle.) A better test is to connect the test tube containing the test material with a rubber stopper and bent delivery tube (see directions on glass bending, P. xix). Have the end of the delivery tube dipping in some limewater in a 10-cm test tube. On heating the substance, any CO_2 will be expelled into the limewater. Or, if testing for CO_2 when an acid is added, disconnect the rubber stopper just long enough to add a little HCl, reconnect it at once, and if necessary warm

[1] We are not considering here the unusual forces brought into play in modern research to smash atoms, by which different elements, with different properties, are formed. Such changes are not "chemical changes." They are called nuclear transformations.

a little to assist in expelling the evolved gas into the limewater.

(4) *Sulfur dioxide*, SO_2: A heavy, colorless gas with a sharp choking odor.

(5) *Nitrogen dioxide*, NO_2: A heavy, brown gas with a disagreeable odor.

(6) *Hydrogen sulfide*, H_2S: A colorless, poisonous gas, with a very characteristic foul odor.

Experimental Procedure

Chemicals: Cu (turnings), Zn (mossy), Zn (dust), S, I_2, HCl, $Ca(OH)_2$ (solid), $Ca(OH)_2$ (sat. sol.), $CuCO_3$, $Cu(NO_3)_2$, $KClO_3$, Mg (ribbon).

1. Reaction to Litmus. Test solutions of each of the soluble substances in the above list of chemicals with red and with blue litmus paper. Litmus turns red in an acid solution, and blue in a basic solution. (A blue color with iodine solution is due to starch in the paper. It is not basic.)

2. The Effect of Heat on Certain Elements. Heat each of the following elements, as directed. In each case, note any physical changes, and also any evidence that a new substance may have been produced.

(a) *Copper*—hold a small piece of copper sheet, or turnings, with the forceps at the top of the Bunsen flame for a short time.

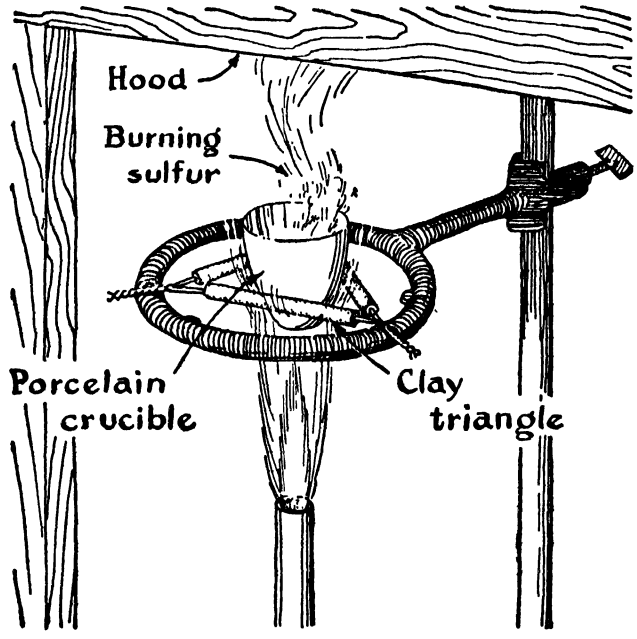


FIG. 3-2. The ignition of sulfur in a crucible.

(b) *Sulfur*—heat a bit of sulfur the size of half a pea in a porcelain crucible, until it first melts, then catches fire as it becomes hotter. Note the odor cautiously. Continue heating until the sulfur is all burned out of crucible. *Keep crucible under a hood.*

(c) *Iodine*—heat one or two small crystals of iodine in a 15-cm test tube, keeping the upper part of the tube cool.

3. The Decomposition of Certain Compounds by Heat. Place small samples each of cupric carbonate, cupric nitrate, and potassium chlorate in separate test tubes. Before you heat them, be prepared to test for any gases which you think may be formed. (See the previous discussion on properties of and tests for common gases, P. 19.) Note the changes occurring on heating, and identify the products, both gaseous and solid. The white residue left on heating potassium chlorate contains no oxygen, and is potassium chloride.

4. The Effect of an Acid on Various Substances. Place small samples each of copper, zinc (use mossy zinc), sulfur, calcium hydroxide (solid), and cupric carbonate in separate test tubes. Be prepared to test for any gases you might anticipate. Add 3 to 5 ml of dilute hydrochloric acid to each. Note changes; identify gases, if any, that form.

5. The Reaction of Zinc and Sulfur.[1] Mix thoroughly an estimated 2 grams of zinc dust (about 1 cm deep in a dry 10-cm test tube) with about twice its volume (1 gram) of powdered sulfur. Place half of the mixture in a 15-cm test tube and add dilute hydrochloric acid. What gas is evolved? Place the remainder on a 7-cm square of asbestos paper, or in your evaporating dish, and ignite it as follows. Hold a 4-cm length of magnesium ribbon with your forceps; light this by heating the tip in the Bunsen burner, and at once touch this burning magnesium to the zinc and sulfur mixture. **(Use reasonable care, and do not get too close, as it burns rapidly.)** To gain additional evidence as to any chemical change which has taken place between the zinc and sulfur, put this residue in a test tube, and add a little dilute hydrochloric acid. Note the odor. What is formed?

[1] To avoid fumes in the laboratory instructors may prefer to demonstrate this.

REPORT: Exp. 3

Some Chemical Properties of Substances

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Reaction to Litmus. List the substances whose solutions are: Acidic_____

Basic_____ Neutral_____

2. The Effect of Heat on Certain Elements. Note any changes in physical state, color, odor, and so forth, and name any new substances produced on heating:

Element	*Observations*	*New Substances*
Copper		
Sulfur		
Iodine		

3. The Decomposition of Certain Compounds by Heat. Note any changes in physical state, color, odor, and so forth, and any tests performed on gaseous products in order to identify them, on heating the substance:

Compound	*Observations, Including Tests for Any Gaseous Products Evolved*	*New Substances*
Cupric carbonate		
Cupric nitrate		
Potassium chlorate		

4. The Effect of Acid on Various Substances. Note any observable effects, such as solution of the solid, color of the solution, tests performed, and results, on any gases evolved, when hydrochloric acid is added to the substance:

Substance	*Observations, Including Tests Performed*	*Identity of Gas, if Any*
Copper		
Zinc		
Sulfur		
Calcium hydroxide		
Cupric carbonate		

5. The Reaction of Zinc and Sulfur. State clearly *all* the evidence in the experiment which leads you to believe that a chemical change did, or did not, take place when

(1) the zinc and sulfur are mixed, before igniting,

(2) the zinc and sulfur mixture was ignited. (**Caution:** Follow experimental directions.)

Interpretation of Data

It is important in drawing conclusions from experimental data that you consider all the facts observed, but also *that you not generalize beyond the data.* Let us consider a hypothetical case:

Example. Six metals were treated with dilute hydrochloric acid. In every case a gas was evolved which, on mixing with air, could be exploded with a sharp report.

Possible Generalizations:

1. Hydrogen can be formed by the action of hydrochloric acid on certain metals. *True.* The behavior noted is characteristic of hydrogen. A sufficient number of cases is given to justify this conclusion.
2. Every metal will displace hydrogen from hydrochloric acid. *Insufficient evidence* to judge. Not all metals were tried, under all possible conditions.
3. When a metal is treated with any acid, hydrogen is liberated. *Insufficient evidence.* One cannot generalize about other acids which were not tried.
4. The gas liberated when the above metals were treated with hydrochloric acid was carbon dioxide. *False.* Contrary to data. While no test for carbon dioxide was made, compounds of carbon were not even included in the reactants.

For each of the following statements, circle the T if sufficient evidence is presented *in Experiments 2 or 3* to justify the statement; circle the F if contrary to the data; or circle the I if insufficient evidence is given to decide.

1. All metals when treated with an acid liberate hydrogen. . . . . T I F
2. Most metals unite with oxygen when heated in the air. . . . . T I F
3. All compounds may be decomposed by heating them. . . . . T I F
4. All compounds containing oxygen decompose to yield oxygen gas when heated. (The symbol for oxygen, O, with or without a subscript, appears in the formula of any compound containing oxygen.) T I F
5. The determination of any one specific property is always sufficient evidence to identify a substance. . . . . T I F
6. Calcium hydroxide is more soluble by reaction with hydrochloric acid solution than by solution in water. (*See* Experiment 2.) . . . . . T I F
7. The aqueous solution of every substance not an acid or base is neutral to litmus. . . . . T I F
8. All salts are soluble. . . . . T I F
9. The disappearance of sulfur on heating always indicates its complete change into different substances. . . . . T I F
10. The decomposition of potassium chlorate by heat is a good example of one of its chemical properties. . . . . T I F
11. Copper oxide will dissolve in hydrochloric acid. . . . . T I F
12. Crystals of a substance are shaken with water, and some crystals remain after shaking. The substance is insoluble. . . . . T I F

The Packing of Atoms or Ions In Crystals 4

College Chemistry, Chapter 2

Review of Fundamental Concepts

The solid state of matter nearly always consists of a regular arrangement of atoms, molecules, or ions. If we represent each atom or group of atoms as a point, then the simplest configuration of points which has all the elements of symmetry of the whole crystal is called the *lattice*. The lattice may be looked on as the unit structure which, repeated indefinitely, gives the crystal. The number of nearest neighbors of a particle in a crystal lattice is called the coordination number.

Crystal Structure of the Elements. Most of the metallic elements crystallize in one of the following structures:

A. *Body-centered cubic packing*, shown by the alkali metals Li, Na, K, Rb, and Cs, and by some of the transition metals in groups Va and VIa, such as V, Nb, Ta, α-Cr, Mo, β-W, and β-U.

B. *Cubic closest packing, or face-centered cubic*, shown by the noble metals Cu, Ag, and Au, some of the transition metals in group VIII, and α-Ca, Sr, and Al.

C. *Hexagonal closest packing*, shown by Mg, Be, and γ-Ca in Group II, and Ti and Hf in Group IVa.

A substance may crystallize in more than one form, as indicated above by the Greek-letter prefixes, but in general each form is stable within a definite range of pressure and temperature.

In the case of the non-metallic elements, molecules such as Cl_2, P_4, and S_8 constitute the building units of the crystals.

The inert gases have an atomic lattice with either cubic closest packing, as A, Ne, and Kr, or hexagonal closest packing, as He.

Crystal Structure of Compounds. Chemical compounds may be conveniently grouped into two broad classes: molecular crystals and ionic crystals.

Molecular crystals contain molecules such as water, H_2O, carbon dioxide, CO_2, hydrogen chloride, HCl, and sugar, $C_{12}H_{22}O_{11}$, as building units. Here the atoms are held together by covalent bonds within the molecule, and the forces holding these neutral molecules together are relatively weak.

Ionic crystals contain positively charged particles called cations or negatively charged particles called anions as the building units. The cation may be a positively charged atom of a metal, such as Na^+, Ca^{++}, or Ag^+, or it may be a complex cation such as $Cu(NH_3)_4^{++}$. The anion may be a negatively charged atom, such as Cl^-, or a complex anion, such as NO_3^- or $PtCl_6^{--}$. Most inorganic salts, such as sodium chloride, NaCl, magnesium bromide, $MgBr_2$, potassium nitrate, KNO_3, and barium sulfate, $BaSO_4$, are members of this class. The structure of an ionic crystal depends on the relative sizes of the ions composing the crystal lattice, and it is possible to determine from geometrical considerations whether the number of nearest neighbors expected is three, four, six, or eight for a given ion. For example, if the ratio of the radius of the cation to that of the anion is greater than 0.73, eight anions can touch a given cation; if the ratio is less than 0.73 but greater than 0.41, only six anions can touch a given cation. The former case is typified by the lattice of the salt Cs^+Cl^- and the latter by the salt Na^+Cl^-.

It is the purpose of this experiment to help the student get some understanding of the various ways that spheres may be packed to form some of the typical crystal arrangements. It must be remembered that when solid spheres are used to represent the relative sizes and shapes of atoms or ions, we are giving them a rigidity which they do not possess. The cloud of electrons surrounding the nucleus of an atom does not have a definite boundary, nor does its influence cease at a definite distance from the nucleus.

As the experiment is performed, it is well to remember the extent of the enlargement of the atoms or ions from their actual radii of 1 or 2 Ångström units (10^{-8} cm) to those of the spheres used in the models. Also bear in mind the large number of particles (Avogadro's number,

6.023×10^{23}) actually involved in forming the gram-atomic weight of a metallic element or the gram formula weight of an ionic compound.

It may also be profitable for you to review some of the simple geometric relationships involved in three-dimensional objects such as a cube and a sphere. For example, how many vertices, how many edges, how many faces does a cube have? What is the relationship between the edges of a cube and a face diagonal? What is the relationship between the body diagonal, the face diagonal, and the edge of a cube? How may a tetrahedron be constructed within a cube? What is the volume of a sphere in terms of its radius? Some simple three-dimensional sketches should help you to determine the relationships desired.

Experimental Procedure

Special supplies: A set of cork balls (27 one-inch, 8 three-fourths-inch and 13 one-half-inch size); 36 pins which have had the heads cut off obliquely (may be conveniently stored in a cork); a small pair of pliers.

1. A Study of Metallic Crystals

Model A. Body-centered cubic packing (not closest packing). Construct the layers illustrated in Figure 4-1, using one-inch cork balls. Always insert the cut-off end of the pin into a ball with the aid of the pliers, and the other ball can then be easily attached to the sharpened end. Try to save wear and tear on the corks by inserting and pulling



FIG. 4-1. Layers of atoms for the body-centered cubic arrangement.

out the pins cleanly. The layers may be assembled without the use of pins by placing the single ball in the depression formed by the four balls of the first layer. Then place the third layer so that the four balls are directly over those in the first layer. As you study this model, you should realize that in an actual crystal there would be an infinite set of these unit cubes with common corners. With the model before you answer the questions in the report sheet.

Model B. Face-centered cubic packing (closest cubic packing). Construct the layers illustrated in Figure 4-2. Note that this time the balls are in actual contact with one another. Assemble the three layers without the use of pins. Place the second layer in a position so that the four balls all contact the center ball of layer one and fit between the outer balls. Then place the third layer so that its balls are directly over those of the first layer. Study this unit cell as you answer the questions in the report sheet. Save this model for comparison with the model for hexagonal closest packing.

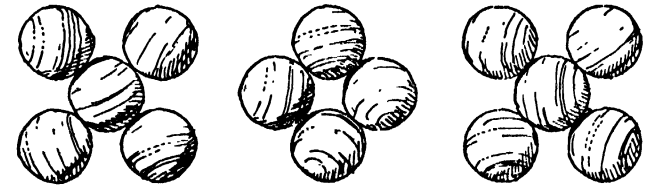


FIG. 4-2. Layers of atoms for the face-centered cubic arrangement.

Model C. Hexagonal closest packing. Construct the layers illustrated in Figure 4-3. Place the first layer so that one of the vertices of the triangle is facing you. Then place the central ball of the

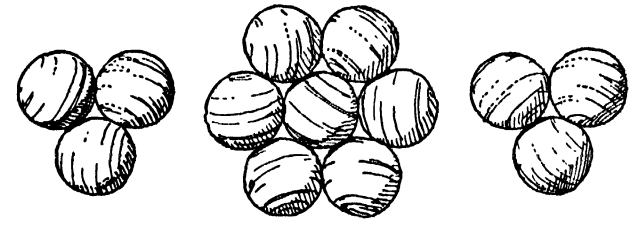


FIG. 4-3. Layers of atoms for the hexagonal closest packing arrangement.

second layer in the depression in the center of the first layer. Be sure that each ball of the first layer is in close contact with three balls of the second layer. Now place the third layer so that each of the three balls is directly over the corresponding ball of the first layer. Answer the questions in the report sheet relative to this model.

Comparison of the two types of closest packing. Place Model B and Model C before you. Remove the top layer of Model B. Rotate the top layer of Model C 60° to the right (or left) so that there is a layer of four balls forming a square facing you. Compare this view with that obtained by

looking down at the bottom two layers of Model B. Place the top layer of Model B on the four balls facing you in Model C to see if you can construct a unit cell of cubic closest packing which resembles Model B tilted at an angle.

2. A Study of Ionic Crystals

Model D. The sodium chloride structure, which is one of the commonest ionic structures for salts which contain an equal number of positive ions and negative ions. Since the sodium ion, Na^+, has a diameter of 1.90 Å and the chloride ion, Cl^-, has a diameter of 3.62 Å, you may approximate the relative sizes of these ions by using one-half-inch balls for Na^+ ions and one-inch balls for Cl^- ions. Construct the layers illustrated in Figure 4-4.



FIG. 4-4. Layers of atoms for the sodium chloride ionic arrangement.

Arrange the three layers so that the sodium and chloride ions are alternately placed. Study this model, and answer the questions in the report sheet.

Model E. The cesium chloride structure. The cesium ion, Cs^+, has a diameter of 3.38 Å compared with 3.62 Å for the chloride ion; so you may approximate the relative sizes of these ions by using three-fourths-inch balls for the cesium ions and one-inch balls for the chloride ions. Construct the first and third layers as illustrated in Figure 4-5. Place four loose three-fourths-inch balls in the

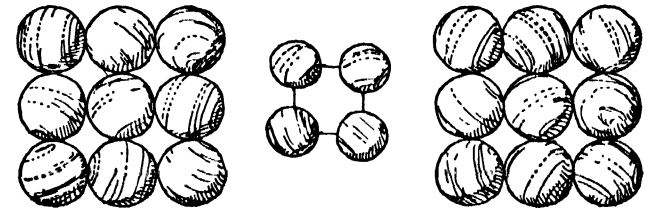


FIG. 4-5. Layers of atoms for the cesium chloride ionic arrangement.

depressions between the nine one-inch balls of the first layer. Then place the third layer directly over the first layer. Answer the questions in the report sheet relating to this model.

REPORT: Exp. 4

The Packing of Atoms and Ions in Crystals

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. A Study of Metallic Crystals

Model A. Body-centered cubic packing.

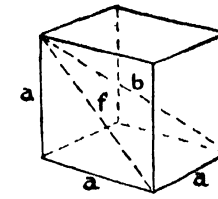
Why is this structure called body-centered cubic?

What is the coordination number of an atom of sodium when packed in a crystal of this type? _____

If this model were extended in all directions, what difference, if any, would there be in the relative positions of the corner spheres and those in the center?

Note: In the calculations below, consider all distances to be measured between the centers of the balls. From a study of the right triangles involved in a cube, as illustrated, where a = the edge of the cube, f = the face diagonal, and b = the body diagonal, the following relationships should be apparent: $b^2 = f^2 + a^2$, and since $f^2 = a^2 + a^2$, it follows that $b^2 = 3a^2$.

In calculating the volumes, note that only one-eighth of each of the corner spheres is inside the cube which has as its corners the centers of the spheres. The volume of a sphere may be calculated from its radius by using the formula $V = \frac{4}{3}\pi r^3$.



What is the length of the body diagonal, b? . . . . . _____ inches, _____ mm

Calculate the length of an edge, a, and also the volume of the cube, a^3: . . . a = _____ mm

a^3 = _____ mm^3

Calculate the volume of the spheres inside the cell: . . . . . _____ mm^3

What fraction of the total volume of the cube is actually occupied by the spheres in this type of packing? . . . . . _____

Model B. Face-centered cubic packing.

Why is this type called face-centered cubic?

What is the coordination number of a copper atom when packed in a crystal of this type? _____

What is the length of the face diagonal, f? . . . . . _____ inches, _____ mm

Calculate the edge of this unit cell from the relation $f^2 = a^2 + a^2$. Also calculate the volume of the cube: . . . . . a = _____ mm

a^3 = _____ mm^3

How many spheres fall wholly within this unit cell? . . . . . _____

Calculate the volume of the spheres inside the cell: . . . . . _____ mm^3

What fraction of the total volume of the cube is actually occupied by the spheres in this type of packing? . . . . . _____

Could you distinguish between the corner spheres and those in the centers of the faces if the model were expanded in all directions? Explain.

Model C. Hexagonal closest packing.

How many spheres are in contact with any one sphere in this type of packing? . . . . _____

How does the coordination number involved here compare with that in Model B with cubic closest packing? . . . . . _____

For the same radius of contact, how should the two types of closest packing compare in density? . . . . . _____

Make a brief statement comparing the packing in Model C with that in Model B.

2. A Study of Ionic Crystals

Model D. The sodium chloride lattice.

Using the actual diameters of the ions in Ångström units as given in the experimental procedure, calculate the radius ratio of sodium ion to chloride ion: . . . . . _____

How many chloride ions are in contact with any one sodium ion in this lattice? . . . _____

How many sodium ions are in contact with any one chloride ion? . . . . . _____

In a crystal of table salt weighing 58.5 grams, how many sodium ions and how many chloride ions would be present? . . . . . _____ Na^+

_____ Cl^-

Molten salts, such as fused sodium chloride, are good conductors of electricity. How do you account for this?

Using the actual diameters of the ions, record each of the following:

The shortest distance between the center of a Na^+ ion and a Cl^- ion. . . . . _____ Å

The shortest distance between two Na^+ ions. . . . . _____ Å

The shortest distance between two Cl^- ions. . . . . _____ Å

Model E. The cesium chloride lattice.

Using the actual diameters of the ions as given in the experimental procedure, calculate the ratio of the radius of the Cs^+ ion to that of the Cl^- ion. _____

What is the coordination number of each of the ions in this type of lattice? . . For Cs^+ = _____

For Cl^- = _____

How do you account for the change in coordination number from Model D to Model E?

Water solutions of salts are good conductors of electricity, whereas solutions of organic substances such as sugars are poor conductors. Explain.

Substances in the Atmosphere

College Chemistry, Chap.

Review of Fundamental Concepts

Look up, in your text,[1] the composition of the atmosphere. Note that it contains two gases in relatively large proportion, nitrogen and oxygen, three others in much lesser, but significant amounts, water vapor, argon, and carbon dioxide, and traces of several others. None of the constituents react readily with one another. Nitrogen and oxygen will combine in limited amount at extremely high temperatures, and water and carbon dioxide partially react in solution to form carbonic acid, H_2CO_3.

In the previous experiment, we have noted the reactivity of the oxygen in the air with a metal, copper, and a nonmetal, sulfur. In this experiment, we shall obtain qualitative evidence of the presence of water, carbon dioxide, and nitrogen, and quantitative evidence of the amount of oxygen in the atmosphere.

Experimental Procedure

Chemicals[2]*:* 0.1 *F* $Ba(OH)_2$, $CaCl_2$ (4-mesh, anhydrous), Fe (filings), Mg (ribbon), 30% pyrogallol solution (freshly prepared).

1. Some Qualitative Observations

(a) *Water Vapor.* Place several granules of anhydrous calcium chloride on a watch glass and leave it exposed to the air. At the close of the period, or the next laboratory period, observe any change that has occurred. (The reasons for the absorption of water by very soluble substances like calcium chloride will be considered when you study solutions. In extremely dry weather, calcium chloride may absorb no water at all.)

(b) *Carbon Dioxide.* Place about 15 ml of 0.1 *F* $Ba(OH)_2$ in a 500-ml flask. Stopper the flask, and shake it for a moment. Observe the change. (A barium hydroxide solution provides a more sensitive test for carbon dioxide than does the more commonly used limewater, or calcium hydroxide, solution, which you used in Experiment 3. The reaction is similar, and forms a precipitate of barium carbonate, $BaCO_3$.)

Just as a comparison, check on the relative amount of carbon dioxide in the breath, by opening the flask, inhaling deeply, and then exhaling your breath through a piece of glass or rubber tubing, into the flask. Close and again shake the flask. Compare the relative amount of precipitate in the two cases.

(c) *Nitrogen.* Place about 15 cm of magnesium ribbon, packed rather compactly, into a crucible, and cover it with the crucible lid. Heat this intensely with the Bunsen burner for about 15 minutes. Cool the crucible, and replace the lid with a small watch glass, to the under side of which is attached a moist piece of red litmus paper. Lift this watch glass just enough to moisten the white residue with a few drops of water. Warm the crucible slightly. Note any change in the litmus. The reactions are as follows: Along with the reaction of magnesium to form magnesium oxide, some of the magnesium reacts, at high temperature, with nitrogen in the air to form magnesium nitride,

$$3\,Mg + N_2 \longrightarrow Mg_3N_2.$$

This, by reaction with water, forms ammonia (NH_3) and the slightly soluble base magnesium hydroxide ($Mg(OH)_2$). Ammonia gas dissolves in water to form the weak, unstable base ammonium hydroxide.

$$Mg_3N_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,NH_3$$

$$NH_3 + H_2O \rightleftarrows NH_4OH.$$

It may be possible to detect the odor of ammonia gas above the moist white solid magnesium hydroxide.

[1] Learn to use your text as a reference book. Consult the index to locate a topic which may be in advance of your present lecture assignments.

[2] The "*F*" preceding a formula indicates a solution of a specified concentration. Thus, a 0.1 *F* solution contains 0.1 of the gram formula weight (as defined in Experiment 10) per liter of solution. For the present, you only need to recognize that a 0.1 *F* solution is a moderately dilute solution of the substance whose formula is given. Units of concentration are discussed in Experiment 20.

How many spheres a

How does the

cubic closest p

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densit

Determination of the Oxygen in Air.

First Method. Absorption of Oxygen by Pyrogallol. Prepare the apparatus as sketched in Figure 5-1. Remove the stopper and fill the flask, with the

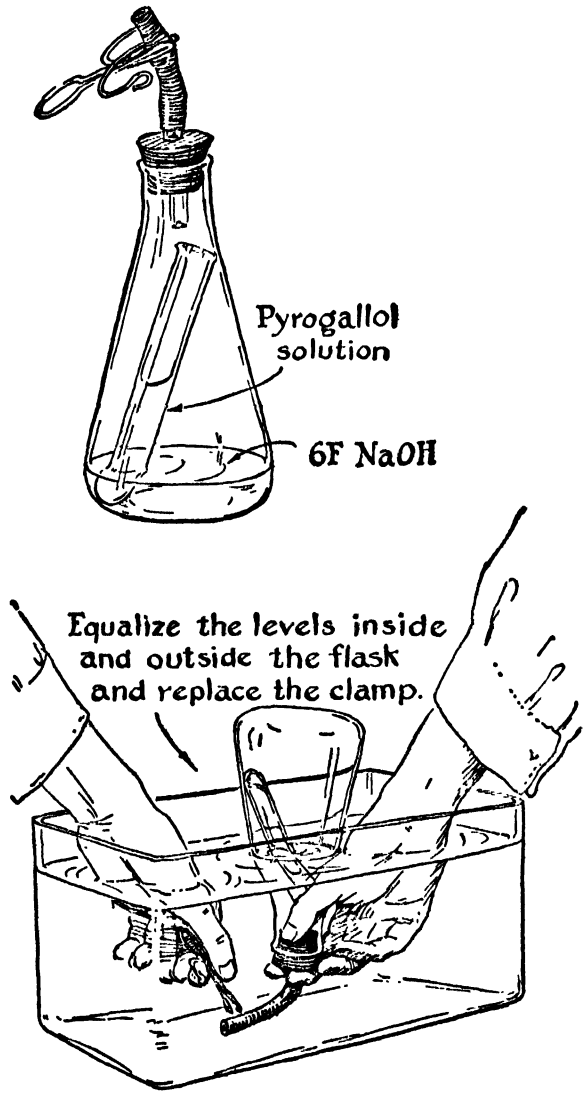


FIG. 5-1. Apparatus for the absorption of oxygen from the air by pyrogallol solution.

10-cm test tube still in it, with tap water. Temporarily disconnect the rubber tube and clamp, and re-insert the stopper and glass tube firmly into the flask so that no air bubbles are trapped. Remove the stopper and accurately measure the volume of the water with your graduated cylinder, to obtain the capacity of the apparatus. Record this volume and all subsequent data, at once, in your report sheet.

With the apparatus empty, but not dried, accurately measure about 20 ml of 6 *F* NaOH into the flask, and 5 to 6 ml of a 30% solution of pyrogallol,[1] (also called pyrogallic acid) into the test tube. Record the exact volumes used. Now firmly close the flask with the stopper (there must be no leak), and re-attach the rubber tube. Avoid undue handling of the flask, as this would warm it above room temperature. When all is ready, tightly clamp the rubber tube just above the glass tube. Repeatedly invert the apparatus, and shake it moderately, at intervals, to mix the contents. After about 15 minutes, during which time the oxygen should completely react chemically with the alkaline pyrogallol, invert the flask so that the rubber tube is completely under water in a large vessel, such as a pneumatic trough. Open the clamp to permit the entry of water, which will replace the volume of oxygen absorbed. With the flask cooled to room temperature, adjust the levels inside and outside the flask so they are equal, then close the clamp. (Again avoid handling that part of the flask which is exposed to the remaining air within.) This procedure will equalize the pressure so that all measurements are made under the same conditions. Place the flask upright at the table top.

At this point in the procedure, test the character of the residual gas by removing the stopper just as you thrust a burning splint into the flask. Results? With your graduated cylinder, carefully measure the volume of the brown liquid contained in the flask. From these data, calculate the volume of oxygen absorbed and the original volume of air, taking account of the volume of all liquids used, and the percentage of oxygen in the air.

(b) *Second Method. Reaction of Oxygen with Iron.* Moisten the inside of your 50- or 100-ml graduated cylinder and sprinkle the walls with fine iron filings. Leave one side clear for observation.[2] Lower the inverted graduate, vertically, into a 400-ml beaker which is two-thirds filled with water, so that bubbles of air do not escape. Note that while the water level rises a little at once due to the in-

[1] A 30% solution means 30 g of solute dissolved in 70 g of water. This should be freshly prepared for class use, or you may use 2.0 g of pyrogallic acid dissolved in 5 ml of water.

[2] A 100-ml cylinder is preferable, if available. If a 50-ml cylinder is used, place a rubber band about it before inverting it in the beaker, to assist you in marking the water level, as mentioned in the next paragraph.

creased pressure, the graduated cylinder is completely filled, initially, with air at atmospheric pressure. Leave this undisturbed until the next laboratory period, during which interval the oxygen (and some water vapor) will react with the iron to form a hydrated iron oxide, or ordinary rust, $Fe_2O_3 \cdot xH_2O$. See Figure 5-2.

Without lifting the graduated cylinder out of the water, adjust the levels inside and outside so they are equal, and carefully read the volume of the residual gas. If the water level is below the graduation marks olume cannot be read directly. nd carefully at the water l ime of residual nd e ne cylinder, by iest graduation graduated cyl- ater needed to nd also to fill it te the percentage

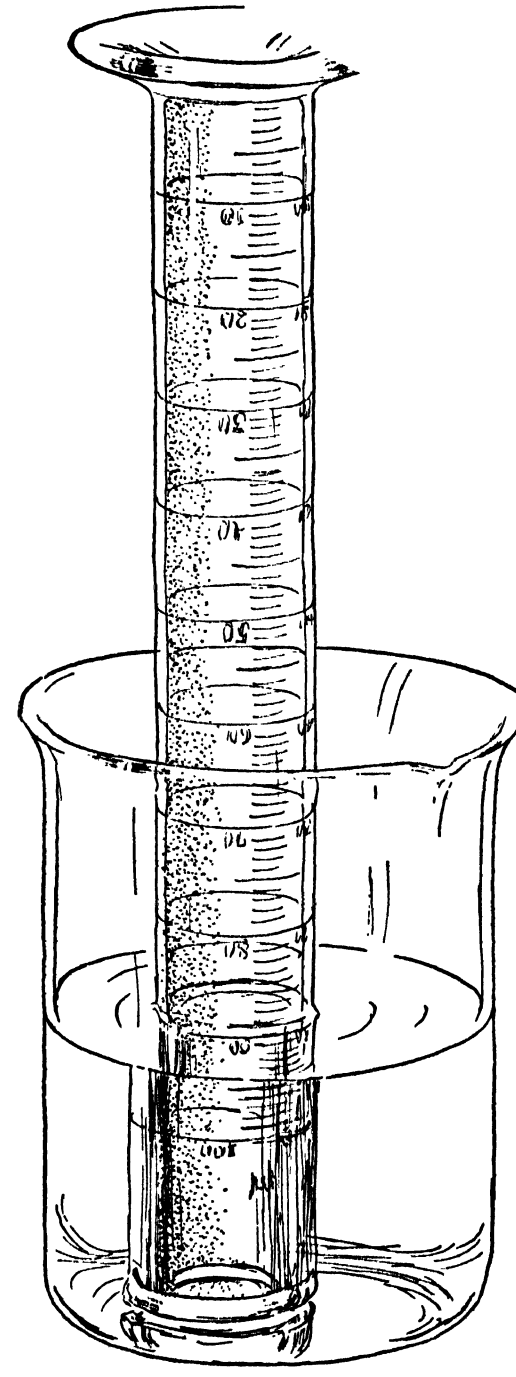


FIG. 5-2. **The absorption of oxygen by iron filings.**

REPORT: Exp. 5

Substances in the Atmosphere

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Some Qualitative Observations

Describe briefly the qualitative evidence which you obtain for the presence in the air of:

A. *Water Vapor*

B. *Carbon Dioxide*

C. *Nitrogen*

2. Quantitative Determination of Oxygen in the Air

A. *First Method. Absorption of Oxygen by Pyrogallol*

	1.	2.
Volume of water required to fill flask with test tube in it	_____ ml	_____ ml
Volume of 6 *F* NaOH	_____ ml	_____ ml
Volume of pyrogallol solution	_____ ml	_____ ml
Volume of all solutions in flask (after absorption)	_____ ml	_____ ml
Volume of oxygen absorbed	_____ ml	_____ ml
Volume of air originally in the stoppered flask	_____ ml	_____ ml
Percentage of oxygen in the air	_____ ml	_____ ml

Method of calculation:

B. *Second Method. Reaction of Oxygen with Iron*

	1.	2.
Volume of air originally in the graduated cylinder	_____ ml	_____ ml
Volume of residual gas in the graduated cylinder	_____ ml	_____ ml
Volume of oxygen absorbed	_____ ml	_____ ml
Percentage of oxygen in the air	_____ ml	_____ ml

Method of calculation:

Questions

1. Judging from the equipment used, the technique employed, and the volumes measured, comment on the relative precision and accuracy of the two methods for the analysis of oxygen.

2. What effect on the results would there be if: (1) All the measurements were carried out at a higher, but constant, temperature? (2) The temperature of the initial measurements of gas volume differed from that of the final measurements?

3. The amount of water vapor in the air is variable, up to a maximum of 2.0% (at room temperature, 20° C). If dry air contains 20.99% oxygen, what would be the corresponding percentage of oxygen in this same air, when saturated with water vapor? (Hint: 20.99 parts of oxygen in 100 parts of dry air would correspond to 20.99 parts oxygen in 102 parts of moist air.)

4. Calculate your percentage error[1] for each method of analysis for oxygen, assuming that the air you analyzed was saturated with water vapor, as the vessels were wet.

(a)_____

(b)_____

5. The carbon dioxide in the air, 0.03%, is likewise absorbed, by the sodium hydroxide in the solution, in method (a) How much of an error in the calculation of the percentage of oxygen is caused by neglecting this factor?

6. Summarize any physical and chemical properties of oxygen and of nitrogen which you have observed, or which it was necessary to assume, in the performance of these experiments.

7. List as many reasons as you can in support of the statement that the air is a mixture, rather than a compound, of its principal constituents.

[1] See Appendix I, Section C on Experimental Errors.

The Preparation of Pure Substances by Chemical Changes 6

College Chemistry, Chapter 4

Review of Fundamental Concepts

The Purity of Substances

A really pure substance, that is one made up of only one kind of molecules, probably does not exist. Even when made with the most refined methods, traces of impurities are likely to be present in a substance. For many purposes, impure substances are satisfactory and more economical, while in other cases chemicals of the purest grade obtainable are required.

The principal grades used in science and industry are: "Commercial" or "Technical" (relatively crude, impure, and cheap); "Purified" (comprising an intermediate grade, often of a rather high degree of purity); "U.S.P." (meeting the standards of the United States Pharmacopoeia for the drug trade); "C.P." (the so-called chemically pure grade); and "Reagent" (comprising the purest and consequently most expensive grade, used in analytical and much scientific work). It is an important part of the training of a chemist to learn methods of purification and tests for purity.

Methods of Purification

The method of removing undesirable constituents from an impure substance may be based on purely physical properties, such as differences in solubilities in suitable solvents, or differences in boiling points as in distillation procedures. Again, we may resort to methods in which one component is changed chemically into some other substance which has a different solubility, or boiling point, thus permitting a separation of the substance as a precipitate (solid substance), or perhaps as a volatile (gaseous) substance.

Types of Chemical Change

Chemical changes are characterized by the formation of one or more new substances, each with its own specific properties, and by the loss or gain of energy. Simple types of chemical changes are: (1) *combination*, in which two or more substances form a more complex one, e.g. the formation of copper sulfide from copper and sulfur; (2) *decomposition*, in which a more complex substance breaks down into two or more simpler ones, e.g. the decomposition of potassium chlorate ($KClO_3$) into potassium chloride (KCl) and oxygen; (3) *displacement or single replacement*, in which one element displaces another from its compound, e.g. the replacement of hydrogen in hydrochloric acid by zinc; (4) *exchange or double replacement*, in which two compounds interchange radicals to form two new compounds, e.g. silver nitrate ($AgNO_3$) and sodium chloride (NaCl) react to form silver chloride (AgCl) and sodium nitrate ($NaNO_3$). This last type of change usually occurs in solution, especially between substances whose solutions are good conductors of electricity. It is known that these substances are separated or dissociated in solution into electrically charged atoms or groups of atoms (radicals) called *ions*. Silver nitrate in solution consists of a mixture of silver ions and nitrate ions. Similarly a sodium chloride solution contains sodium ions and chloride ions. The formation of the precipitate of silver chloride consists of a combination of the silver ions and the chloride ions to form a compound that does not dissolve appreciably in water. The sodium ions and nitrate ions still remain in solution. Unless the solution is evaporated to dryness, forming crystals of sodium nitrate, we really have only a simple combination. A discussion of ions and their properties is given in later experiments.

Chemical Changes Occurring in this Experiment

We shall start with a sample of a silver-copper alloy (such as one of the several alloys used in jewelry manufacture) which has the approximate composition of American coinage silver. By a succession of chemical and physical changes, we shall separate this so as to obtain pure silver and pure copper metals. In succeeding experiments we shall convert these pure metals quantitatively into pure compounds, and calculate the formulas of the com-

pounds thus formed. The reactions will be carried out in the following steps:

(1) Silver-copper alloy is dissolved with nitric acid (HNO_3) to give a solution of silver nitrate ($AgNO_3$) and cupric nitrate ($Cu(NO_3)_2$).

(2) This solution is treated with sulfuric acid (H_2SO_4), evaporated to the point of the appearance of dense white fumes, and then diluted with water. The solution now contains silver sulfate (Ag_2SO_4) and cupric sulfate ($CuSO_4$).

(3) Copper metal is added to this solution, precipitating the silver as the free metal, and forming additional cupric sulfate in solution.

(4) Pure metallic copper is then obtained from this cupric sulfate solution by replacement with metallic zinc, in a manner similar to that of the replacement of silver above.

These successive changes may be summarized as follows:

$$\text{Ag-Cu} \xrightarrow{HNO_3} \underset{Cu(NO_3)_2}{AgNO_3} \xrightarrow{H_2SO_4} \underset{CuSO_4}{Ag_2SO_4} \xrightarrow{Cu} \underset{CuSO_4}{\underline{\quad Ag \quad}} \xrightarrow{Zn} \underset{ZnSO_4}{\underline{\quad Cu \quad}}$$

The experiment as a whole serves to illustrate the various types of chemical change, especially replacement reactions of a more active metal for a less active metal from its salts. (See Table VIII, Appendix II.)

Preliminary Work

Fill in the data called for in Table A, "Physical Properties of Various Substances," of the report sheet. This will give you information helpful in understanding the experiment.

Experimental Procedure

Special supplies: Ag-Cu alloy.[1]

Chemicals: Copper wire, No. 18, 0.1 *F* $Cu(NO_3)_2$, 0.1*F* $K_4Fe(CN)_6$, 0.1 *F* $AgNO_3$. Mossy zinc, 0.1 *F* $Zn(NO_3)_2$.

1. Pure Silver from a Silver-Copper Alloy.[2] Obtain a sample of silver-copper alloy weighing approximately 1.5 g. Using a balance sensitive to 0.01 g (such as the agate, knife-edge, triple-beam balance), weigh the alloy carefully, recording the weight on the report sheet. (Get instructions on the use of the balance. Be sure the balance's knife-edge support is released and the balance properly adjusted to zero, with all weight slides at zero position, before adding the alloy. A piece of metal may be weighed directly on the scale pan.) Place the weighed alloy in a 150-ml beaker and add 10 ml of dilute nitric acid (HNO_3). *Caution: Do not spill nitric acid on your hands or clothing—if this occurs flush well with water, neutralize acid on clothing with ammonium hydroxide.* Place the beaker on a wire gauze supported on a ring stand *under the hood,* and warm gently if needed, but only intermittently to maintain a moderate rate of solution of the metal.

If a brown gas (what is it?) ceases to be evolved before all the metal dissolves, it may be necessary to add a little more nitric acid. After complete solution of the metal, add 25 ml of dilute sulfuric acid, and continue the gentle heating in a manner to avoid any loss of solution by spattering, until the solution is evaporated to a syrupy liquid. This consists of concentrated sulfuric acid and dissolved salts. This point will be indicated by the very copious emission of dense, white, choking fumes of sulfur trioxide (SO_3). The beaker may then be covered with a watch glass to prevent the further escape of these fumes into the room. *Use caution,* as concentrated sulfuric acid is very corrosive. *Let the beaker cool,* then add cautiously about 125 ml of distilled water from your wash bottle. Heat the solution quite hot, but do not boil it, and stir with a glass stirring rod to dissolve the salts. (Silver sulfate, $(Ag)_2SO_4$, which is only slightly soluble at room temperature, is much more soluble in this strongly acid solution. In this case it is present largely as the acid salt, silver hydrogen sulfate, $AgHSO_4$. This should dissolve readily on heating and stirring the solution.)

Obtain a 30-cm length of about No. 18 copper wire, shape this into a very loose coil, and place in the warm solution of dissolved salts, leaving an end

[1] Silver-copper alloy of the composition of a dime, or of various percentages in order to provide for "unknowns" if desired, may be obtained from dealers in the noble metals—silver, gold, and platinum. The cost is only about three cents per student.

[2] *Caution:* Wash off any silver salt solutions spilled on the hands or clothing at once, otherwise a black stain of metallic silver will result. This is difficult to remove, but may be dissolved by treating the stain first with a few drops of tincture of iodine (to form AgI) and then with a saturated solution of sodium thiosulfate ($Na_2S_2O_3$), to remove excess iodine and dissolve the AgI.

of the wire bent up out of the solution as a handle. Leave the copper wire quietly in the solution for ten to fifteen minutes, to observe the beautiful deposit. Then stir, or shake the wire gently, at intervals, to loosen the precipitated silver and to

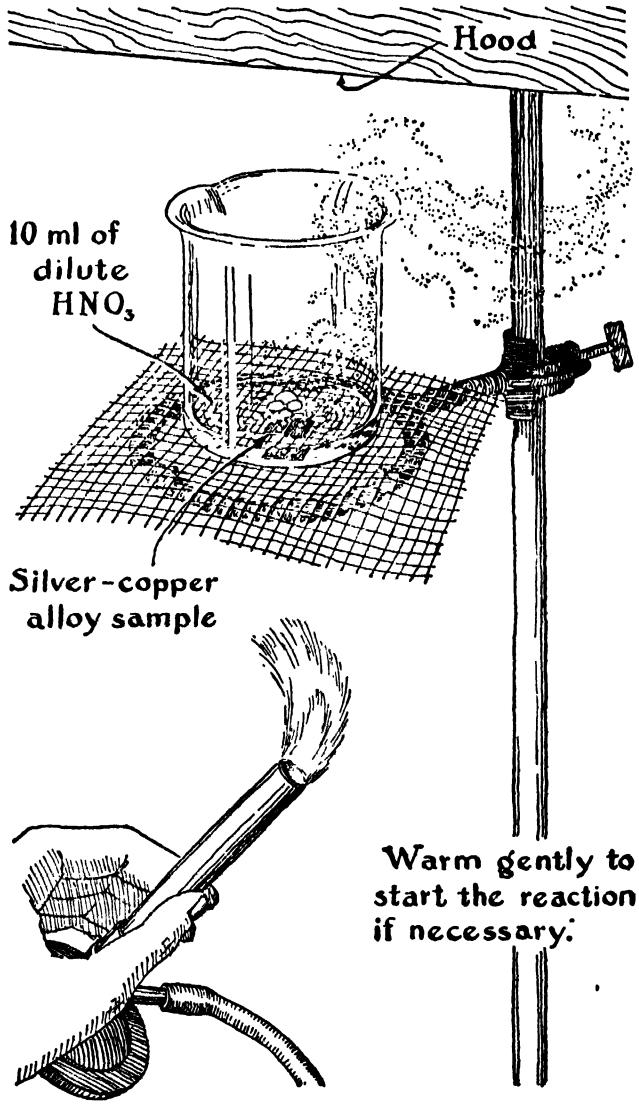


FIG. 6-1. Dissolving the silver-copper alloy.

expose fresh copper to the solution. While this reaction is proceeding, carry out the test tube reactions in the following paragraph, so as to learn suitable methods of qualitative tests which you will need to know in this experiment.

Qualitative Tests for Silver, Copper, and Zinc Salts. We shall test solutions of silver, copper, and zinc salts, and mixtures of these salts, with three reagents: hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), and potassium ferrocyanide ($K_4Fe(CN)_6$), respectively. Refer now to the report sheet, Table B. Place 1-ml samples of the salt solutions, as specified in the left column of Table B, into 10-cm test tubes. Add a drop of dilute hydrochloric acid to each, and note the results. Prepare another set of the salt solutions, and test each with 1 ml of dilute ammonium hydroxide. *Mix well*, and then note the results. (With cupric nitrate, ammonia forms a complex addition compound of the formula $Cu(NH_3)_4(NO_3)_2$, which contains the deep blue ion, $Cu(NH_3)_4^{++}$.) Test still a third set of the salt solutions with 1 ml of potassium ferrocyanide solution. In the silver nitrate salt mixtures be sure to use an excess of the potassium ferrocyanide, about 2 ml. State suitable methods (on the report sheet) for detecting the presence of silver, copper, and zinc salts in a solution.

To return to our reaction, after the copper wire has been in the solution of the alloy metals for about a half hour, transfer a few drops of the solution to a small test tube, and test this for silver ion. If a positive test is obtained, leave the wire in the solution for a longer period, until there is no more silver ion in the solution, this being shown by repeated tests.[1] When the reaction is complete, the resulting solution is much richer in cupric sulfate solution than it was before. Remove the copper wire from the solution, and carefully shake loose all of the precipitated silver. Let the silver settle, and carefully decant (see Fig. i-12, P. xix) as much of the clear solution as you can into a clean beaker, taking care that no silver is transferred. Add 5 ml of distilled water to the silver residue to wash it, mix this thoroughly, let it settle, and decant again, catching this first wash water in the cupric sulfate solution. Save this solution for paragraph 2, which follows. Continue to wash the silver metal by decantation, using first a 5-ml portion of dilute ammonium hydroxide as the wash solution (to remove any impurity of silver chloride), then using 5-ml portions of distilled water, until the washings show no positive test for cupric ion when 5 drops

[1] The rate of reaction of silver sulfate solution with copper metal varies a great deal with the concentration of acid. It is quite slow in a neutral solution, requiring five to ten hours for completion. However with 25 ml of dilute sulfuric acid present in the 125 ml of solution, the replacement should be completed in 30 to 45 minutes. If your reaction is proceeding too slowly, you may add an additional 5 ml of sulfuric acid.

of ammonia are added to 1 ml of the wash water. Finally drain off the last wash water from the silver. Discard all wash solutions after the first.

Heat a clean evaporating dish to dry it thoroughly. Let it cool, and weigh the dish carefully on the balance. With a stirring rod, transfer all the silver to this dish, without loss, and heat it until it is thoroughly dry. Cool, and reweigh it. Calculate the percentage of silver in your alloy sample.

To check on the purity of your silver, take a very small amount of it, not over one twentieth of the total amount, dissolve it in a half milliliter of dilute nitric acid by warming it gently, and test it for cupric ion as above. (Be sure to add an excess of ammonia, so the solution smells of ammonia after mixing.) Show this test to your instructor, together with the recorded results of the test, for his approval. Preserve your dry silver carefully in a covered vessel for use in Experiment 10.

2. Pure Copper from a Cupric Sulfate Solution. To your cupric sulfate solution from the above preparation of pure silver, add several grams of mossy zinc. (A large excess is not necessary.) Let this stand, with frequent stirring or shaking, until the blue color of the solution has disappeared. Test a few drops of this solution in a test tube with ammonia to see whether the copper is completely replaced. When a positive test for copper is no longer obtained, carefully decant the clear liquid, which may be discarded, leaving the solid material in the beaker. Pick out with your stirring rod any larger particles of zinc which remain, and add about 5 ml of dilute sulfuric acid, if necessary, to dissolve the remaining zinc. Does any copper dissolve? When the reaction is complete, decant the solution, and wash the copper by decantation with 5-ml portions of tap water, and finally with distilled water, until the last washing gives no test for zinc ion when 1 ml of potassium ferrocyanide is added to it. The washed copper may be dried at room temperature, but should not be heated, as it oxidizes readily when warm.

To check on the purity of your copper, dissolve a very small portion of it in a half milliliter of warm dilute nitric acid, and test this for the presence of silver ion. Show this test to your instructor, together with the recorded results of the test, for his approval.

REPORT: Exp. 6

Preparation of Pure Substances

Preliminary Work

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

TABLE A.

PHYSICAL PROPERTIES OF VARIOUS SUBSTANCES

The data for this table are to be obtained, before performing the experiment, from reference sources available, such as a table of physical constants of inorganic compounds in a handbook of chemistry.

Substance	*Color*	*Solubility g/100 g H_2O, at 20°C*	*Melting Point*	*Decomposition Temp.*
Cupric nitrate $Cu(NO_3)_2 \cdot 3H_2O$				
Cupric oxide CuO			(No entry)	
Cupric sulfate $CuSO_4 \cdot 5H_2O$			(No entry)	
Potassium nitrate KNO_3				
Silver chloride $AgCl$				(No entry)
Silver nitrate $AgNO_3$				
Silver oxide Ag_2O			(No entry)	
Silver sulfate Ag_2SO_4				

TABLE B.

QUALITATIVE TEST FOR SILVER, COPPER AND ZINC IONS

Obtain these data experimentally, as directed. In the proper square, indicate any results obtained, such as "white curdy precipitate," "no effect," the color of any solution formed, etc.

Reagents / *Test Solutions*	*Hydrochloric Acid (1 drop)*	*Ammonium Hydroxide 1 ml*	*Potassium Ferrocyanide 1 ml*
Pure silver nitrate solution			
Pure cupric nitrate solution			
Cupric nitrate solution and 1 drop silver nitrate			
Silver nitrate solution and 1 drop cupric nitrate			
Pure zinc nitrate solution			
Zinc nitrate solution and 1 drop cupric nitrate			

Utilizing the preceding results, name a reagent or reagents which will prove satisfactory when testing for the metal ions listed below, and give the name and color of any distinctive precipitates or solutions formed:

Metal Ions	*Reagent(s)*	*Name and Color of Distinctive Product Formed*
Silver nitrate (silver ion)		
Cupric nitrate (cupric ion)		
Zinc nitrate (zinc ion)		

1. Pure Silver from Silver-Copper Alloy

Weight of silver-copper alloy taken . . . . . _____ g

Weight of evaporating dish plus pure silver . . . . . _____ g

Weight of evaporating dish, empty and dry . . . . . _____ g

Weight of pure silver obtained . . . . . _____ g

Percentage of silver in the alloy . . . . . _____ %

Method of calculation:

Test for purity of solid silver metal obtained:

Method _____

Observed result of test _____ Instructor's approval _____

2. Pure Copper from Cupric Sulfate

Test for purity of solid copper metal obtained:

Method _____

Observed result of test _____ Instructor's approval _____

3. Chemical Changes Involved in This Experiment

For each of the cases (a) to (i) on the next page, decide on the nature of the reaction, if any, which will occur. If you have had no previous chemistry, simply write the *names* of the products formed. At the right, indicate the type of the reaction: C for combination, D for decomposition, S for single replacement, and DR for double replacement. If you have studied chemistry, you may wish to write balanced equations for the reactions. Study Assignment A, Page 5, and Table XVI, Ionic Valences, in Appendix II, will help you to write the formulas correctly. As an example, we have given below both the names of the products and the equation for the solution of your alloy in nitric acid. This is a more complex, oxidation-reduction type of reaction.

Example: | *Types of Reactions*

(x) Silver (or copper) is dissolved in nitric acid:

Silver nitrate, nitric oxide, and water or $3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + NO + 2\,H_2O$ | (*A complex oxidation reduction*)

Types of Reactions

(a) Silver nitrate and sulfuric acid solutions are evaporated:

_____ _____

(b) Hydrochloric acid is added to silver sulfate:

_____ _____

(c) A copper wire is placed in silver sulfate solution:

_____ _____

(d) Zinc metal is added to dilute sulfuric acid:

_____ _____

(e) Copper metal is added to dilute sulfuric acid:

_____ _____

(f) Zinc metal is added to cupric sulfate solution:

_____ _____

(g) Potassium ferrocyanide and cupric nitrate solutions are mixed:

_____ _____

(h) Potassium ferrocyanide and zinc nitrate solutions are mixed:

_____ _____

(i) Copper metal is heated in air:

_____ _____

(j) Silver oxide is heated:

_____ _____

(k) Silver metal is heated in air:

_____ _____

4. Replacement Series of the Metals

Considering only the reactions in solution above which you marked SR (single replacement), make a list of the elements copper, zinc, silver, and hydrogen in such an order that each element comes above another that it replaces from solution.

_____

_____

_____

_____

Interpretation of Data, and Problems

In answering this section, use any of your data or Table A in this experiment, and also Table VIII in the Appendix.

1. (a) Predict two single replacement reactions which you did not try, but would expect to occur:

_____

_____

(b) Predict a combination of a metal with a solution of a salt of another metal in which no reaction would occur:

_____

2. Choose the method that you would use to separate the following pairs of substances. If a chemical change is required, encircle the C. If the separation is based on a difference in solubilities, encircle the S, or, if based on a difference in boiling points, encircle the B.

(a) Silver chloride and cupric sulfate . . . . . C S B
(b) Water and silver nitrate . . . . . C S B
(c) Zinc nitrate and cupric nitrate . . . . . C S B
(d) Water and silver . . . . . C S B
(e) Zinc and copper . . . . . C S B
(f) Silver oxide and silver nitrate . . . . . C S B
(g) Cupric oxide from nitrogen dioxide and oxygen . . . . . C S B

In case a chemical change takes place in any of the above, record the change involved in your separation:

( )_____

( )_____

3. Three unknown solutions, which may contain salts of silver, zinc, and copper, but no other salts, are tested as indicated below. For each case, indicate what you know about the presence or absence of each metal ion in the solution. Encircle the P if the given metal is definitely proved present in the solution, A if it is definitely absent, and D if the test is insufficient to decide.

(a) Unknown solution (a) is tested by adding ammonium hydroxide in excess, giving a clear, colorless solution.

Silver P D A
Zinc P D A
Copper P D A

(b) Unknown solution (b) is tested by adding a drop of hydrochloric acid, giving a white precipitate.

Silver P D A
Zinc P D A
Copper P D A

(c) Unknown solution (c) is tested by adding a drop of hydrochloric acid, with no noticeable effect, then adding a little potassium ferrocyanide, giving a white precipitate.

Silver P D A
Zinc P D A
Copper P D A

4. Cupric oxide contains 79.9% copper. What weight of American coinage silver, which is 90% silver, would be needed to produce, by suitable chemical reaction, 10.0 grams of cupric oxide? . . . . . _____

5. What weight of silver nitrate, which is 64% silver, could be produced from a U. S. dime weighing 2.5 grams? . . . . . _____

The Reduction of Metallic Oxides by Hydrogen and Other Reducing Agents

7

College Chemistry, Chapters 4, 6

Review of Fundamental Concepts

Oxidation and Reduction

As a first simple definition, we may say that a substance is *oxidized* when it combines with oxygen (or with some other nonmetallic element, as chlorine). The *oxidizing agent* for the reaction may be either free oxygen gas or some compound which supplies oxygen or another nonmetallic element. In general, when a substance is oxidized, the extent of its combination with nonmetallic elements is increased.

A substance is *reduced* when the extent to which it is combined with oxygen, or other nonmetallic elements, is decreased. The *reducing agent* is the substance—for example, hydrogen gas or some metallic element—which removes the nonmetallic element by combining with it. A detailed study of oxidation and reduction is given in Experiment 17, and other subsequent experiments. Study Table VIII in Appendix II, and note the variation in the ease with which the oxides of different metals may be reduced.

In this experiment, directions are given for the reduction of certain metallic oxides by the use of: (1) hydrogen gas, (2) your domestic fuel gas, and (3) the blowpipe, with a charcoal block. Use as many metallic oxides, and methods, as your instructor directs. In observing your results, look for such characteristics as change in color and physical form, luster, malleability, hardness, magnetic properties (in the case of iron), and ease of melting.

Experimental Procedure

Special supplies: Thistle tube, calcium chloride tube, blowpipe, magnet.

Chemicals: $CaCl_2$ (anhydrous, 4-mesh), cotton, zinc (mossy), 0.1 *F* $CuSO_4$, charcoal stick, powdered charcoal, various metallic oxides for reduction, as CuO, Fe_2O_3, PbO, Pb_3O_4, PbO_2, SnO_2.

1. Reduction with Hydrogen. Prepare the apparatus as illustrated in Figure 7-1. Place about 2 to 4 g of the metallic oxide to be reduced in the pyrex test tube. Put about 15 g of mossy zinc, together with 10 ml of water, in the generating flask. *Before generating hydrogen have your apparatus approved by the instructor,* and have him initial the report sheet. He will not approve it later.

When all is ready, pour 20 ml of dilute sulfuric acid down the thistle tube. If the gas is slow in generating, add 2 or 3 ml of cupric sulfate solution, as a catalyst. More acid may be added from time to time, so as to maintain a moderate rate of evolution of gas. (*Wrap the generating flask in a towel to catch flying glass in case an explosion should occur.*)

Test for the purity of hydrogen gas throughout the system by inverting a 10-ml test tube over the exit tube to catch a tube full of the issuing gas, as illustrated in Figure 7-2. Repeat this test until the gas burns quietly, and then use this test tube of burning hydrogen to ignite the gas issuing from the capillary tip. *As a safety precaution, ignite the tip in no other way.*

Now heat the metallic oxide to a moderate temperature, maintaining a steady evolution of hydrogen all the while by adding acid as needed. When the change is complete, warm the other part of the test tube to dry out all the water (where did it come from?), but do not burn the rubber stopper. Remove the flame and permit the free metal to cool, still keeping the tube filled with hydrogen gas so that no air will enter to oxidize the metal.

2. Reduction with Domestic Fuel Gas. Coal gas or a mixed gas usually contains free hydrogen and is an excellent reducing agent. Natural gas, which is largely methane (CH_4), is not satisfactory. If your gas supply is suitable, place the oxide to be reduced in the test tube (Fig. 7-1), disconnect the hydrogen generator and connect the gas jet by means of rubber tubing to the $CaCl_2$ drying tube. Pass a slow stream of gas through the system, and ignite the excess at the exit tip. Heat the test tube to reduce the oxide to the free metal.

3. Reduction by the Use of the Blowpipe. Hollow out a piece of charcoal near one end so as to make a depression about 1 cm wide and 5 to 7 mm deep. Fill this with the metallic oxide to be reduced, and heat it with the reducing flame of the blowpipe, as illustrated in Figure 7-3. Your instructor will demonstrate the proper technique, so as to maintain a continuous blowpipe jet. (Learn to maintain a positive air pressure, while inhaling

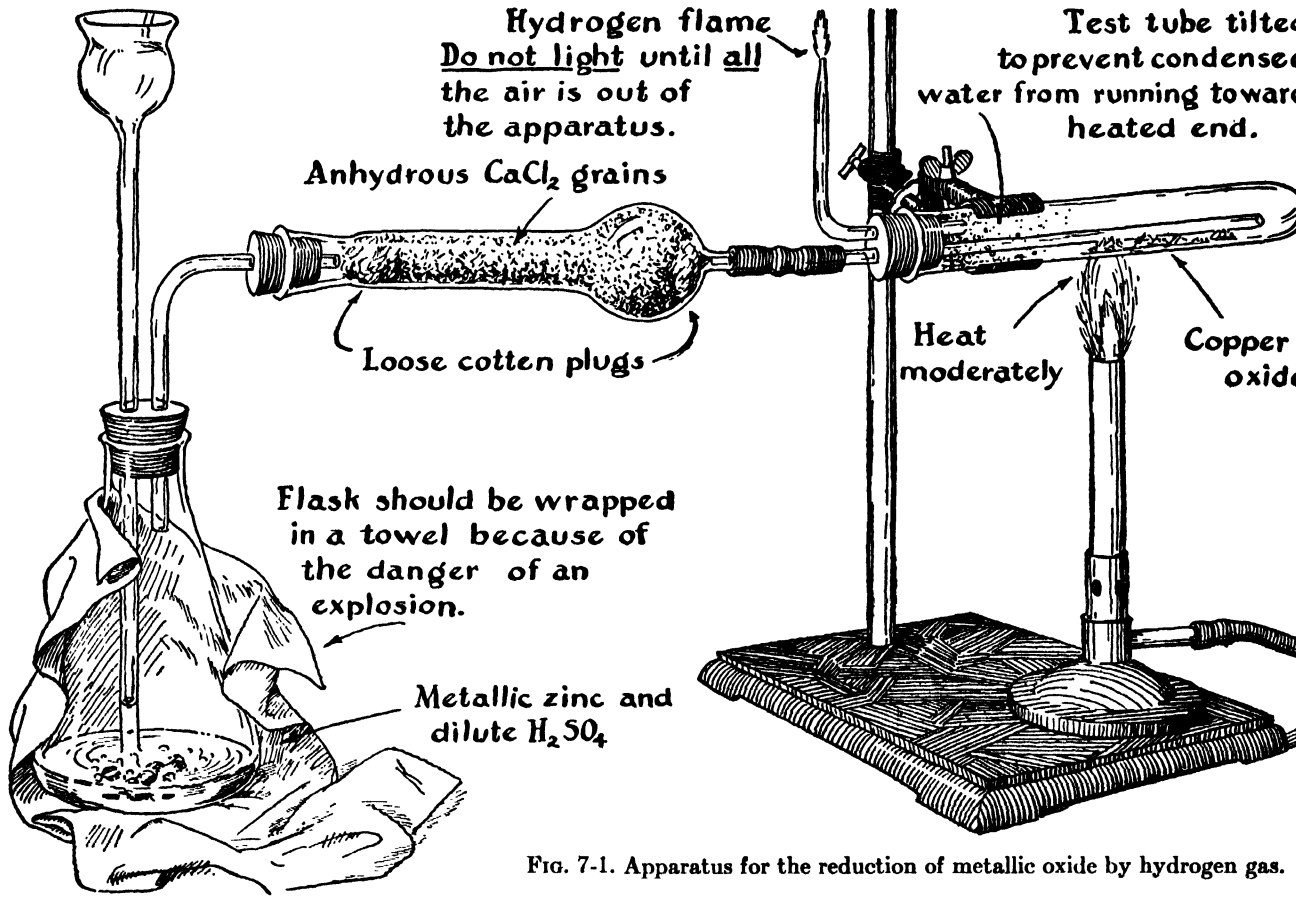


FIG. 7-1. Apparatus for the reduction of metallic oxide by hydrogen gas.

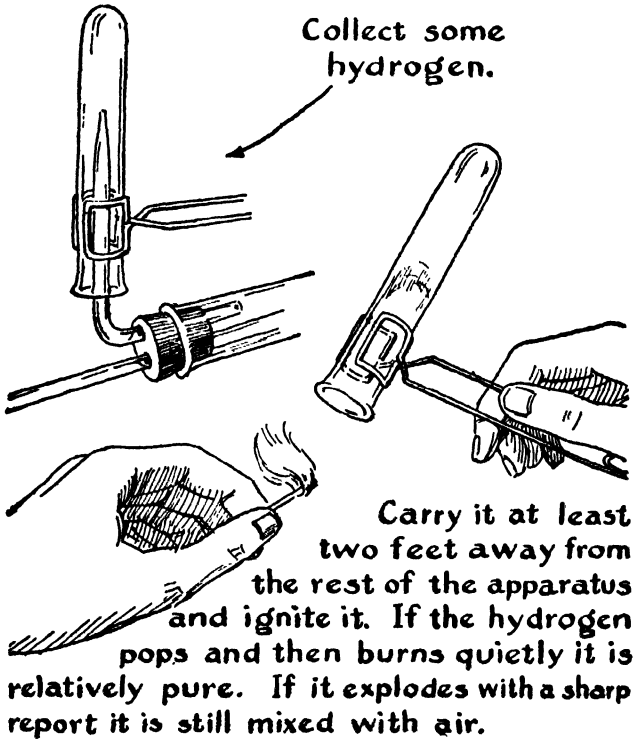


FIG. 7-2. Testing for the purity of the hydrogen from the generator.

at the same time.) Note that the oxide must be kept in the inner portion of the flame, in the presence of the hot reducing gases which may consist both of the hot domestic gas and of carbon monoxide produced by the burning charcoal. Sometimes, it is advisable to mix the metallic oxide with powdered charcoal before placing it on the charcoal block.

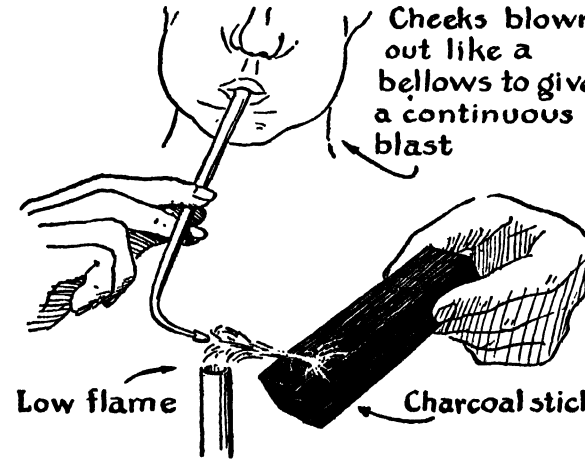


FIG. 7-3. The reduction of a metallic oxide which is placed in a depression in a charcoal block, by the use of a blowpipe.

REPORT: Exp. 7

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Reduction of Metallic Oxides by Hydrogen and Other Reducing Agents

Review Questions

1. Write equations for the preparation of hydrogen gas by the following reactions:

Sodium metal and water_____

Steam and red hot iron_____

Zinc and sulfuric acid_____

Electrolysis of water_____

2. For the equations below, write in the spaces provided, the formulas of the substances designated:

(a) $FeO + CO \longrightarrow Fe + CO_2$

(b) $2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2$

	For Equation (a)	*For Equation (b)*
The substance oxidized		
The substance reduced		
The oxidizing agent		
The reducing agent		

1. Reduction with Hydrogen

Instructor's Approval of Apparatus . . . . _____

1. List at least four physical properties of hydrogen *which you observed in this experiment.*

2. Write the equation for the reaction which occurs in the explosion of impure hydrogen gas:

_____

3. Write equations for the reduction of each of the following oxides by hydrogen gas:

Cupric oxide, CuO . . . . . _____

Ferric oxide, Fe_2O_3 . . . . . _____

Magnetic iron oxide, Fe_3O_4 . . . . . _____

4. List the metallic oxide or oxides which you reduced, and give all physical evidences *which you observed*, fo each case, that a reaction had taken place:

2. Reduction by Other Reducing Agents

1. Write equations for the reduction that takes place on heating stannic oxide, SnO_2, with:

Carbon . . . . . _____

Carbon monoxide . . . . . _____

2. List any metallic oxides which you reduced by the use of the blowpipe, and for each of these reaction indicate all evidences of chemical change *which you observed:*

3. In the reactions of the blowpipe flame, (1) hot oxygen gas can react with the red hot charcoal, and (2) an carbon dioxide formed can likewise react with the red hot charcoal. Write the equations for these processes:

(1)_____

(2)_____

Application of Principles

Consider the results of this experiment, and Table VIII in the Appendix, in answering the following.

1. Suggest three other metals, besides zinc, which might be satisfactorily used, by reaction with an acid, f the preparation of hydrogen gas.

_____

2. List, in each category, two metals whose oxides:

Can be reduced by heat alone, ... _____

Cannot be reduced by heat but can by H_2 or CO, ... _____

Cannot be reduced by H_2 or CO but can by Al, ... _____

Cannot be reduced except by electrolysis. . . . . _____

The Oxides of the Elements and the Periodic Table

8

College Chemistry, Chapters 5, 6

Review of Fundamental Concepts

In this experiment, we shall prepare oxygen gas, and use this gas to prepare a number of representative oxides of various elements. We shall observe the chemical character of the different oxides, by their reactions with water and by the formation of salts, and correlate the general character of the elements with their relative positions in the periodic table.

Acids and Bases from Oxides

In general, the oxide of an element (symbol El) reacts with water to form an addition compound in which there are hydroxide groups,

$$ElO + H_2O \longrightarrow El\begin{matrix}\diagup O{-}H \\ \diagdown O{-}H.\end{matrix}$$

(The number of OH groups, and the corresponding subscripts in the formulas, will, of course, vary with different elements.) The character of this hydroxide depends on the nature of the element to which the OH groups are attached. The product may behave as an *acid*,[1] which is characterized in solution by the presence of hydrogen ions, H^+. We, therefore, write the formula with the hydrogen atoms first, as H_2ElO_2. In solution, it ionizes according to the equation

$$H_2ElO_2 \longrightarrow 2\ H^+ + ElO_2^{--}.$$

On the other hand, the compound may behave as a *base*, which is characterized, in solution, by the presence of hydroxide ions, OH^-, so we write the formula with the hydroxide group together. In solution, it ionizes according to the equation

$$El(OH)_2 \longrightarrow El^{++} + 2\ OH^-.$$

An oxide which with water forms an acid is called an *acidic oxide or acid anhydride*. An oxide which with water forms a base is called a *basic oxide or basic anhydride*. We may compute the formula of a basic or acidic anhydride which is related to a given base or acid by subtracting water so as to eliminate all hydrogen atoms, as for example,

$$Mg(OH)_2 - H_2O \longrightarrow MgO$$

$$2\ H_3BO_3 - 3\ H_2O \longrightarrow B_2O_3.$$

Salts

Salts are ionic-type compounds which consist of an electropositive radical (other than hydrogen ion) combined with an electronegative radical (other than hydroxide ion). An important method of formation of salts involves the reaction of either a base or basic oxide with either an acid or acidic oxide. Typical equations for such reactions are:

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O$$

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$CaO + CO_2 \longrightarrow CaCO_3.$$

If the reactions take place in solution, they more probably are of the first type, while if they take place in a molten mixture, free from water, they would, of course, involve the interaction of the basic and acidic oxides directly. In the study of the geological history of the earth's crust, the formation of many minerals is to be explained in terms of the crystallization of "salts" from the mixture of basic and acidic oxides present in the molten magma, as it cooled. The ceramic industry is based on such reactions, as are also certain metallurgical operations, for example, in the iron and aluminum industries.

Salts may also be formed by the action of the free metal with an acid, in which case hydrogen gas, rather than water, is formed, as in the reaction

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2.$$

Likewise, a salt is formed when a metal combines with a nonmetal, as in the reaction

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl.$$

Chemical Formulas, Valence, Nomenclature

There are many thousands of chemical substances. However, their formulas and names in

[1] A number of important acids are not derived from oxides, however, as the binary hydrides of the nonmetals, i.e., HCl, HBr, H_2S, etc.

general correspond to simple rules, the application of which is not difficult for you to master.

Binary compounds are those consisting of two elements. Their formulas are the simplest to build, and they may be named by remembering only the characteristic ending *ide*. In such compounds, the more electropositive (metallic) element is given first, followed by an abbreviation of the more electronegative (nonmetallic) element, then completed by the ending *ide*. A few examples are: NaCl, sodium chlor*ide;* CaO, calcium ox*ide;* $MgBr_2$, magnesium brom*ide;* H_2S, hydrogen sulf*ide;* AlI_3, aluminum iod*ide;* Mg_3N_2, magnesium nitr*ide;* and K_2O, potassium ox*ide*.

Ionic valence and the periodic table. The subscripts which you note in the above and in other formulas indicate the relative number of atoms of the different elements which are combined together. The relative combining power of an element in a compound is called its *valence*. At this time we shall introduce only the *ionic valence.*[1] This term implies that the atom, or radical, in the compound possesses a definite electrical charge. The metals become electropositive, and the nonmetals become electronegative, in their binary compounds. The theoretical explanation of this positive and negative character will be presented later, when your background is better developed, but it will be to your advantage now to learn a few of the common valences, and to relate them to the position of the element in the periodic table. Note that in the first three groups the positive valence always corresponds to the periodic table group number. Thus we have a valence of +1 for hydrogen and for the metals of group I in their compounds: H^+, Li^+, Na^+, K^+, Rb^+, and Cs^+; a valence of +2 for the metals of group II in their compounds: Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, and Ra^{++}; and a valence of +3 for the metals of group III in their compounds: Al^{+++}, Sc^{+++}, etc.[2]

The typical ionic valences of the nonmetals are, likewise, in accordance with their periodic group. In their binary compounds, we have a valence of −1 for the group VII elements: F^-, Cl^-, Br^-, I^- a valence of −2 for the group VI elements O^{--}, S^{--}, Se^{--}, Te^{--}; and a valence of −3 fo the group V elements, N^{---}, P^{---}, As^{---}, etc. (Note that the negative valence is obtained b subtracting the group number from eight.)

Some elements, notably the *transition metal* (atomic numbers 22 to 32 and those below them i the periodic table), show a *variable valence.* I these cases, the endings *ous* and *ic* are used t show, respectively, the lower and the higher va lence. The more common instances of variabl valence are:

Fe^{++}	Co^{++}	Ni^{++}	Cu^{+}	Au^{+}	Hg_2^{++}	Sn^{++}	*ous*
Fe^{+++}	Co^{+++}	Ni^{+++}	Cu^{++}	Au^{+++}	Hg^{++}	Sn^{++++}	*ic*

The names and formulas of a few correspondin compounds are:

ferr*ous*	bromide	$FeBr_2$	mercur*ous*	oxide	Hg_2O
ferr*ic*	bromide	$FeBr_3$	mercur*ic*	oxide	HgO
cupr*ous*	sulfide	Cu_2S	stann*ous*	chloride	$SnCl_2$
cupr*ic*	sulfide	CuS	stann*ic*	chloride	$SnCl_4$

It will pay you to *learn the names and formula* of a very few *common oxygen acids*, as this, in turn will teach you the valences of the correspondin negative radicals.[4] Note that if the name of th oxygen acid ends in *ic*, the name of the correspond ing negative radical ends in *ate*.

nitr*ic* acid	HNO_3	nitr*ate* ion	NO_3^-
sulfur*ic* acid	H_2SO_4	sulf*ate* ion	SO_4^{--}
carbon*ic* acid	H_2CO_3	carbon*ate* ion	CO_3^{--}
phosphor*ic* acid	H_3PO_4	phosph*ate* ion	PO_4^{---}

In general, acids and salts containing three differ ent elements (ternary compounds) are name according to a different system than binary com pounds. This is considered in detail after Experi ment 18.

To summarize the building of a formula: Note that one simply inserts such subscripts after eac element or radical as will balance the total positive and total negative charges, as, for example $(Na^+)(Cl^-)$ or NaCl, $(Ca^{++})(Cl^-)_2$ or $CaCl_2$

[1] The topic of valence, including other aspects of the problem, such as "covalence" and "coordination number," will be considered more thoroughly later. See *College Chemistry*, Chapters 10 and 11, and Experiments 15, 16, and 35.

[2] The character of boron is such that it is usually present in compounds as a part of an ion which possesses a negative charge, as in boric acid, H_3BO_3, i.e. BO_3^{---}.

[3] As we move from group VII to group V, the chemical bond forme when these elements combine with other elements becomes less ioni and more covalent in character. For the purpose of writing correc formulas, however, it is convenient to ascribe definite negative va lences to these elements.

[4] The term "radical" is applied to a group of atoms which ofte act as a unit in a chemical reaction.

$(Mg^{++})(NO_3^-)_2$ or $Mg(NO_3)_2$, $(Ca^{++})(O^{--})$ or CaO, $(Ca^{++})(SO_4^{--})$ or $CaSO_4$, and $(Ba^{++})_3(PO_4^{---})_2$ or $Ba_3(PO_4)_2$.

Some additional rules of nomenclature. Hydroxides are named according to the rule for binary compounds even though there are three elements present. The hydroxide ion (OH^-) is a rather stable group of elements and is treated as though it were a single nonmetal ion such as chloride (Cl^-). For example, NaOH is sodium hydrox*ide*, and $Al(OH)_3$ is aluminum hydrox*ide*.

The ion NH_4^+ behaves very much like the alkali metal ions (Na^+, K^+, etc.) and is given the name "ammonium ion." It is treated exactly as though it were a simple metal ion. For example, NH_4Cl is ammonium chlor*ide*, NH_4OH is ammonium hydrox*ide*, $(NH_4)_2S$ is ammonium sulf*ide*.

Some special mention should be made of *binary compounds containing two nonmetallic elements.* In these cases the more electronegative element is named last, and a prefix is attached to indicate the number of atoms of this element (rather than the *ous* and *ic* endings used in the case of metals). Some examples are:

SO_2 sulfur dioxide	N_2O_3 nitrogen trioxide
SO_3 sulfur trioxide	N_2O_5 nitrogen pentoxide

Some compounds like water (H_2O), ammonia (NH_3), and phosphine (PH_3) possess common names which were given them before the nomenclature of compounds was systematized.

The *hydrogen compounds of some of the nonmetals* (HF, HCl, HBr, HI, H_2S, H_2Se, etc.) form acid solutions when dissolved in water, and when they are used in this sense they are named according to the following simple convention:

HCl (hydrogen chloride) becomes *hydro*chlor*ic acid*

HBr (hydrogen bromide) becomes *hydro*brom*ic acid*

H_2S (hydrogen sulfide) becomes *hydro*sulfur*ic acid*

The Writing of a Chemical Equation

A chemical equation is simply the chemist's shorthand expression of a chemical reaction which takes place. Fundamentally, it expresses the *quantities* of the substances used and produced. All of the atoms included in the molecules of the reactants must reappear in the molecules of the products, that is, *an equation must balance.* Thus, to write

$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$

is false. It is necessary to use 2 HCl, since two atoms each of hydrogen and of chlorine are involved on the right side of the equation. We, therefore, write

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2.$$

In writing a correct, balanced equation, note these points:

First—be sure that the formulas of the substances used, and of those produced, are correct, and then *do not change the subscripts* in order to balance the equation.

Second—place such coefficients in front of the formulas as are needed to have the same number of atoms of each element on each side of the equation. This usually can be done by a simple inspection. A good policy is to start with the most complicated formula.

For example, when steam is passed over red hot iron, analysis of the oxide formed shows that it is Fe_3O_4, magnetic iron oxide. We, therefore, first write down the correct formulas of reactants and products:

$$Fe + H_2O \longrightarrow Fe_3O_4 + H_2 \text{ (unbalanced).}$$

To balance it, start with the Fe_3O_4 noting that 3 Fe and 4 H_2O will be required, and then 4 H_2 will be produced:

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2 \text{ (balanced).}$$

Experimental Procedure

Special supplies: Deflagrating spoon, 6 glass squares, pneumatic trough, 6 250-ml wide mouth bottles.

Chemicals: Ca (metal shavings), Cu (turnings), Fe (steel wool), Mg (ribbon), P (red), S, small pieces of charcoal, litmus solution, $KClO_3$, MnO_2 (powdered), H_3BO_3, 60% solution of $HClO_4$, Na_2O_2.

1. The Preparation of Oxygen. Assemble the apparatus as illustrated in Figure 8-1. Mix about 10 g of potassium chlorate with 2 g of manganese dioxide. First place a very small sample of this mixture in the test tube and heat it enough to melt the potassium chlorate. If it decomposes smoothly, without obvious sparks and combustion, it is safe to use.[1] Let the test tube cool, then add the re-

[1] If organic materials are present, or if possibly the wrong chemicals are mixed, a dangerous explosion might result. It pays to treat potassium chlorate with due caution and respect.

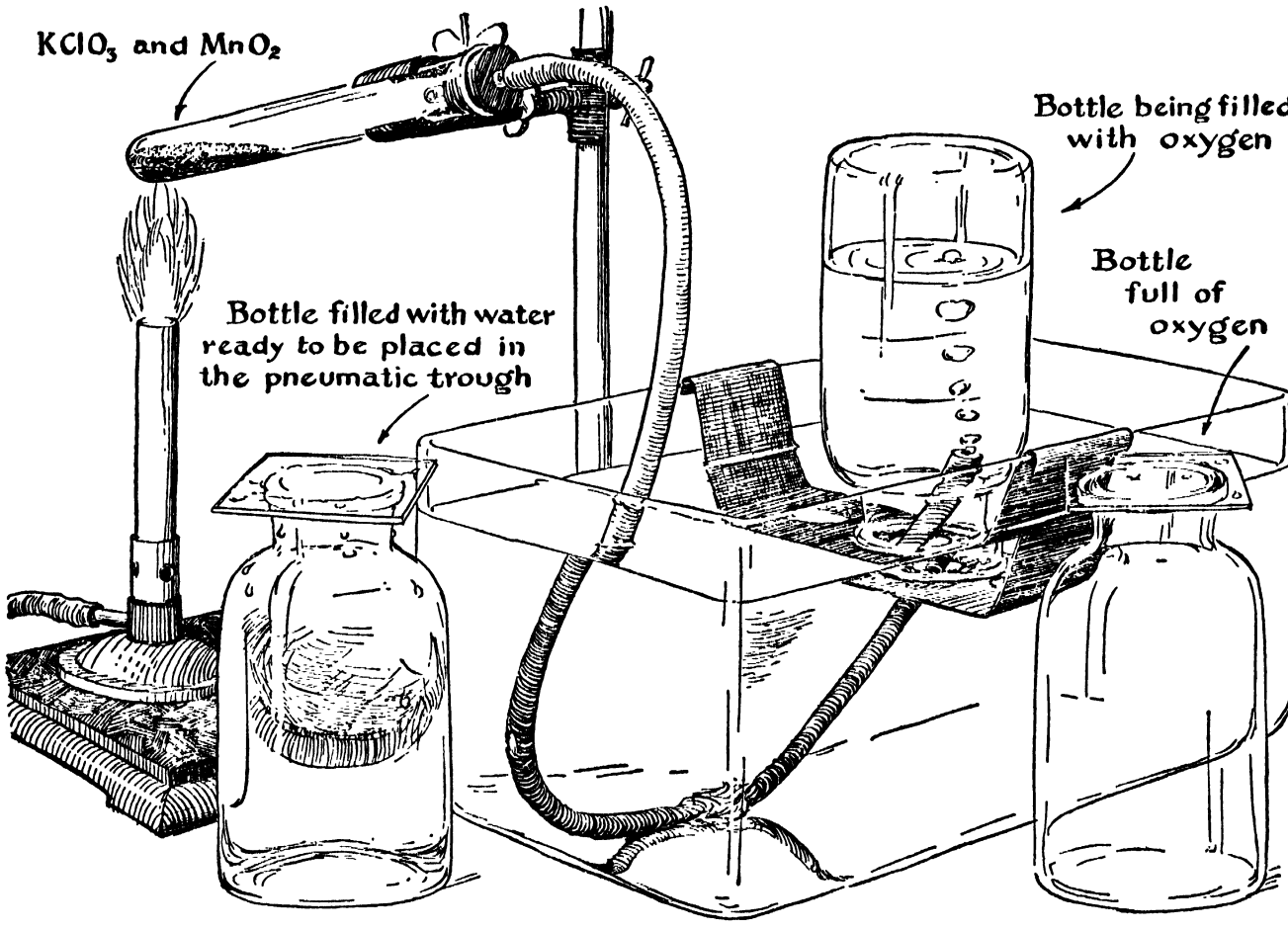


FIG. 8-1. The laboratory preparation of oxygen gas.

mainder of the mixture and connect the delivery tube. Fill six 250-ml wide mouth bottles with water and invert these in the pneumatic trough as needed. When all is ready, gently heat the potassium chlorate and manganese dioxide mixture just enough to maintain a moderate evolution of oxygen. First let a little of the gas escape into the air, to permit the generator to fill with pure oxygen, and then collect the six bottles of oxygen by displacement of water. Cover each with a glass square as soon as it is filled, and place it right side up on the table. Take the delivery tube out of the water before the generation of oxygen ceases or before you remove the flame. Why?

2. The Preparation of Oxides. Prepare oxides of the following elements by burning them in oxygen gas. Keep the bottles covered as much as possible. Number or label each to avoid confusion. Immediately after each combustion, add 30 to 50 ml of water, replace the cover, shake the bottle to dissolve the oxide formed, and set it aside for later use.

Magnesium. Ignite a 10-cm length of magnesium ribbon, held with the crucible tongs, and at once thrust it into a bottle of oxygen. (Do not injure your eyes by looking directly at the brilliant light.)

Calcium. Calcium metal is difficult to ignite, but burns very brilliantly. **Use caution.** *Your instructor may wish to demonstrate this.* Prepare a deflagrating spoon by lining it with a little asbestos paper or shreds, and ignite this to burn out any carbon. Heat a shaving of calcium metal, on the deflagrating spoon, quite hot. At once add a 2-cm length of magnesium ribbon as a fuse, re-heat the calcium and ignite the magnesium, and then quickly thrust this into a bottle of oxygen. See Figure 8-2.

As an alternative procedure, you may place a shaving of calcium in a crucible, and ignite it in the

air at the maximum temperature over a Bunsen burner for 15 minutes, then wash out the product with water into a beaker.

Iron. Add a little water to a bottle of oxygen, to form a protective layer on the bottom. Heat a little steel wool, held by the tongs, in the Bunsen flame to ignite it, and at once thrust it into this bottle.

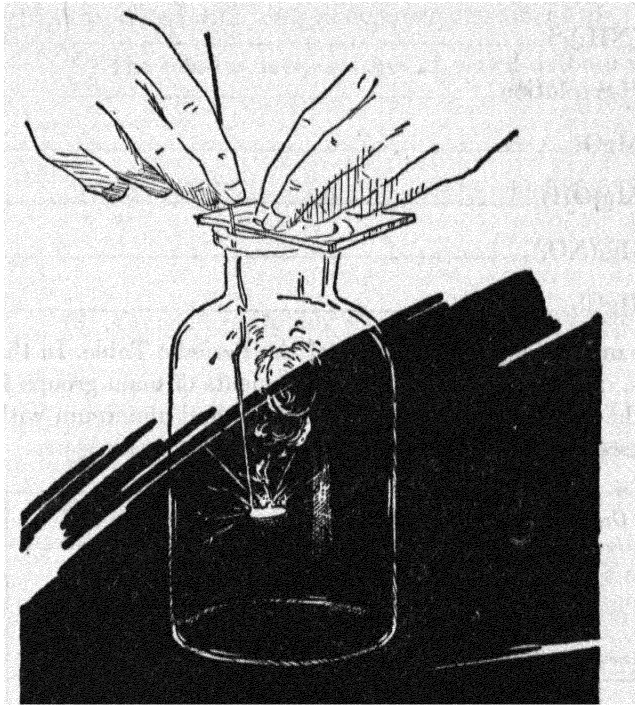


FIG. 8-2. The use of a deflagrating spoon to burn a substance in oxygen.

Carbon. Ignite a small piece of charcoal, held by the tongs or in a clean deflagrating spoon, and thrust the glowing charcoal into a bottle of oxygen.

Phosphorus and Sulfur. For each of these, clean and re-line the deflagrating spoon, and ignite it to burn out any combustible residue. Add a bit of sulfur, or phosphorus (use *red* phosphorus, no more in volume than half a pea). Ignite each of these over the burner, then thrust them into bottles of oxygen gas. In each case, after the combustion dies down, re-heat the deflagrating spoon to burn out all remaining phosphorus or sulfur.

3. Acids and Bases from Oxides. To each of the above bottles, in which the oxide of an element has been formed and to which water has been added to form a solution, add 1 to 2 ml of litmus solution.[1] Correlate the chemical character of the reaction product with the position of the element in the periodic table.

Other oxides. The above tests include representative elements from groups 2, 4, 5, 6, and the transition group 8, in the periodic table. To complete the series, let us examine an oxide or hydroxide from each of the other principal groups 1, 3, 7, and another example from group 5. (Why not include an element from group 0?)

The normal *alkali oxides*, as Na_2O, are difficult to obtain. Sodium peroxide forms when sodium burns in oxygen. The final reaction product with water, however, is the same as when Na_2O reacts with water. The extra "peroxide oxygen" is liberated as free oxygen gas. Compare the equations

$$Na_2O + H_2O \longrightarrow 2\ NaOH$$

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2.$$

Boil a very small amount of sodium peroxide in 5 ml of water in a 15-cm test tube for a moment to complete the above reaction. Cool the solution, and test it with litmus. Also note the slippery, soapy feeling of such a caustic solution. *Wash your fingers thoroughly.*

The *oxide of boron*, B_2O_3, is not readily available, and in some forms is very insoluble. Dissolve a small amount of boron hydroxide in 5 ml of hot water. Cool it, and test it with litmus. Decide which formula, $B(OH)_3$, or H_3BO_3, is preferable. How is the substance usually named?

To test the character of an *oxide of nitrogen*, connect a bent delivery tube to a 15-cm test tube which contains a small amount of metallic copper. Add 1 ml of water and 3 ml of concentrated HNO_3, then quickly close the tube, and bubble the evolved nitrogen dioxide through 5 ml of distilled water contained in a second test tube. Boil this solution a moment, cool it, and test it with litmus. The reaction is

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO.$$

The *oxides of chlorine* are all very unstable. Dissolve several drops of a 60% solution of a hydroxide of chlorine (whose formula may be written $ClO_3(OH)$ or $HClO_4$), in 5 ml of water, and test the solution with litmus. Decide which of the two formulas you regard as the preferable one.

[1] Ferric oxide or hydroxide is so insoluble that litmus has no effect on the solution. The effect may be somewhat feeble in one or two other cases, but should be sufficient to indicate the acidic or basic character of the hydroxide.

Drill on Formulas and Nomenclature

Note: Use this material, as needed, to help you learn how to write correct formulas and name compounds. Check your answers with your instructor, but they need not be handed in unless called for.

1. Name the following:

FeI_2	H_2CO_3
I_2	$CaCO_3$
$FeCl_3$	CaC_2
$Fe_2(SO_4)_3$	$SnSO_4$
FeS	$(NH_4)_2S$
NCl_3	H_2S solution
PCl_5	MgO
$La(NO_3)_3$	$Mg(OH)_2$
Mg_3N_2	$Hg_2(NO_3)_2$
SnS_2	$HgCl_2$

2. The spaces below represent portions of some of the main groups and periods of the Periodic Table. In the proper squares, write the correct formulas for the chlorides, oxides, and sulfates of the elements of main groups I, II, and III, respectively. Likewise, write the formulas of the compounds of sodium, calcium, and aluminum with the elements of main groups VI and VII. Two of the squares have been completed for you as examples.

	Group I	*Group II*	*Group III*	*Group VI*	*Group VII*
Period 2	$LiCl$ Li_2O Li_2SO_4		(omit the sulfate)		
Period 3				Na_2S CaS Al_2S_3	
Period 4					
Period 5					

3. Give the valence (including the + or − sign) for the italicized element or radical in each of the following formulas:

Cu_2O	$La_2(SO_4)_3$	NH_4OH	H_3PO_4	SnS_2	XO_2
$CuSO_4$	Ca_3N_2	SnO	$ZrCl_4$	$MgNH_4PO_4$	ZrZ_2

4. From the valences which you found for the hypothetical elements X and Z above, what would be the formulas of the following? Fill in the proper subscripts:

$H_{(\ )}Z_{(\ )}$ $X_{(\ )}(OH)_{(\ )}$ $(NH_4)_{(\ )}Z_{(\ )}$ $X_{(\ )}S_{(\ )}$ $X_{(\ )}(PO_4)_{(\ )}$ $X_{(\ )}Z_{(\ )}$

REPORT: Exp. 8

The Oxides of the Elements and the Periodic Table

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Preparation of Oxygen. Write the equation for the reaction by which you prepared oxygen.

_____

Compare (*a*) the heating of potassium chlorate alone, and (*b*) the heating of the same amount of potassium chlorate, mixed with some manganese dioxide, as to:

(1) The relative temperatures at which decomposition readily takes place:

(2) The relative amounts of oxygen which may be obtained:

(3) Any changes taking place in the manganese dioxide:

(4) The name applied to a substance used like manganese dioxide is used in this reaction:

_____

2. The Preparation of Oxides. Describe any changes occurring during the reaction of each element with oxygen, and any distinctive characteristics of the products formed. Write the equation for the reaction, in each case.

Magnesium:

Calcium:

Iron:

Carbon:

Phosphorus:

Sulfur:

3. The Reaction of Oxides with Water. On the line corresponding to its periodic group, write the formula of each oxide (or hydroxide, if the oxide was not available) which you studied in this experiment. Indicate the reaction to litmus of its water solution, and write the equation for the formation of the acid or base.

Group	*Formula of Oxide*	*Reaction to Litmus*	*Equation for Reaction, if Any*
I			
II (two elements)			
III			
IV			
V (two elements)			
VI			
VII			
VIII (transition)			

Comment on the acidic or basic character of the oxide of an element, as compared to its position in the periodic table.

Application of Principles. From the position of the elements in the periodic table, write the formulas of three other oxides, which, in each case, would behave as:

Acidic oxides_____ Basic oxides_____

Write the formulas of the anhydrides of:

H_2SO_3_____ $Ba(OH)_2$_____ HNO_2_____ H_2CO_3_____

H_2SO_4_____ H_3PO_4_____ HNO_3_____ $Al(OH)_3$_____

Complete and balance the following equations:

____ HCl + ____ $Ba(OH)_2 \longrightarrow$

____ MgO + ____ $H_2SO_4 \longrightarrow$

____ Al + ____ $HCl \longrightarrow$

____ Na_2O + ____ $CO_2 \longrightarrow$

____ $Ca(OH)_2$ + ____ $H_3PO_4 \longrightarrow$

____ Na_2O + ____ $P_2O_5 \longrightarrow$

The Chemistry of Nitrogen and Ammonia 9

College Chemistry, Chapters 5, 15

Review of Fundamental Concepts

We have noted already, in Experiment 5, that free nitrogen gas is quite inactive at room temperature. This is in accord with its relative abundance in the atmosphere, and in accord with the scarcity of nitrogen compounds.

Impure nitrogen, which still contains the inert gases, principally argon, may be obtained from the air by any reagent which will remove the oxygen. This may be accomplished by the use of phosphorus, pyrogallol or metallic iron as in Experiment 5, by the passage of air over hot metallic copper, or commercially by the fractionation of liquid air. Pure nitrogen, as we shall learn in this experiment, can be obtained by the chemical reaction of some of its compounds. We study ammonia this early in the course, because of its constant use as a laboratory reagent. The oxides and acids of nitrogen will be considered in Experiment 22.

Experimental Procedure

Special supplies: Three 250-ml wide mouth bottles, 3 glass plates, pneumatic trough, deflagrating spoon, asbestos fiber, wooden splints.

Chemicals: NH_4Cl, $NaNO_2$, Mg (ribbon), S, P (red), $Ca(OH)_2$, CuO, litmus solution, 1 *F* NH_4Cl.

1. The Preparation of Pure Nitrogen. Assemble the apparatus as illustrated in Figure 9-1. Prepare to collect three bottles of the gas by displacement of water. Place 4 g of ammonium chloride (NH_4Cl), 5 g of sodium nit*rite* ($NaNO_2$), and 30 ml of water in the flask.

Since the reaction is an exothermic one (releases energy as it proceeds), be prepared to loosen the clamp and immerse the generator in the pneumatic trough to cool it, in case the reaction becomes too

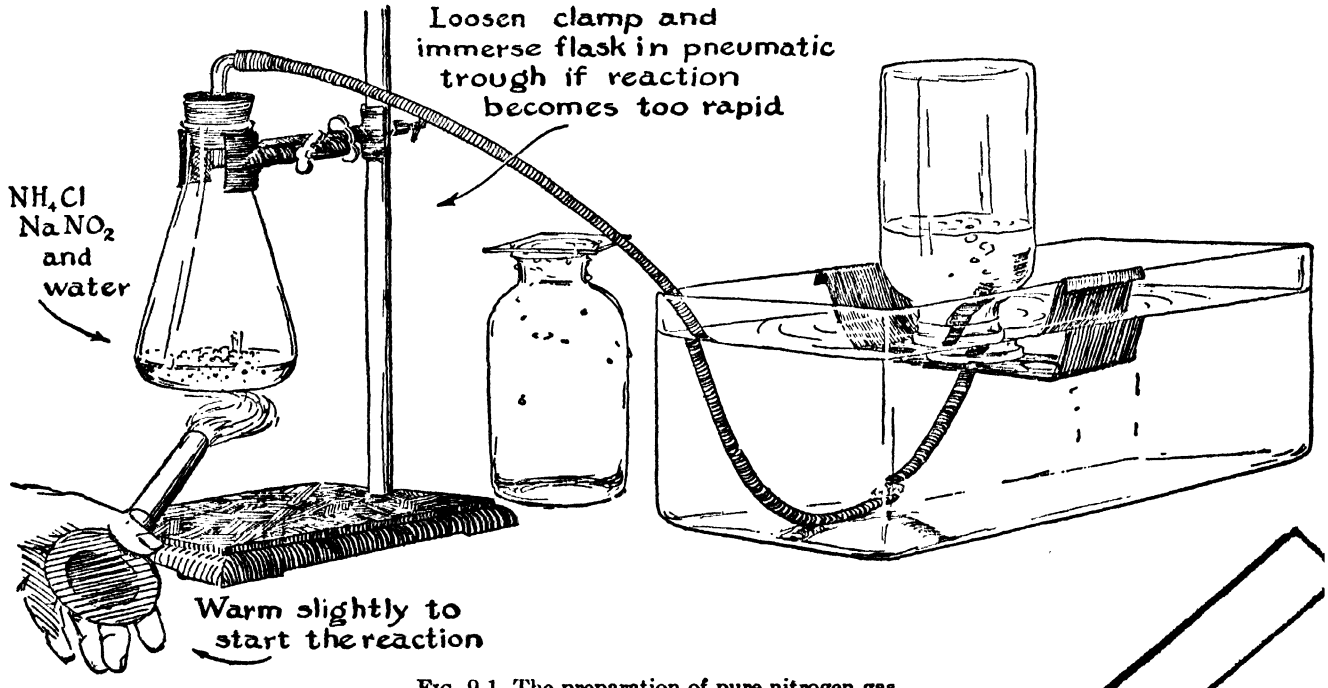


FIG. 9-1. The preparation of pure nitrogen gas.

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rapid. Warm the flask just enough to start the reaction, *then withdraw the flame.* Permit the first gas generated (which will be mixed with the air of the flask) to escape, and then collect three bottles of nitrogen.

Properties of Nitrogen. Observe the usual physical properties of the gas, as color, odor, solubility in water, etc. Test the ability of nitrogen gas to burn or to support combustion by inserting a burning splint into a bottle of the gas. Try, also, substances which undergo a more vigorous reaction in the air, as a piece of magnesium ribbon, and a little sulfur or phosphorus on a deflagrating spoon which has been lined with asbestos.

2. The Preparation of Ammonia. (a) *Formation.* Place a mixture of several grams each of ammonium chloride and calcium hydroxide in a 15-cm test tube, and warm it. Note the odor. Also, expose a piece of moist, red litmus to the vapors.

(*b*) *Preparation.* A more convenient method for our use is as illustrated in Figure 9-2. Assemble this apparatus. The generator flask contains about 30 ml of concentrated ammonium hydroxide solution. The drying tube should be well filled with fresh, anhydrous, 4-mesh calcium chloride ($CaCl_2$), with loose plugs of cotton at either end. Note the relative length of the delivery tubes in the collection bottles, and in the test tube. Place about a gram of cupric oxide in the test tube. In the receiving flask, place about 35 ml of water, and adjust the delivery tube so that it almost touches the water.

To generate ammonia, gently warm the flask just enough to maintain a moderate rate of evolution of bubbles in the final receiving flask. After the gas has been generating a minute or two, heat the cupric oxide in the test tube, with a second burner. When ammonia reaches the hot cupric oxide, two changes should be obvious to you. When the change in the cupric oxide is complete, let the test tube cool, but continue generating ammonia for a few minutes more to form a solution in the receiving flask, and then withdraw all heat and permit the operation to subside.

3. Properties of Ammonia. (a) *Reducing Action.* You have already carried out this operation during the preparation of the gas. Record your observations of this in the report sheet.

(b) *Behavior on Burning.* Disconnect the two bottles of ammonia from the collection system, and cover them at the same time with a glass plate so as to lose as little ammonia as possible. Thrust a burning splint into one bottle of ammonia. Note whether the gas is inflammable, and whether it will support combustion.

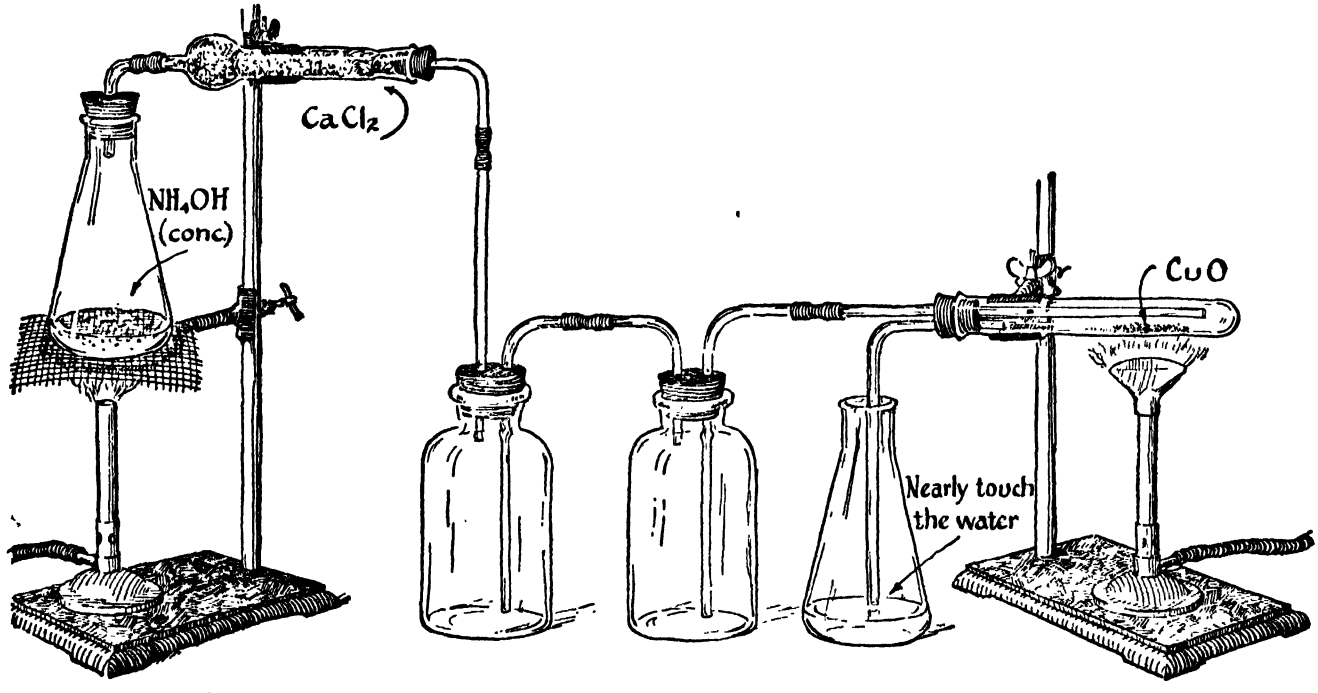


FIG. 9-2. The preparation of ammonia gas.

(c) *Behavior with Water.* Place about 300 ml of water in a 400-ml beaker, add 1 to 2 ml of litmus solution and 1 ml of dilute HCl to turn the litmus red. Now immerse the second bottle of ammonia gas, mouth down, into the beaker of acidified water, and observe the results.

Test 5 ml of the solution of ammonia gas in water (from the flask) with red litmus. Boil this solution a few minutes, then test the residual solution again with red litmus. If necessary, repeat the boiling.

In order to compare this behavior with that of a solution of hydrogen chloride, boil 5 ml of dilute hydrochloric acid solution as you did the ammonia, and test the residue each time with blue litmus.

(d) *Volatility.* Place not over 1 g of ammonium chloride (NH_4Cl) in an evaporating dish, and heat it strongly as long as any action occurs.

Vary this procedure by placing a little solid NH_4Cl in a dry 15-cm test tube, and then place a loose plug of asbestos fiber about half way down the tube. Moisten a piece each of red and blue litmus paper, and attach them to the inside wall of the upper part of the test tube. Heat the NH_4Cl and explain any change in the litmus in terms of the relative rates of diffusion of the gases present.

(e) *Test for Ammonium Ion.* To determine the conditions necessary for a positive test, place 1 ml of 1 *F* NH_4Cl in an evaporating dish, and cover this with a watch glass, to the under side of which is attached a moist piece of red litmus paper. Warm the dish slightly (do not boil the solution) to discover whether ammonia gas will be liberated on warming ammonium salt solutions. After you observe the result, add 1 ml of 6 *F* NaOH to the solution, replace the watch glass, and watch for any change in the litmus. Warm again if necessary. (The NaOH solution is not volatile. Convince yourself of this by repeating the above test, without the NH_4Cl present.)

REPORT: Exp. 9

The Chemistry of Nitrogen and Ammonia

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Preparation and Properties of Nitrogen

Write the equation for the reaction by which you prepared nitrogen gas:

_____

Summarize your observations on the physical properties and general chemical behavior of nitrogen gas.

Recall the reaction of nitrogen gas on very hot, active metals, by re-writing here the equation for its reaction with magnesium, and the equation for the reaction of the product with water.

_____

_____

2, 3. The Preparation and Properties of Ammonia

Write the equation for the reaction which occurs on warming a mixture of solid ammonium chloride and calcium hydroxide.

_____

(1) Write the equation for the reaction of ammonia with cupric oxide. (The nitrogen is liberated as N_2 gas.)

_____

In this reaction, which substance is the

Reducing agent?_____ Oxidizing agent?_____

(2) Does ammonia support combustion?_____ Does ammonia burn?_____

(3) When ammonia is dissolved in water, what evidence is there of any chemical action?

What is the equation for the change that takes place:

When ammonia dissolves in water?_____

When a solution of ammonia is boiled?_____

Compare the behavior which you observe on boiling ammonia solution, and on boiling hydrogen chloride solution.

(4) Comment on the volatility of ammonium salts.

Write the equation for the reaction that takes place when solid ammonium chloride is heated.

Interpret the change in the litmus paper when solid ammonium chloride was heated in a test tube containing an asbestos fiber plug.

(5) Compare the results of warming an ammonium chloride solution, first without, and then with, the addition of sodium hydroxide solution.

What is the equation for this reaction?

Outline the procedure you would follow in the testing of a commercial product, for example a fertilizer, for the presence of ammonium salts.

Equations

Write the equation for:

(1) The formation of white fumes when concentrated HCl solution is brought in contact with ammonia gas.

(2) The neutralization of ammonium hydroxide solution by hydrochloric acid.

(3) The neutralization of ammonium hydroxide by sulfuric acid.

The Determination of the Formula of a Compound from Experimental Data — 10

College Chemistry, Chapter 8

Review of Fundamental Concepts

Units of Quantity as Used in Chemistry

The terms, **atomic weight** and **molecular weight,** refer to the weights of the atoms and molecules of the various elements and compounds, respectively, relative to the mass of an oxygen atom which is arbitrarily taken as 16.0000. Because atoms and molecules are the units in which chemical reactions occur, and since they are such minute particles that it is impossible to deal with them individually, for practical purposes we use larger unit quantities *which contain equal numbers of atoms or molecules per unit.* These are defined in the following paragraphs.

The **gram-atomic weight** (usually referred to as a **gram-atom**) of an element is defined as a weight in grams numerically equal to the atomic weight of the element. Thus, 12 grams of carbon (atomic weight 12) is one gram-atom of carbon. Likewise, a quantity of sulfur (atomic weight 32) which weighs 64 grams, is two gram-atoms of sulfur. A **chemical symbol,** as C, or S, represents in a rather loose sense simply the name of the element. Very frequently the symbol is used to designate one atom of an element. In chemical calculations we must use a large enough unit to be practical, in which case a symbol represents one gram-atom of an element. Thus the symbol C stands for 12 grams of carbon, and O for 16 grams of oxygen.

The **gram-molecular weight, or mole,** of a substance, likewise, is defined as a weight in grams numerically equal to the molecular weight of the substance, *or* is the sum of the gram-atomic weights of the constituent elements as represented by the formula of the substance. Thus one mole of carbon disulfide (1 CS_2) contains 1 C (12 grams) and 2 S (2 × 32 grams) and weighs 76 grams.

It is important to remember that one gram-atom of any element, or one mole of any compound, contains the same number of individual atoms or molecules, respectively. This is Avogadro's number, 0.6023 × 10^{24} particles. Thus 12 grams of carbon (1 C), 207.2 grams of lead (1 Pb), 76 grams of carbon disulfide (1 CS_2), and 18 grams of water ($1H_2O$), each contains this same number of atoms or molecules, respectively.

The gram-formula weight. In many substances, such as the salts (NaCl, $CuCl_2$ for example), the units of crystal structure are not molecules, but are ions—the same ions as those formed when the substance dissolves to form a solution. Strictly speaking, then, we may say there is no such thing as a particle of "NaCl," or "$CuCl_2$" in which these formulas represent a single molecule. Such formulas express merely the simplest proportion of the constituent ions. The term "gram-molecular weight," or "mole," although frequently used in such cases, is thus a misnomer. Throughout this manual we shall use the term "*gram-formula weight,*" abbreviated to *gfw,* to express the weight in grams as represented by the formula given. The term "mole" will be reserved for substances in which the molecular species is known and represented by the formula used.

Study Figure 10-1 to further clarify the meanings of the terms gram-atom, mole, and formula weight. Some examples will help you to learn to think in terms of chemical units of quantity. Remember that the gram-atomic weight means grams per gram-atom, and that the gram-molecular weight means grams per mole. Thus, the defining equations are:

$$(1)\quad \text{g at wt} = \frac{\text{grams}}{\text{g at}}, \text{ and } (2)\quad \text{g mol wt} = \frac{\text{grams}}{\text{moles}}.$$

For example, to calculate the weight of ten gram-atoms of sulfur, we transpose (1) thus, g at × g at wt = grams, and write

$$10 \text{ g at S} \times 32 \frac{\text{g}}{\text{g at}} = 320 \text{ grams S}.$$

Conversely, for example, to calculate the number of moles in 38 grams of carbon disulfide, we transpose (2) thus, $\frac{\text{grams}}{\text{g mol wt}} = \text{moles}$, and write

$$\frac{38 \text{ g } CS_2}{76 \text{ g/mole}} = 0.500 \text{ moles } CS_2.$$

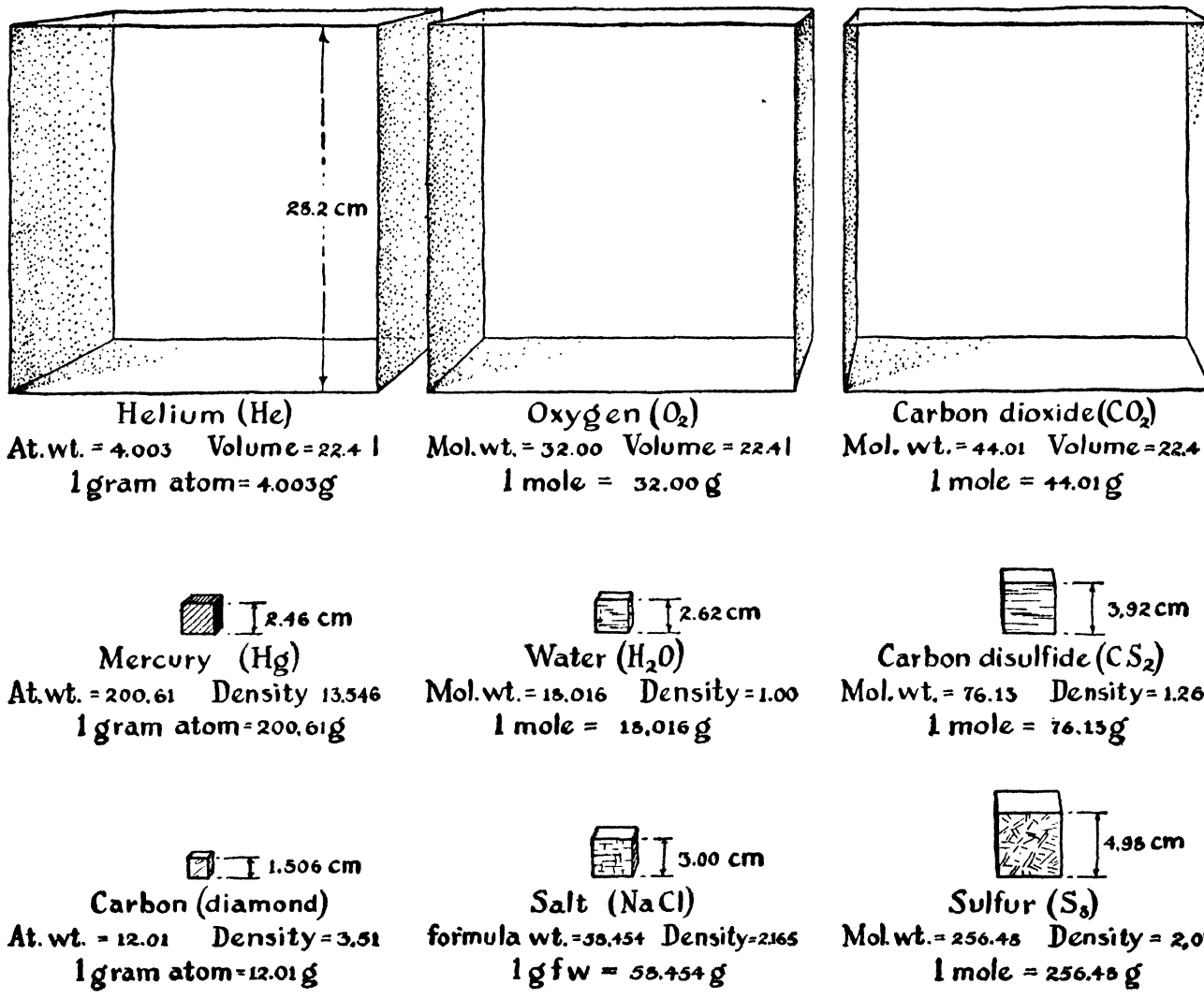


FIG. 10-1. Gram-atoms, moles, and formula weights. Although the weight in grams is very different for different substances, the number of atoms or molecules per gram-atom or mole is the same in all cases, namely the "Avogadro number."

The Calculation of the Formula from the Data

While experimental data express the relative weights (in grams) of the constituent elements, a formula expresses the relative number of gram-atoms of each constituent element. Furthermore, this number of gram-atoms is always capable of being expressed as an integral ratio of small whole numbers. (This is a consequence of the atomic theory.) We need therefore only to calculate the number of gram-atomic weights of each element from the number of grams of each in any given amount of the compound, and find the simplest integral ratio of these.

For example, in finding the formula of a chloride of copper, it was analyzed and 5.00 grams of it was found to contain 2.35 grams of copper and 2.65 grams of chlorine. We may calculate the respective number of gram-atoms of each as follows:

$$\frac{2.35 \text{ g Cu}}{63.5 \text{ g/g at}} = 0.0370 \text{ g at Cu}$$

$$\frac{2.65 \text{ g Cl}}{35.5 \text{ g/g at}} = 0.0746 \text{ g at Cl.}$$

Dividing each of these numbers by the smaller one, we have a ratio of 1 Cu to 2.02 Cl. The simplest formula is, therefore, $CuCl_2$.

For some substances, where there is a definite molecule as the unit of structure of the substance, we can write a definite correct "molecular formula." The formula of hydrogen peroxide is H_2O_2,

not HO, because the molecular weight of this substance has been determined experimentally, and has a value of 34, not 17. Note that the two formulas correspond to the same percentage composition. The determination of molecular weights is considered in Experiment 13.

In this experiment a weighed sample of silver is dissolved in nitric acid (HNO_3) and precipitated as silver chloride. From the weight of silver and the weight of silver chloride the percentage composition of the silver chloride may be calculated. The formula may then be calculated as in the case of $CuCl_2$ above.

Experimental Precision vs. Significant Figures

This experiment and the following one present the first strictly quantitative experiments, in which you are expected to carry out your weighings with care and with as great a precision as the data justify. Before going ahead with the experimental procedure, read the section under "Laboratory Manipulations" on **The Care and Use of the Balance,** page xx. Follow any special instructions which your instructor gives you.

When experimental data are recorded and when calculations involving these data are made, it is very important to record the answer in such a way as to convey the proper estimate of the precision of measurement. Study Section B in Appendix I on **Significant Figures,** and answer the questions in the report sheet on this point.

Experimental Procedure

Special supplies: Analytical weights.

Chemicals: Sample of pure silver (your preparation from Exp. 6, if pure).

Heat, cool, and weigh (to 0.001 g if possible) a clean evaporating dish. (It is worth while to keep a record of the individual weight denominations used in each weighing, on a separate sheet, as a check against errors in counting weights.) Enter this weight in the report sheet, and then carefully transfer to the dish from 0.5 g to 1.0 g of pure dry silver metal. (Use your preparation from Experiment 6, if it is pure.) Again weigh the dish with its contents, and record this weight. Place the dish on a wire gauze supported on an iron ring. Add 3 ml of dilute nitric acid, and cover the dish with a watch glass. If action does not begin immediately, warm the dish momentarily, but avoid any loss of solution by spattering. When all the silver has been dissolved, remove the watch glass. Rinse the under side of the watch glass into the dish, by holding it edgewise over the dish, and spraying it with distilled water from your wash bottle, as illustrated by Figure 10-2.

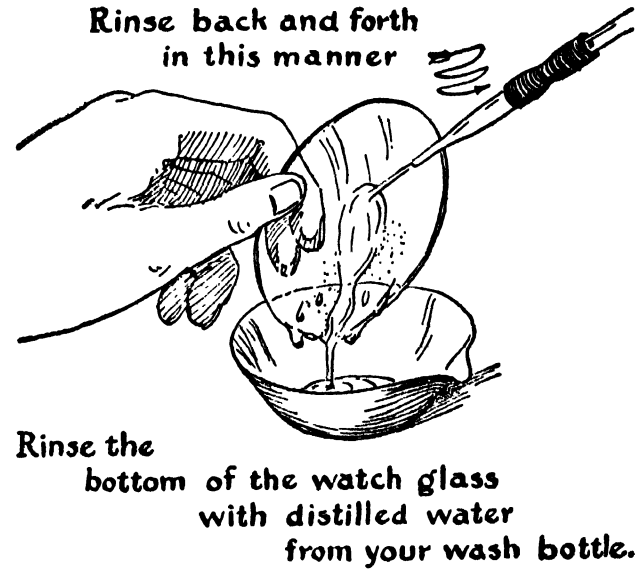


FIG. 10-2. The technique of rinsing a watch glass.

Now add 3 to 5 ml of dilute hydrochloric acid to the solution, and evaporate the mixture very gently by placing the wire gauze with the dish on it at a height of two or three inches above a low (¾") flame. Use great care to avoid any spattering of the precipitate. (See Fig. 10-3.) As the mixture approaches dryness, it may be wise to transfer the dish to the top of a beaker of boiling water (Fig. 10-4) to complete the evaporation. When the precipitate is apparently dry, again heat the dish cautiously directly on the wire gauze, wafting the flame back and forth under the dish until it is quite hot and thoroughly dry. Do not melt the residue, but be sure all vapors of water and acid have ceased to be evolved. Cool and weigh the dish and residue, being careful to avoid all unnecessary handling of the dish, as it will reabsorb moisture

from the hands. Record the weight. From these data, calculate the formula of silver chloride, as outlined in the report sheet.

Optional experiments, for students who have the time and interest to do further work. Some details of experimental procedure are left to the student to devise. Also, prepare a suitable report sheet for the entry of all data *before they are obtained.*

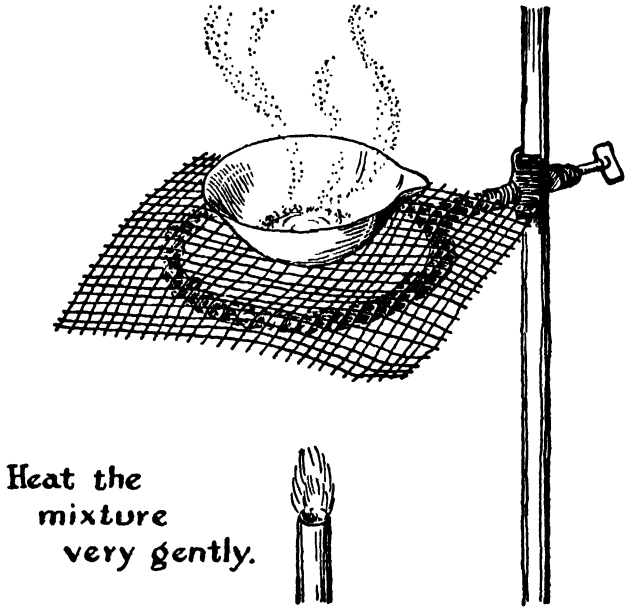


FIG. 10-3. The evaporation of liquid contained in an evaporating dish. The liquid may simmer very gently, but you should avoid boiling it vigorously.

(1) *A sulfide of copper.* First heat a clean crucible, supported on a clay triangle, for a moment. Cool the crucible and weigh it accurately, without the cover. Add about 2 grams of copper, as wire or coarse turnings, and press this well down in the crucible. Weigh this accurately. Add 1 to 1.5 g of powdered sulfur. Avoid a large excess, as it takes longer to burn out. Now place the crucible, with lid in place, under the fume hood, and heat it moderately to form the compound and vaporize excess sulfur. Also play the flame around the sides and top of the crucible and lid. *Do not remove the cover while the crucible is hot,* as atmospheric oxidation would take place. Avoid heating longer than necessary. When sulfur ceases to burn around the lid, let the crucible cool, and examine the conten for vaporization of all excess sulfur (a black stain will remain). Finally weigh the crucible and contents. Calculate the formula of the compound.

(2) *A chloride of lead.* The same general procedure as for silver chloride may be used; use about 0.5 g of lead, which has been cut in thin shavings to facilitate solution. After accurately weighing the dish, and the dish plus the lead, add about 10 ml of

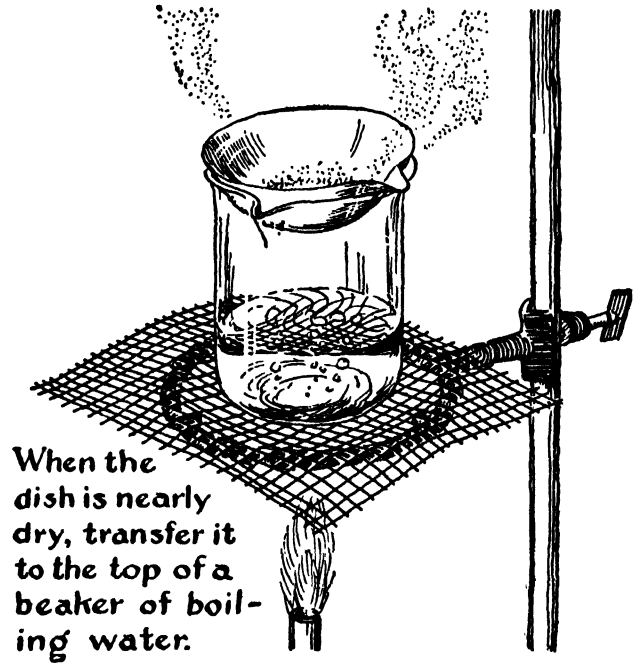


FIG. 10-4. The evaporation of a liquid over a water bath.

conc nitric acid. Cover the dish with a watch glass, and warm it occasionally as needed to promote solution of the metal, which is *very* slow. It may be necessary to leave this over night. When the metal is all dissolved (solid lead nitrate will remain), use a water bath (Fig. 10-4) to evaporate most of the acid. Then add 5 ml conc hydrochloric acid to convert the salt to lead chloride. Evaporate just to dryness, and again moisten the salt with a few drops of hydrochloric acid, and evaporate. Finally heat with the bare flame, very gently to avoid spattering, until all acid vapors are gone and the salt is thoroughly dry. Avoid a high temperature. Let the dish cool, and weigh it. Calculate the formula of the compound.

REPORT: Exp. 10

Percentage Composition and Formula of a Compound

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Data[1]	*1*	*2*
Weight of dish and silver chloride	g	g
Weight of dish and silver	g	g
Weight of dish, dried, at start	g	g
Gram atomic weight of silver[2]	g	g
Gram atomic weight of chlorine	g	g

	Calculations[3]	*1*	*2*
Weight of silver chloride		g	g
Weight of silver		g	g
Weight of chlorine		g	g
Number of gram atoms of silver in weight taken[4]		g at	g at
Number of gram atoms of chlorine in weight taken		g at	g at
Simplest integral ratio between gram atoms of Ag and Cl (from your data)			
Formula of the compound (from your data)			
Theoretical % silver in compound, from its formula		%	%
Experimental % silver in compound (from your data)		%	%
Percentage error		%	%

Approval of Instructor_____

[1] Data are listed in the order most convenient for subtraction, rather than in the order in which they are obtained. Columns are provided for two samples, or for repetition of the experiment, as desired.

[2] An atomic weight table is given inside the cover of the manual.

[3] Indicate the method of all calculations in the spaces provided, but do not carry out the actual multiplication, division, and so forth, here. As soon as you have finished your calculations, report the result to your instructor.

[4] Calculate the number of gram atoms to 3 significant figures, not just to "3 decimal places."

Significant Figures, Problems

"How far shall I carry out my figures?" To learn the principles governing this common problem of the beginning science student study Appendix I, Sec. B, on "Significant Figures," and answer the following questions.

Note: In general, in this course, calculate the answers to problems to three significant figures (slide-rule accuracy), except where the data given indicate that greater or less precision should be indicated in the answer.

Answers

1. How many significant figures are there in each of the numbers (a) 35.6, (b) 3.56, (c) 742.0, (d) 7.0058, (e) 0.0058, (f) 0.6023×10^{24}?

1 (a)_____(b)_____

(c)_____(d)_____

(e)_____(f)_____

2. To a flask the following volumes of water were added: 4.27 ml, 101 ml, and 36.4 ml. The total volume of water should be recorded as:

2_____

3. In finding the percentage of silver in silver chloride, the weight of silver was 0.552 gram. The weight of chlorine was 0.178 gram. The percentage of silver should be recorded as: (a) 70%, (b) 75%, (c) 75.6%, (d) 75.62%, (e) 75.616%, (f) 75.6164%.

3_____

4. How many gram atoms in one pound (454 g) of

magnesium? . . . 4_____

copper? . . . . _____

gold? . . . . . _____

5. How many moles in one pound (454 g) of

sugar, $C_{12}H_{22}O_{11}$? . . 5_____

oxygen? . . . . _____

water? . . . . . _____

6. Methanol (wood alcohol) contains 37.5% carbon, 12.5% hydrogen, and 49.9% oxygen. What is its formula? *Note:* A 100-gram sample of methanol contains 37.5 g of carbon, 12.5 grams of hydrogen, and 49.9 grams of oxygen.

6_____

7. A compound of bismuth and chlorine is found to consist of 3.15 g of Bi and 1.60 g of Cl. What is the formula?

7_____

The Atomic Weight of Magnesium 11

College Chemistry, Chapter 8

Review of Fundamental Concepts

Exact atomic weight determinations constitute some of the most fundamental of all scientific data. They are determined with the most painstaking care, with many elaborate precautions, and with the finest of balances and other equipment. As you know, they are based on the weight of a given element which combines with, or is equivalent to, one gram atom of oxygen, which is arbitrarily assigned a value of 16.0000 g. Since oxygen has a valence of two in most of its compounds with other elements, one half of its gram-atomic weight, namely 8.0000 g, is often taken as the standard of reference in determining the relative combining weights of other elements. The "combining weight" thus obtained, or some simple integral multiple of it, will be the true atomic weight of the given element.

The factor by which this equivalent or combining weight must be multiplied to give the correct atomic weight can be decided by several methods, as outlined in your text. At the present time the known position of the element in the periodic table, and its atomic number as experimentally determined by the Moseley method, give unmistakable evidence of the approximate value of its atomic weight. In earlier days, as first discovered by Dulong and Petit, an experimental determination of the specific heat of the element enabled chemists to obtain approximate atomic weight values.

For some elements, direct measurements by comparison with oxygen are inaccurate or impractical. For these, "secondary standards"—other elements whose atomic weights have been most carefully obtained—are used. The elements silver, chlorine, and bromine are such standards. Note that their atomic weights are known to *five or six significant figures.*

The procedures of this experiment are quite simple. The precision you are able to attain will be limited primarily by your technique and by the limitation of the balance you use. If a balance equipped with a rider (which enables you to weigh to 0.001 g) is not available, estimate the nearest thousandth of a gram as near as you can by the technique illustrated by Figure i-17, Page xxii.

Experimental Procedure

Special supplies: Analytical weights.

Chemicals: Mg ribbon. Other metals as needed in wire or thin sheet form, for optional experiments.

Heat, cool, and weigh (to 0.001 g if possible) a clean crucible[1] and lid. (It is worth while to keep a record of the individual weight denominations used in each weighing, on a separate sheet, as a check against errors in counting weights.) Enter this weight in the report sheet. Now add to the crucible about 0.5 to 0.8 g (about 3 feet) of magnesium ribbon, which has been crumpled so as to fit into the lower part of the crucible and still allow good exposure to the air. Do not pack it down too tightly. Again weigh the crucible and lid with its contents, and record the weight. Place the crucible on a clay triangle over the burner. Adjust the lid to allow a small amount of ventilation (see Figure 11-1), and heat to oxidize the magnesium. *Avoid heating the crucible too rapidly*, or with too much ventilation, in order to prevent an appreciable amount of "smoke" (magnesium oxide) from escaping. You can also regulate the rate of burning by using your crucible tongs to adjust the position of the crucible lid.

Continue the heating until oxidation is about complete. This you can determine by lifting the lid slightly with your crucible tongs and seeing whether now the contents of the crucible do not glow brightly. When you are sure, remove the lid to one side, to provide an abundance of air, and continue the heating at the maximum temperature

[1] Since this experiment causes damage to the glaze of the crucible, you may use old crucibles. Concentrated HCl will afterwards remove any dark stain you may find.

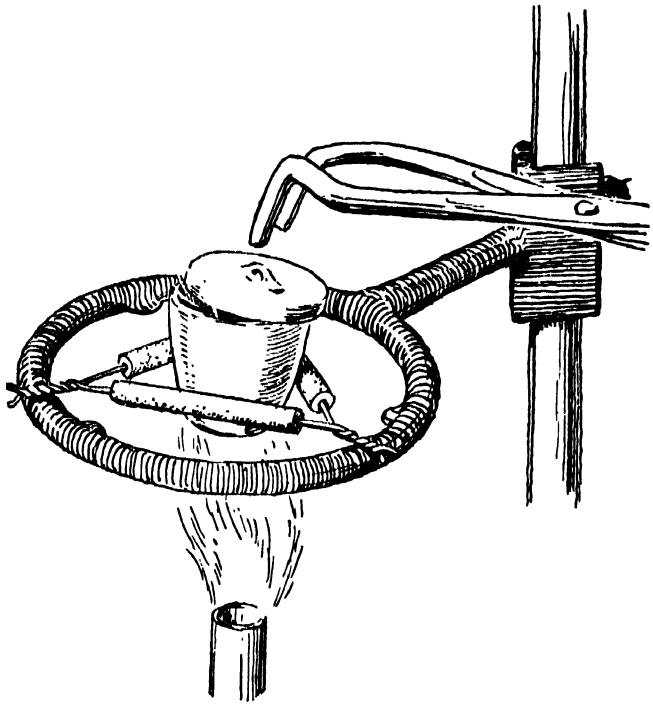


FIG. 11-1. The rate of oxidation of magnesium may be controlled so as to avoid smoke, by regulating the amount of ventilation and the size of the flame.

for another five minutes.

After the crucible becomes cool, gently crush into a powder the product that has been formed, using the smooth end of a glass stirring rod. Make the powder lie compactly on the bottom of the crucible for thorough reheating in subsequent operations. Any powder adhering to the stirring rod may be tapped back into the crucible without loss. (A camel's hair brush is often used to loosen such powder from the rod. Your instructor may assist you with this operation if necessary.)

Now moisten the product with 10 to 15 drops of distilled water from a medicine dropper. This will change the magnesium nitride, some of which was formed at the same time, into magnesium hydroxide. Warm this and note the odor of ammonia, which has also been formed.

Finally, reheat the crucible with the lid fully in place, at first gently to avoid spattering, then at full heat (to give the crucible bottom a good red heat) for at least 5 to 10 minutes. This is necessary to achieve complete decomposition of the magnesium hydroxide.

The equations for the reactions are:

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

$$3\ Mg + N_2 \longrightarrow Mg_3N_2$$

$$Mg_3N_2 + 6\ HOH \longrightarrow 3\ Mg(OH)_2 + 2\ NH_3$$

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

When the crucible, lid, and contents are completely cool, weigh[1] them accurately and record the weight.

From these data you can calculate the combining weight of magnesium (the weight of the metal that combines with 8.0000 g of oxygen). From the known position of magnesium in Group II in the Periodic Table, and from its atomic number, you can decide by what integral factor you should multiply its combining weight to get the true atomic weight.

Optional Experiment. *The Atomic Weight of Tin.* An oxide of tin may be formed by adding about 10 ml of concentrated nitric acid to a weighed sample of tin metal, in a weighed evaporating dish. After complete disintegration of the metal, evaporate the liquid very carefully (see Figures 10-2, 10-3, and 10-4 in the preceding experiment) so as to avoid spattering. Finally ignite the residue at the maximum temperature of the burner for at least 20 minutes, making certain that all portions of the dish become very hot, so that the metastannic acid first formed is completely decomposed to the oxide. Cool the dish and weigh it.

From these data you can calculate the combining weight of tin (the weight of the metal that combines with 8.0000 g of oxygen). From the known position of tin in the Periodic Table (Group IV elements characteristically have a valence in their compounds of two or four), and from its atomic number, you can decide by what integral factor you should multiply its combining weight to get its true atomic weight.

---

[1] Weigh the MgO within about 20 minutes after it is completely cool, as it tends to regain moisture from the air and form $Mg(OH)_2$ again. If excessive time elapses, reheat and cool the crucible before weighing it.

REPORT: Exp. 11

The Atomic Weight of Magnesium

Name _____

Date _____

Section _____

Locker Number _____

Data	*1*	*2*
Weight of crucible, lid, and magnesium oxide	g	g
Weight of crucible, lid, and magnesium	g	g
Weight of crucible and lid	g	g

Calculations

Weight of magnesium	g	g
Weight of oxygen	g	g
Combining weight of magnesium, from data	g	g
Atomic weight of magnesium, from data	g	g
Percentage error	%	%

Evaluation of Experimental Work

1. A student completes his experiment a half hour before the close of the laboratory period. The first thing he should do is: (a) clean and lock his locker, (b) make his calculations and report his answer, (c) go home, (d) consult his neighbor's calculations.
2. A student's magnesium oxide spatters on drying out the added water, and some is lost. He should: (a) estimate how much was lost and make allowance for it in his answer, (b) repeat the experiment with a new sample, (c) repeat the experiment with a new sample after devising a method to prevent spattering.
3. A student weighs his magnesium to four significant figures, and the weight of the magnesium oxide obtained from it to two significant figures. His experimental results should be reliable to (a) 2, (b) 3, (c) 4, (d) 6 significant figures.
4. Assuming that you used approximately 0.5 gram of magnesium, and that your balance is capable of weighing to 0.001 g, to how many significant figures are you justified in expressing your answer? Explain your answer:

5. Suppose you did not bother to transform the impurity of magnesium nitride (Mg_3N_2) in your sample to magnesium oxide (MgO). Would this cause your value for the atomic weight of magnesium to be: (a) too low, (b) too high, (c) unaffected by the impurity? Explain your answer:

Answers

1 _____

2 _____

3 _____

4 _____

5 _____

Problems

Answers

1. Calculate the percentage composition of the elements in common salt, NaCl. (Use such atomic weight values as are necessary to give the correct answers to 3 significant figures.)

1_____

2. Ethyl chloride is composed of 37.2% carbon, 7.8% hydrogen, and 55.0% chlorine. What is its simplest formula?

2_____

3. A sample of an oxide of lead, which weighs 2.50 g, is reduced by heating in a stream of hydrogen gas, thus forming 2.27 g of lead. What is the simplest formula of this oxide?

3_____

4. The hemoglobin of the blood, a protein, is known to contain 0.335% iron. There must be at least one atom of iron per molecule of the protein. On this basis, what must be the minimum weight of a mole of hemoglobin?

4_____

5. (a) If the specific heat of element E has been determined and has a value of 0.0508 cal/g deg, what is the approximate atomic weight of the element? (b) If 1.218 g of this element, when combined with oxygen, gives a total weight of 1.458 g, what is its combining weight (weight combined with 8.0000 g of oxygen)? (c) What is its exact atomic weight? (d) What is the formula of the oxide?

5 (a)_____

(b)_____

(c)_____

(d)_____

The Molal Volume of a Gas — 12

College Chemistry, Chapter 9

Review of Fundamental Concepts

Avogadro's Law and the Molal Volume

In order that you may understand the behavior of gases, we review two important facts that are related to each other. The first of these we considered in Experiment 10, namely, that one mole of any substance contains the same number of molecules as a mole of any other substance. (This is inherent in the definition of a mole.) The second fact, which is a consequence of the kinetic theory of gases, and was first propounded by the Italian chemist Avogadro about 1811, states that equal volumes of all gases, measured under similar conditions of temperature and pressure, will contain the same number of molecules. As a necessary corollary of these two facts, then, *one mole of any gas* will have a volume equal to that of one mole of any other gas measured under similar conditions. This volume is called **the molal volume of a gas.**

The Molal Volume at Standard Conditions. The Perfect Gas

To evaluate this volume in metric units, recall that the symbol O stands for 16.0000 grams of oxygen, and that one mole of oxygen gas, O_2, therefore weighs 32.0000 grams. As you will verify in this experiment, this has been found experimentally to have a molal volume of 22.4 liters at standard conditions (0°C and 760 mm Hg pressure). Every other gas, likewise, will have a molal volume at standard conditions of 22.4 liters.

Since all real gases deviate more or less from the behavior of a perfect gas, their respective molal volumes will vary slightly. Only in cases of perfect gases, were they to exist, would the molal volumes not vary. **A perfect gas is that idealized gas in** which the molecules would have no attractive forces whatever for one another, and likewise would be mere "points," without any significant volume. The standard molal volume for such a perfect gas has been calculated from measurements on real gases at very low pressures to be 22.4140 liters. Most ordinary gases, unless they have a high molecular weight or are measured quite near their boiling point, have molal volumes which do not deviate more than about 1% from this value.

The Calculation of Gas Volumes. The General Gas Law Equation

It is much easier to measure the amount of a given gaseous substance by measuring its volume than by weighing it. Of course, this necessitates also the measurement of the temperature and the pressure for its volume is dependent on these variables. The relationship is expressed by the *General Gas Law Equation*, which in its most general form is stated thus:

$$PV = nRT. \qquad (1)$$

In this, n is the number of moles of gas, of volume

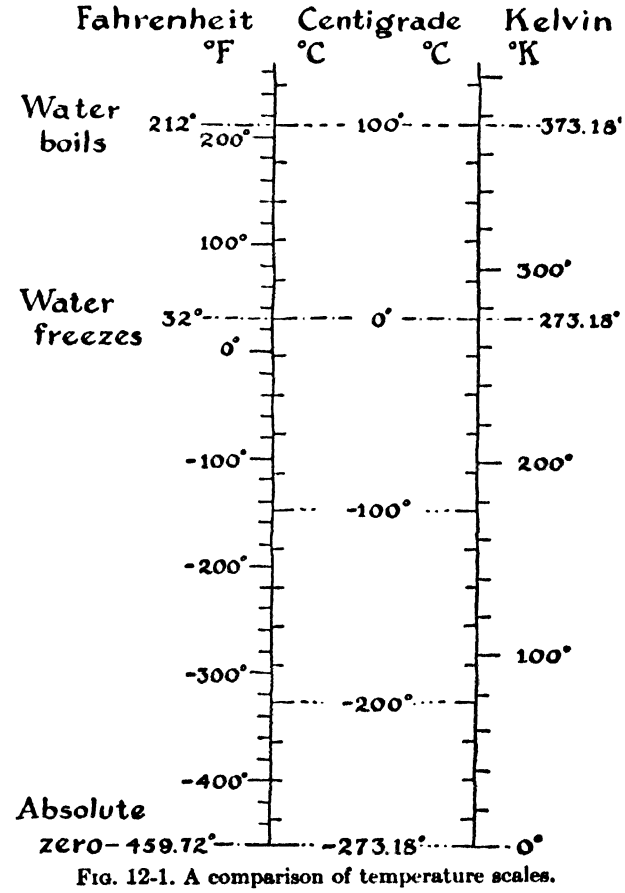


FIG. 12-1. A comparison of temperature scales.

V, at the absolute temperature T and the pressure P. R is a proportionality constant called the "gas constant," and has the same value for all gases. It occurs in many fundamental equations of chemistry and physics.

In all cases where the same amount of a gas is involved, the value of nR will also be constant, and we may write

$$PV = kT, \quad \text{or} \quad \frac{PV}{T} = k. \qquad (2)$$

Now if P_1, V_1, and T_1 represent the corresponding pressure, volume, and temperature of a given quantity of gas, and P_2, V_2, and T_2 represent some other set of related values of pressure, volume, and temperature (for example, standard conditions) for this same quantity of gas, then we may express the relation existing between them by

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}. \qquad (3)$$

This may be transposed to give

$$V_1 = V_2 \times \frac{T_1}{T_2} \times \frac{P_2}{P_1}. \qquad (4)$$

It will be noted that, in equations (3) or (4), if the temperature is constant ($T_1 = T_2$), the inverse proportionality of pressure and volume (Boyle's Law) is expressed. Likewise for constant pressures ($P_1 = P_2$) the direct proportionality of volume and absolute temperature (Charles' Law) is expressed. (See also Study Assignment A, Sec. C, Page 7.) If any five of the quantities in equation (3) are known, the sixth can of course be calculated by simple algebraic means.

Many students and instructors prefer to reason out the relationships, rather than blindly "to follow a formula," and to apply the pressure and temperature (corrective) factors according to whether the pressure change, and the temperature change, will cause an increase or a decrease in the volume. Either point of view gives the same result. An example: 300 ml of CO_2 gas, measured at 30°C and 780 mm Hg pressure, when changed to standard conditions, 0°C and 760 mm Hg pressure, will have its volume decreased by decreasing temperature, and increased by decreasing pressure, in accordance with the equation

$$V_1 = 300 \text{ ml} \times \frac{273^\circ}{303^\circ} \times \frac{780 \text{ mm}}{760 \text{ mm}} = 277 \text{ ml}.$$

The general form of the gas law equation (1), permits many direct calculations. One must know the value of the gas constant R. When V is given in milliliters, and P in atmospheres, R has the value 82.0 ml atm per degree per mole. An example: What weight of chlorine gas, Cl_2, would be contained in a 5.00 liter flask at 20°C, and 600 mm (600/760 atm) pressure? Substituting in the equation (1)

$$PV = nRT, \qquad \text{we have}$$

$$\frac{600}{760} \text{ atm} \times 5000 \text{ ml} = n \times 82.0 \frac{\text{ml atm}}{\text{deg mole}} \times 293^\circ, \text{ or}$$

transposing,

$$n = \frac{600}{760} \text{ atm} \times 5000 \text{ ml} \times \frac{\text{deg mole}}{82.0 \text{ ml atm}} \times \frac{1}{293^\circ} = 0.164 \text{ mole}.$$

And, in grams,

$$0.164 \text{ mole} \times 71 \frac{\text{g}}{\text{mole}} Cl_2 = 11.6 \text{ g } Cl_2.$$

Aqueous Vapor Pressure, Dalton's Law of Partial Pressures

When any gas in a closed container is collected over, or exposed to, liquid water, the water evaporates until a saturated vapor results, that is, until the opposing rates of evaporation and condensation of water molecules at the liquid surface reach a "balance." These gaseous water molecules exert their due share of the total gas pressure against the walls of the container. Thus if 3% of all the gas molecules are water, and 97% are oxygen molecules, then 3% of the total pressure is the vapor pressure of water, and 97% is the pressure due to the oxygen. *Each gas exerts its own pressure regardless of the presence of other gases.* This is **Dalton's Law of Partial Pressures.** Stated as an equation, we have

$$P_{total} = P_{H_2O} + P_{O_2}, \text{ or transposing, } P_{O_2} = P_{total} - P_{H_2O}.$$

To illustrate Dalton's Law, in Figure 12-2 we have shown in (a) a mixture of oxygen molecules and water vapor molecules. In (b), the water molecules have been removed, but all the oxygen gas is still present, in the same total volume. The pressure has thus been reduced by an amount equal to the vapor pressure of water.

Experimental Procedure

Special supplies: Analytical weights, 600-ml beaker, 100°C thermometer, 500-ml graduated cylinder.

Chemicals: prepared unknown mixture of $KClO_3$, KCl and MnO_2; or $KClO_3$, MnO_2.

Prepare the apparatus as illustrated in Figure 12-3. Note the details carefully. Test tube A must be clean and *thoroughly dry*. Fill the flask B with water, and have a small amount of water in the beaker D. Fill the rubber tube C with water by blowing in the rubber tube A momentarily. Syphon water back and forth through tube C by raising and lowering the beaker, to expel all air bubbles. Finally, with the flask nearly filled, but not quite to the top (water must not enter the short glass tube connected to the rubber tube A), close the clamp which has been placed on tube C near the flask.

Obtain an unknown mixture of $KClO_3$, KCl, and MnO_2 from the instructor and at once record its code number on your report sheet.[1] By completely decomposing a weighed sample of this and measuring the volume of the oxygen liberated at a known temperature and pressure, the molal volume of oxygen, and also the percent of $KClO_3$ in the sample, may be determined. First weigh the empty test tube A, together with its connecting stopper and glass tube, as precisely as your balance permits, to the nearest milligram if possible. Then add from 1.5 to 4.0 g of the $KClO_3$ mixture to the test tube. (Your instructor will suggest the approximate amount for you to use, as you must not use an amount that will generate oxygen in excess of the capacity of the flask B.) Again weigh the test tube assembly.

Connect the test tube and stopper to tube A, and make sure that your apparatus is air tight by opening the clamp on tube C, and noting that water does not flow out of the flask, even when the water levels are quite uneven. Have your apparatus approved by the instructor (see report sheet).

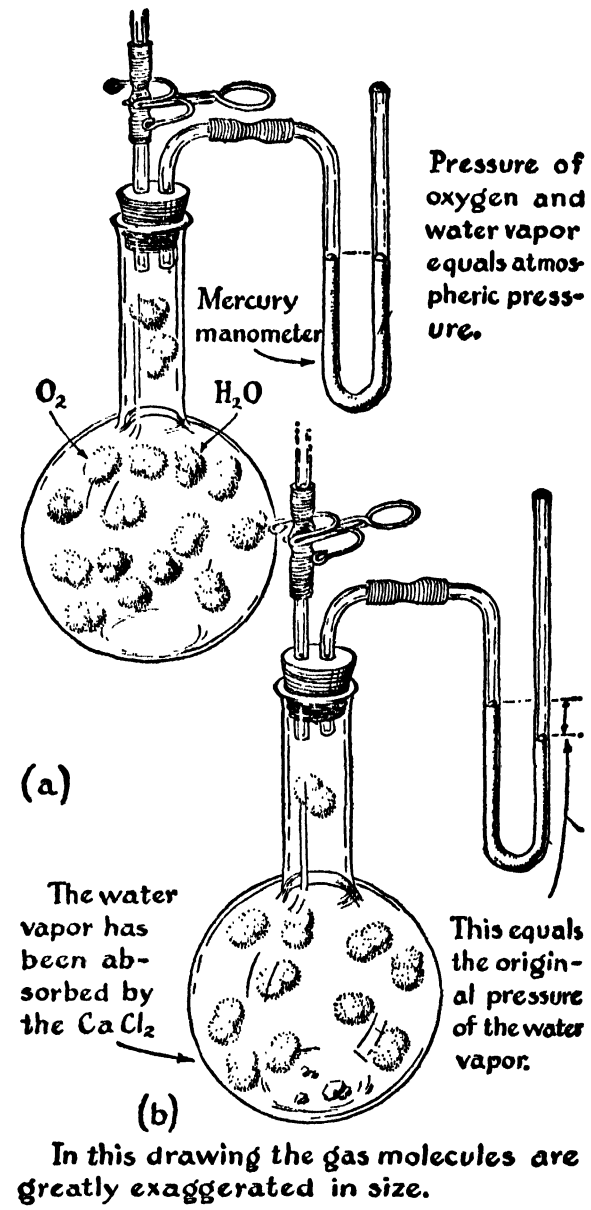


FIG. 12-2. Illustrating an application of Dalton's law of partial pressures.

Equalize the pressures inside and outside the flask by raising the beaker until both water levels are the same. Water can syphon in or out of the flask until the internal and external pressures are equal. Close the clamp and discard the water in the beaker. Drain the beaker carefully and completely, but do not dry it. Replace the tube in the beaker, and open the clamp. During the heating that fol-

[1] If you are not using an unknown mixture, and are determining only the molal volume of O_2, about 5g $KClO_3$ may be dried by just melting it in test tube A (disconnected and held by a test tube holder, and heated throughout its entire length). Let this cool, then add a very small amount (10-15 mg) of dry MnO_2. Weigh the test tube and connecting stopper and glass tube with the contents. **As a safety precaution,** it is wise to test a small amount of the $KClO_3$, mixed with a little of the MnO_2 you will use, as you did in Exp. 8, by melting it to see if it decomposes quietly without obvious combustion.

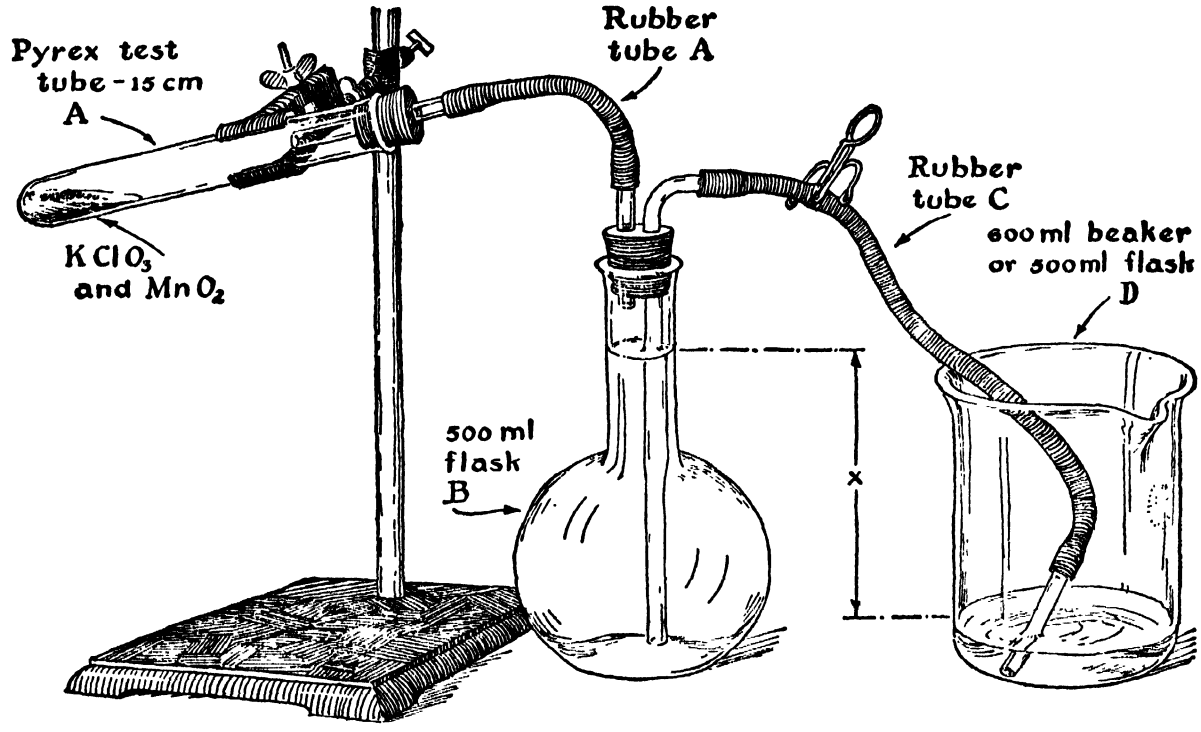


FIG. 12-3. Apparatus to determine the molal volume of oxygen.

lows see that the end of the tube C is kept under the water in the beaker.

Heat the $KClO_3$ mixture gently at first, then more strongly, to maintain a moderate rate of evolution of oxygen gas. If white vapors appear in the tube, decrease the heating until this stops. Continue the heating as long as any oxygen gas is liberated, until there is no further transfer of water into the flask. (If you have prepared your own mixture, using excess pure $KClO_3$ and MnO_2, *stop the heating* in time so that the water level does not go lower than 1 or 2 cm above the end of the tube in the flask.) Do not remove the tube from the beaker until the apparatus has cooled completely to room temperature and the internal and external pressures have been equalized. *Also do not handle the flask* in such a way that the gas contained will be warmed by the hands. Adjust the levels in the flask and beaker so they are equal, and then close the clamp on tube C. Obtain the final weight of the test tube, its contents, and its tube connection. Take the temperature of the oxygen by placing a thermometer directly in the gas. Measure the volume of oxygen by carefully measuring the water in the beaker, using a 500-ml graduated cylinder. The aqueous vapor pressure may be obtained from Table IV in Appendix II. Obtain the barometer reading for the day. This must be corrected for the unequal expansion of the mercury and the brass scale (Table V, Appendix II). The correction is to be subtracted from the direct barometer reading, and is necessitated by the fact that atmospheric pressures are always translated into terms of the barometer at 0° C.

Calculate from your data (a) the volume, at standard conditions, of 32 grams (1 mole) of oxygen gas, and (b) the percentage of $KClO_3$ in the unknown sample issued to you.

REPORT: Exp. 12

The Molal Volume of a Gas

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Unknown sample number_____ Instructor's approval of apparatus_____

Data	*1*	*2*
Weight of tube and contents before heating	g	g
Weight of tube and residue after heating	g	g
Weight of empty tube	g	g
Temperature of the oxygen	°C	°C
Volume of oxygen collected	ml	ml
Barometer reading (uncorrected at .... °C)	mm	mm
Aqueous vapor pressure at temperature of gas	mm	mm

	Calculations	*1*	*2*
Weight of oxygen		g	g
Temperature, absolute		°K	°K
Barometric pressure, corrected for expansion of scale (total gas pressure)		mm	mm
Pressure of oxygen alone, in the flask		mm	mm
Volume of your oxygen at standard condition		ml	ml
The molal volume of oxygen		l	l
Percentage error		%	%
Moles of your oxygen		moles	moles
Moles of $KClO_3$ decomposed		moles	moles
Weight of $KClO_3$ in sample		g	g
Percent of $KClO_3$ in sample		%	%

Exercises on Laboratory Technique

1. Why should not the glass tube connected to rubber tube A extend to the bottom of the flask? What would happen at the conclusion of the heating if it did reach to the bottom?

2. Why is it necessary that the other tube in the flask reach to the bottom?

3. Should the end of the delivery tube C remain under water while the apparatus is cooling? Why?

4. Why should the end of delivery tube C be under water when the pressure in the apparatus is equalized with atmospheric pressure?

5. Why should the test tube be allowed to cool before the water volume is measured?

6. What objection is there to weighing an object, such as the tube of potassium chlorate, on the balance while the tube is still warm?

7. What purpose does the clamp on tube C serve?

8. If the water level in the flask were 10.3 cm above the water level in the beaker (x in Fig. 12-3), would the gas pressure in the flask be greater or less than atmospheric pressure? By how much would the pressures differ? (Express in mm of mercury. See the sketch and explanation.)

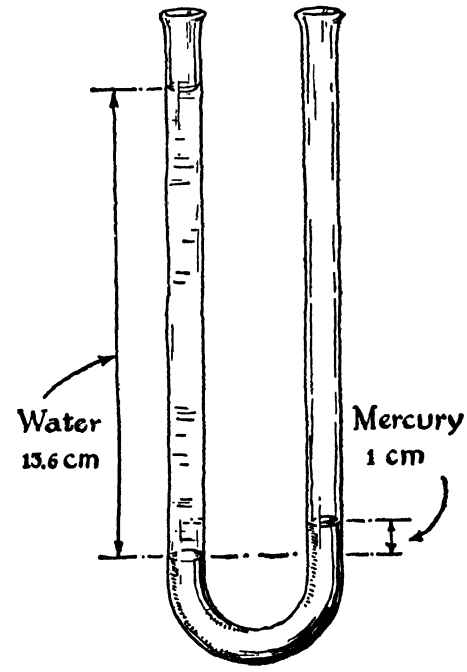


FIG. 12-4. The mercury equivalent of a water column. Since the density of mercury is 13.6 times that of water, a mercury column will stand only 1/13.6 times as high as a water column which balances the same pressure.

Exercises on Experimental Errors

(*Note:* Study thoroughly the section in Appendix I on "Experimental Errors.")

1. Calculate the percent of uncertainty of the data in your experiment, as follows:
   (a) the weight of oxygen (note that two weighings are required for each determination),

   (b) the volume of oxygen liberated,

   (c) the pressure of the oxygen (after correction for barometer scale expansion and for vapor pressure).

2. From the answers to question 1, above, calculate the maximum percent of uncertainty of your experimental value for the molal volume of oxygen, due to these causes.

3. Considering the number of significant figures in your weight, volume, and pressure of oxygen, respectively, to how many significant figures should your result for the molal volume be expressed?

Answers

1 (a)_____%

(b)_____%

(c)_____%

2_____%

3_____

4. How does your percentage error in the experiment compare with the percent of uncertainty as calculated above? If your error is less, would you attribute this to chance, to more careful technique, or to some other cause? In general, what type of error (method, equipment, or observation) do you feel is responsible for any error in your result? Is a "blunder" indicated?

5. List any other factors you can suggest that affect the amount of error in this experiment, which were not considered above.

Problems on the Gas Laws and Molal Volumes

Answers
(label and give units)

1. A pilot balloon filled with 100.0 liters of H_2 at a pressure of 740 mm Hg and 17°C rises to a height of 14,000 ft, where the pressure is 370 mm, and the temperature is −33°C. To what volume will the H_2 expand? . . . . . 1_____

2. A liter of air at 29°C and saturated with water vapor, is dried by bubbling it through conc. H_2SO_4. What is the volume of dry air, if the atmospheric pressure is 750 mm of Hg? 2_____

3. Dry air is 78.0% N_2 and 21.0% O_2. What is the partial pressure of each of these constituents when the total atmospheric pressure is 750 mm Hg? . . . . . 3_____

4. 6.0 liters of H_2 at 80 cm Hg pressure is mixed with 8.0 liters of He at 75 cm Hg pressure, in a 12 liter container. What is the partial pressure of each constituent, and what is the total pressure? . . . . . 4_____

5. A mixture of $KClO_3$ and KCl, weighing 61.3 g was heated intensely, giving 5.60 liters of O_2, at standard conditions. Write the equation for the reaction:

_____

How many moles of O_2 were liberated? How many formula weights, and grams of $KClO_3$ were present, and what was the percentage of $KClO_3$, in the mixture? . . . . . 5_____

6. All real gases deviate to some extent from the behavior of perfect gases. At standard conditions the density of O_2 is 0.0014290 g/ml, of H_2 is 0.00008988 g/ml, and of CO_2 is 0.0019769 g/ml. Using these values, and the exact atomic weights, calculate the molal volume of each of these, in milliliters, to 5 significant figures. . . . . 6_____

The Molecular Weight of a Gas — 13

College Chemistry, Chapter 9

Review of Fundamental Concepts

Review the relationships between Avogadro's Law, the molal volume, and also the general gas law equation as developed in the last experiment. From these considerations we may state that *the molecular weight of any gas is the weight in grams of 22.4 liters of that gas at standard conditions.* Likewise the molecular weight of a volatile liquid or solid, whose vapor may be readily measured at known conditions and then calculated to standard conditions, can be determined by this same method.

In this experiment we shall make direct measurements of the weight and corresponding volume of a given gas at the laboratory temperature and pressure. We shall first obtain the weight of the gas container, a 200 to 300-ml flask, filled with dry air. From a knowledge of the density of air and the volume of the flask, the weight of the contained air, and hence the weight of the empty (evacuated) flask, can then be calculated. The difference between this weight, and the weight when the flask is filled with the gas under consideration, will of course give the weight of the volume of the gas contained in the flask.

Various gases, such as carbon dioxide (CO_2), sulfur dioxide (SO_2), ammonia (NH_3), nitrogen (N_2), nitrous oxide (N_2O), methane (CH_4), or acetylene (C_2H_2), may be used in the experiment. When tanks of the compressed gas are available, they are convenient; but you will learn more chemistry if you prepare your own sample of gas. You should study, in a general chemistry text, the properties and method of preparation of the gas to be used. Directions will be given here for the preparation of carbon dioxide. Sulfur dioxide may be prepared in a similar apparatus by substituting sodium bisulfite ($NaHSO_3$) in place of the marble chips, and warming the mixture slightly to drive the more soluble sulfur dioxide gas out of solution.

Experimental Procedure

Special supplies: Analytical weights, thistle tube, calcium chloride drying tube, 110°C thermometer.

Chemicals: $CaCO_3$ (marble chips) for CO_2, $NaHSO_3$ for SO_2, etc.

The apparatus to be used is sketched in Figure 13-1. First clean and thoroughly dry a 200-ml flask C, fitted with a one-hole rubber stopper and a glass tube extending very nearly to the bottom of the flask. This tube is connected by a section of rubber tubing to a drying tube B, filled with 4-mesh calcium chloride which is protected at each end by a loose plug of cotton. Leave the stopper in C loose so as to permit gas to escape, and connect the drying tube to the compressed air supply. Pass a very gentle stream of dried air through C for at least five minutes. If C has been warmed previously, and the air passed through while it is cooling, more complete drying will be assured. (If compressed air is not available, a two-hole stopper, with a short exit tube, may be used in C, and this connected to a water aspirator to suck air through B and C. In this case the second hole in the stopper should be plugged when making all weighings, so as to prevent undue diffusion of CO_2.)

In the meantime, prepare the carbon dioxide generator A, using a 200-ml Erlenmeyer flask having a thistle tube reaching almost to the bottom, and having a short, right-angle exit tube, to be connected to the calcium chloride tube when ready to generate the gas. Place about 25 g of marble chips ($CaCO_3$) in the generator, and add about 10 ml of water to cover the end of the thistle tube. Do not add acid until ready to generate the carbon dioxide.

Disconnect the rubber tube from the flask C, and weigh this flask, including the stopper and glass tube, to an accuracy of 0.001 g. After this weighing, avoid all unnecessary handling of the flask. Hold it by the rim, and reattach it to the drying tube and CO_2 generator, placing it on a clean dry square of paper to avoid contamination by the table. Be sure the stopper is left loose so the displaced air and excess gas can escape between it and the flask. When ready add dilute hydrochloric acid (HCl) through the thistle tube, a little at a time as needed, so as to maintain a gentle evolution of CO_2. (You

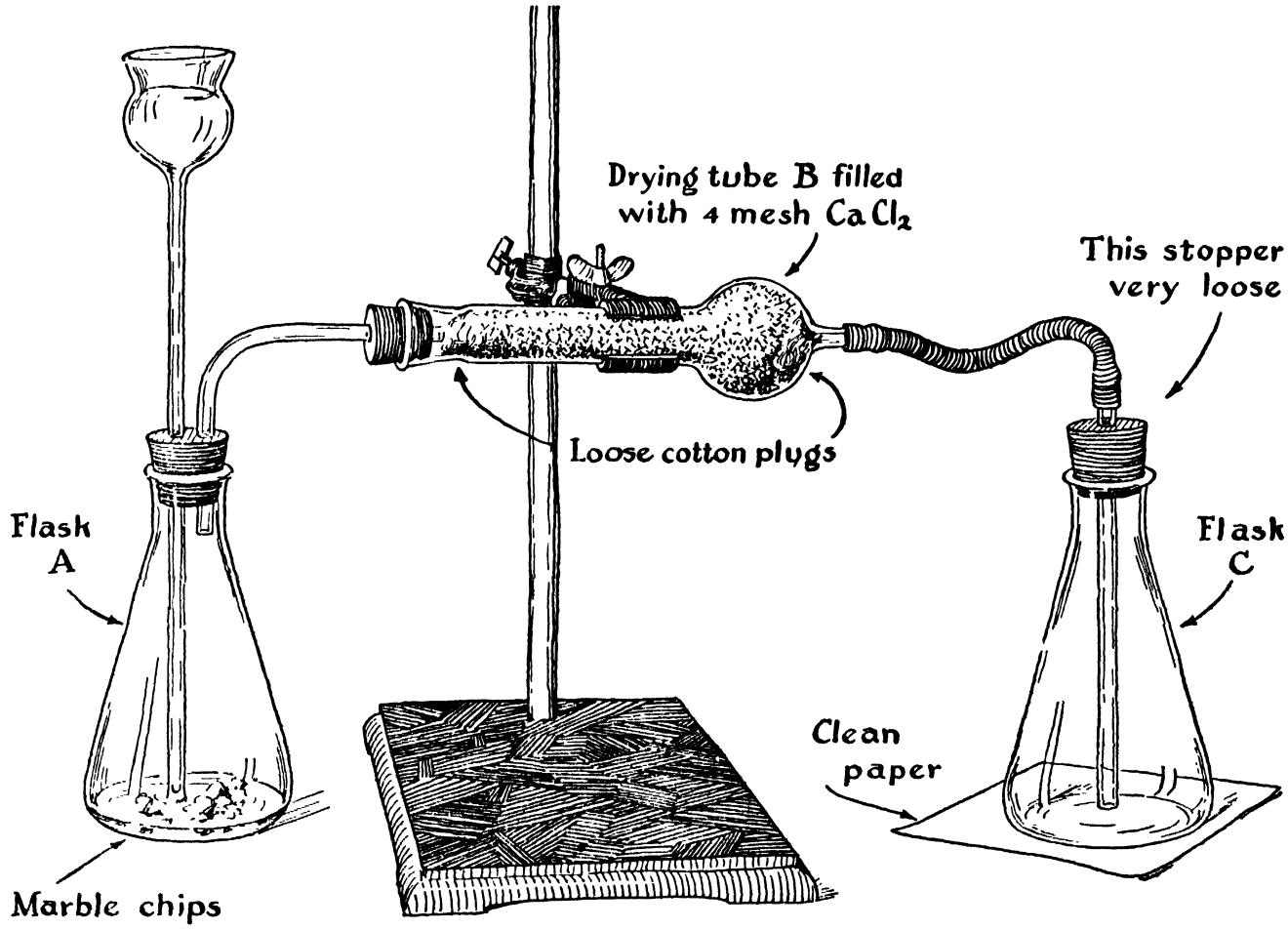


FIG. 13-1. Apparatus to determine the molecular weight of a gas.

may momentarily tighten the stopper in C and note the rate at which liquid backs up in the thistle tube, in order to estimate the rate at which gas is being generated.)

Let the generator run for at least twenty minutes to displace all the air in C by CO_2 gas. Finally detach the rubber tube from C and push in the stopper firmly. Without undue handling, at once weigh the flask and contents. It is necessary to weigh at once to avoid undue diffusion of air into C through the glass tube. Again connect C to the drying tube, gently release the stopper in C and pass CO_2 through it for an additional ten to fifteen minutes. Weigh the flask C as before. The two weights should agree if the flask was filled with CO_2 the first time.

Take the temperature of the gas with a thermometer placed in the gas shortly after the last weighing, and obtain the barometer reading for the day. To measure the exact volume of the flask to the bottom of the stopper, fill the flask with water, replace the stopper and glass tube, and wipe off excess water. Weigh this on the platform balance to the nearest gram. (This heavy a weight might injure an analytical balance, hence the more rugged platform balance is used. Furthermore, great precision is not required for this weight. Why not?) How does the weight of water enable you to calculate its volume? Look up in a reference source the density of dry air at your laboratory conditions. Enter all data and calculations on the report sheet.

From the volume of CO_2, calculated to standard conditions, and the weight of this CO_2, calculate its molecular weight (the weight in grams of the molal volume).

REPORT: Exp. 13

The Molecular Weight of a Gas

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Data	*1*	*2*
Weight of flask and stopper, filled with CO_2	g	g
Weight of flask and stopper, filled with water	g	g
Weight of flask and stopper, filled with air	g	g
Temperature of flask	°C	°C
Barometer reading (uncorrected at .... °C)	mm	mm
Density of dry air at flask temperature and pressure Reference:.....	g ml	g ml

	Calculations	*1*	*2*
Temperature, absolute		°K	°K
Barometer reading, correction		mm	mm
Volume of flask[1]		ml	ml
Volume of carbon dioxide at standard conditions		ml	ml
Weight of air in flask at the start		g	g
Weight of empty flask and stopper		g	g
Weight of carbon dioxide contained in the flask		g	g
Molecular weight of CO_2 (from your data)			
Percentage error		%	%

[1] Why can we neglect the weight of the air in the flask when obtaining the weight of the water (from which we calculate the volume of the flask), but cannot neglect it when calculating the weight of the carbon dioxide? Explain.

Problems

1. Write the chemical equation for the reaction taking place in the preparation of carbon dioxide.

2. How many gram formula weights are there in the 25.0 g of $CaCO_3$ used? Calculations:

3. How many liters of carbon dioxide could be generated at standard conditions by this weight of $CaCO_3$?

4. What volume would this amount of carbon dioxide occupy at ordinary laboratory conditions? (Assume 27°C and 740 mm.)

5. A liter of ethyl chloride vapor weighs 2.87 g, recalculated to standard conditions. Find the approximate molecular weight.

6. What is the density relative to oxygen (ratio between the density of the gas and the density of oxygen) of a gas which has a gram molecular weight of 160 g?

7. What is the weight of a liter of each of the following gases at standard conditions: chlorine, Cl_2; butane, C_4H_{10}; phosgene, $COCl_2$? (Use no other data except atomic weights and the molal volume.)

8. 100.0 g of water is vaporized at 100°C and 740 mm pressure. What is the volume of the steam formed? (Hint: first convert the weight to moles.)

Answers

2 _____ gfw

3 _____ l

4 _____ l

5 _____

6 _____

7 _____ g Cl_2

_____ g C_4H_{10}

_____ g $COCl_2$

8 _____ l

The Solution of Problems Based on Equations — B

College Chemistry, Chapters 8, 9

A Study Assignment

This review is inserted at this time, after you have completed the study of weight relations in Experiments 10 to 13, in order that we may bring together and compare the methods for the solution of problems involving the weights and volumes of reacting substances. In solving problems, the quantitative relationships inherent in an equation are most conveniently expressed in terms of the appropriate "chemical units" of quantity—gram-atoms, formula weights, or moles. In the final answer, these may then be converted into units of weight (grams), or in the case of gases into units of volume (liters). This is illustrated as follows.

When aluminum is dissolved in hydrochloric acid, the skeleton equation is

$$Al + HCl \longrightarrow AlCl_3 + H_2 \quad \text{(unbalanced)}.$$

To balance this, note that the least common multiple of the 3 Cl atoms and the 2 H atoms is 6, so that we need 6 HCl. The balanced equation is, therefore,

(balanced)	$2\ Al$	$+\ 6\ HCl \longrightarrow$	$2\ AlCl_3$	$+\ 3\ H_2$.
gfw, moles:	2	6	2	3
grams:	$2 \times 27 = 54$	$6 \times 36.5 = 219$	$2 \times 135.5 = 271$	$3 \times 2.016 = 6.05$
liters (Applies only to gases at standard conditions):				$3 \times 22.4 = 67.2$

Under each formula, we have written its meaning in various units. Note that:

(1) the coefficients give directly the number of gram-atoms, moles, or formula weights involved.

(2) In the case of a gas, we may express the quantity involved either by weight (grams) or by volume (liters), whichever is called for in the problem.

The practical solution of problems involving the relative quantities of substances in chemical reactions is best explained by several illustrative problems.

Example 1. Weight-Weight Relations. What weight of sulfuric acid would be needed to dissolve 50.0 grams of aluminum?

The equation is:

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2$$

The given weight, 50 g Al, is first expressed as gram-atoms:

$$\frac{50.0\ g\ Al}{27\ g/g\ at} = 1.852\ g\ at\ Al$$

Then, from the equation, we note that 3 formula weights of H_2SO_4 react with 2 gram-atoms of Al. Therefore, we need

$$\frac{3}{2} \times 1.852 = 2.78\ gfw\ H_2SO_4$$

Finally, we convert the formula weights of H_2SO_4 back to grams:

$$2.78\ gfw \times 98\ \frac{g}{gfw} = 272\ g\ H_2SO_4.$$

Example 2. Weight-Volume Relations. What weight of aluminum will be required to produce 12.0 liters of hydrogen gas at standard conditions, by reaction with sulfuric acid?

The equation is:

$$2\ Al + 3\ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3\ H_2$$

First express the 12.0 liters of hydrogen as moles:

$$\frac{12.0\ l\ H_2}{22.4\ l/mole} = 0.536\ mole\ H_2$$

From the equation, we note that 2 g at Al are needed to produce 3 moles of H_2. Therefore, we need

$$\frac{2}{3} \times 0.536\ g\ at\ Al = 0.357\ g\ at\ Al.$$

Finally, we convert the gram-atoms of Al back to grams:

$$0.357\ g\ at\ Al \times 27\ \frac{g}{g\ at} = 9.64\ g\ Al.$$

Example 3. Weight-Volume-Gas Law Relations. What volume of hydrogen gas, measured at 27° C and 640 mm Hg pressure, will be produced by the

reaction of 25.0 g of zinc with an excess of hydrochloric acid?

The equation is:

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$$

Therefore, as many moles of hydrogen will be produced as there are gram-atoms of zinc:

$$\frac{25.0\ g\ Zn}{65.4\ g/g\ at} = 0.382\ g\ at\ Zn, \text{ or also } 0.382\ mole\ H_2.$$

We may now use the general gas law equation, $pv = nRT$, to convert the 0.382 moles of gas (n in the equation) to liters at the conditions given. Note that when R = 0.082 liter atm/mole deg, the pressure must be expressed in atmospheres, i.e., p = 640/760 = 0.842 atm. Also, T = 273 + 27 = 300° K.

Transposing the equation, and substituting:

$$v = \frac{nRT}{p} = \frac{0.382\ mole \times 0.082\ liter\ atm/mole\ deg \times 300°K}{0.842\ atm}$$

$$= 11.2\ l.$$

Example 4. Volume-Volume Relations. What volume of air, 20% oxygen, is needed to burn 10.0 liters of butane gas, C_4H_{10}, completely to carbon dioxide and water?

The equation is:

$$2\ C_4H_{10} + 13\ O_2 \longrightarrow 8\ CO_2 + 10\ H_2O.$$

The volumes of gases will be in the same ratio as the number of molecules, or moles, of the gases (Avogadro's Law), therefore, from the equation:

2 liters C_4H_{10} is equivalent to 13 liters O_2 (pure),

and

$$10.0\ liters\ C_4H_{10}\ is\ equivalent\ to\ 10.0 \times \frac{13}{2} = 65\ liters\ O_2.$$

Finally, since the air is only 20% oxygen, the volume of air required will be

65 liters/0.20 = 325 liters of air.

To summarize, in solving problems based on chemical equations:

Step 1. Write the balanced equation for the reaction concerned.

Step 2. Read the problem carefully, taking note of the data given, and the items to be found.

Step 3. Express the data given in the appropriate chemical units of quantity (gram-atoms, formula weights, or moles) and from the equation find how many gram-atoms, formula weights, or moles of the desired substance this will give or require.

Step 4. Finally, convert the latter back into the units of weight or volume asked for in the problem. When both substances are gases, the coefficients in the equation give directly the relative volumes.

REPORT: Assignment B

The Solution of Problems Based on Equations

*Name*_____

Date _____

*Section*_____

*Locker Number*_____

Problems

Show the solution, in good order, below each problem. The first step is always to write the equation for the reaction. Express the answers to three significant figures.

1. How many grams of zinc metal will react with three gram-formula weights of (a) hydrochloric acid, (b) sulfuric acid, (c) phosphoric acid? (Assume that all hydrogen atoms in each case react.)

2. In Experiment 6, suppose that 1.30 g of silver was obtained by reaction of the silver sulfate solution with metallic copper. What weight of copper metal dissolved from the copper wire?

3. How many formula weights, and how many grams, of calcium sulfate would be formed from 222 grams of calcium hydroxide, by reaction with sulfuric acid?

4. What volume of carbon dioxide at standard conditions may be obtained by heating 250 grams of limestone, $CaCO_3$?

5. What volume of oxygen is needed to burn 25.0 liters of butane C_4H_{10}, completely to carbon dioxide and water?

Answers

1_____g

_____g

_____g

2_____g

3_____gfw

_____g

4_____l

5_____l

6. 175 grams of calcium chloride is treated with excess silver nitrate solution. How many gram-formula weights of calcium chloride are there? How many grams of silver chloride will be produced?

6_____gfw

_____g

7. 50.0 grams of cupric sulfate crystals, $CuSO_4 \cdot 5\ H_2O$, is dissolved in water and treated with excess aluminum metal. How many grams of aluminum will dissolve? How many grams of copper will precipitate?

7_____g Al

_____g Cu

8. 12.6 grams of sodium bicarbonate, $NaHCO_3$, reacts with dilute nitric acid to form water, carbon dioxide, and sodium nitrate. What volume of carbon dioxide, at 27° C and 700 mm Hg pressure, is liberated by the reaction?

8_____l

9. What volume of air, at 25° C and 740 mm Hg pressure, is required to burn a pint of gasoline completely to carbon dioxide and water? (Assume air is 20% O_2, gasoline is C_7H_{16}, and that a pint of gasoline weighs 350 grams.)

9_____l

10. 135 grams of aluminum metal is dissolved in hydrochloric acid. The solution is then treated with sulfuric acid and evaporated, to change the aluminum chloride to aluminum sulfate. Water and potassium sulfate are added, and the solution evaporated to form alum crystals, $KAl(SO_4)_2 \cdot 12\ H_2O$. What weights of (a) sulfuric acid, (b) potassium sulfate, are needed, and (c) what weight of alum crystals will be produced? (*Note:* Write the three equations, then, by a comparison of the relative number of gram-atoms and formula weights involved, solve directly for the desired substances. Avoid any unnecessary intermediate steps.)

10_____

Group Relationships in the Periodic Table 14

College Chemistry, Chapters 5, 6

Review of Fundamental Concepts

In Experiment 8, we studied the chemical character of the oxides of a number of elements in relation to their positions in the periodic table. In this experiment, we shall continue this study, particularly in relation to the variation in electropositive and electronegative character as we move from element to element vertically in a group. We identify increasing electropositive character with increasing basic tendencies of the compounds of the metals, and increasing electronegative character with increasing acidic character of the compounds of the nonmetals. It will be of interest to compare these tendencies in the more active metallic groups I, II, and III, and in the very active nonmetallic group VII—the halogens.

Experimental Procedure

Special supplies: Five 150 to 250-ml wide mouth bottles, 5 glass squares, deflagrating spoon, asbestos pieces, tin foil, colored cotton cloth, colored flowers, newspaper, lead dish, paraffin.

Chemicals: Na, K, Ca, Mg, Al metals, CaF_2, CCl_4, Br_2 water, Cl_2 water, 0.1 *F* I_2, phenolphthalein indicator, 5% NaClO (commercial brand), P, KBr, KI, NaCl, MnO_2, steel wool, Sb (powdered), 0.1 *F* KBr, 0.1 *F* KI, 0.1 *F* NaCl.

1. The Behavior of the Metals of Groups I, II, and III. (1) Fill a 15-cm test tube with water, close the opening with your thumb, and invert the test tube into a 400-ml beaker half filled with water, so that no air enters the tube. Now wrap a small piece of sodium metal (size of a small pea) with a little tin foil. (**Caution:** *Sodium metal and also potassium metal must be handled with extreme care. Use forceps or tongs. Never touch the metal with your hands. Observe all precautions which your instructor gives.*) Punch several holes in the tin foil wrapped around the sodium. Hold this with tongs or forceps, and quickly insert it under the open end of the test tube. See Figure 14-1. When the reaction has subsided, remove the tube full of gas from the beaker, and at once ignite it. Also, test the solution in the beaker with phenolphthalein solution, or litmus. (Phenolphthalein is colorless in an acid, and red in a basic solution.)

(2) Compare the relative activity of sodium and potassium metals with water, as follows. Place a watch glass over a beaker which is a third full of water. By means of forceps or tongs, drop a small piece of sodium (size of half a pea) into the water. Keep the beaker covered during the reaction, as a precaution. Repeat the experiment, using a small piece of potassium metal in place of the sodium.

(3) Invert a test tube filled with water in a beaker of water. Drop a piece of calcium metal into the beaker and cover it with the test tube, so as to collect the evolved gas. Identify the gas, and also the solid which precipitates from the solution. Note the comparative rate of the reaction as com-



Fig. 14-1. The reaction of sodium metal with water.

pared with that of the other metals you used. Does magnesium react with cold water?

(4) Compare the relative rates of reaction of small pieces of magnesium, calcium, and aluminum, with 3 ml of dilute (6 *F*) hydrochloric acid mixed with an equal volume of water.

2. The Behavior of Chlorine. Because of its very corrosive characteristics, *caution must be exercised* so as to avoid all unnecessary release of chlorine gas into the atmosphere. *Work in the hood.*

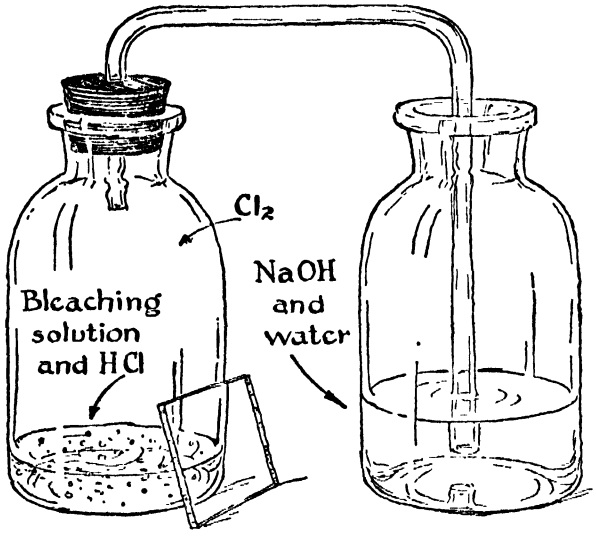


FIG. 14-2. A simple method for the preparation of samples of chlorine gas. The escape of excess chlorine into the atmosphere is prevented by absorption into NaOH solution.

(a) *Preparation from Bleaching Solution.*[1] Arrange a 150 to 250-ml wide mouth bottle with a stopper and delivery tube as illustrated in Figure 14-2. The delivery tube leads into a second bottle or flask containing a solution of about 20 ml of 6 *F* NaOH with 50 ml of water, in order to absorb any excess chlorine. Place 20 ml of a standard brand of bleaching solution, which contains 5% sodium hypochlorite (NaClO), and 5 ml of concentrated hydrochloric acid, in the wide mouth bottle, and *at once* insert the stopper. Let this stand a few minutes to complete the reaction, for which the equation is

$$2\ HCl + NaClO \longrightarrow Cl_2 + NaCl + H_2O.$$

[1] The preparation of chlorine by the usual laboratory method, namely, the oxidation of HCl by MnO_2, will be carried out in Experiment 18. Our purpose here is to obtain samples of Cl_2 gas in a simple manner, with a minimum contamination of the atmosphere. Your instructor may designate different students to perform the various tests for others to observe in order to decrease the amount of chlorine liberated in the laboratory.

Quickly cover each bottle of chlorine gas with a glass square, as you remove the stopper. Prepare a bottle of gas for each of the tests of paragraph (b), immediately before you perform the test. Recharge the generator bottle with fresh reagents for each bottle of Cl_2 which you prepare. The solutions used to prepare the chlorine may be left in the bottles. They will not interfere with the tests.

Keep each bottle of chlorine which you use covered as completely as possible during the test. After completing each observation, add 15-25 ml of the wash solution of NaOH from the second bottle to the covered bottle and mix it well. This will react with excess chlorine and thus avoid releasing it into the atmosphere when you clean the bottle.

(b) *Reactions of Chlorine.* Test the behavior of chlorine with metals by sprinkling a little powdered antimony into a bottle of chlorine. The product is antimony trichloride ($SbCl_3$). Into a second bottle, insert a little steel wool which has been ignited by holding it momentarily in a flame.

Try the reaction of chlorine with a nonmetal by inserting a bit of burning phosphorus into a third bottle of chlorine. The phosphorus should be contained in a deflagrating spoon which is lined with asbestos. Phosphorus trichloride (PCl_3) is formed as a vapor. (It is a liquid at room temperature.)

Test the bleaching action of chlorine by inserting into a bottle of chlorine such materials as a moist strip of colored cotton cloth, a colored flower, a moist strip of paper with fountain pen ink on it, and a moist strip of newspaper with printer's ink on it. (The latter contains carbon black.)

Prepare a glass jet by drawing down a piece of glass tubing (Fig. i-4, P. xiii). Connect this by rubber tubing to the gas supply, ignite the jet, and adjust the gas to give a one-inch flame. Now lower this burning gas into a bottle of chlorine gas. (For the purposes of this experiment, consider the gas to be methane (CH_4). If it is coal gas, it will also contain considerable hydrogen gas.) By noting the appearance, and by exposing a piece of moist, blue litmus to the fumes, identify the products which are formed.

3. The Formation of Bromine and Iodine. Into a 250-ml flask, place 1 to 2 g of potassium bromide (KBr), a little manganese dioxide (MnO_2), and 1 to 2 ml of concentrated sulfuric acid. Warm this mixture just enough to note the product

formed. (Bromine can be distilled from such a mixture and condensed to liquid bromine under cool water.) Observe the properties of a sample of liquid bromine, as exhibited by your instructor. Wash the contents of the flask down the drain with plenty of water.

Place 1 to 2 g of potassium iodide (KI) and a little manganese dioxide in an evaporating dish. Add 1 to 2 ml of concentrated sulfuric acid and cover this with a watch glass which contains a little water (see also Fig. 2-3, P. 16). Warm the dish gently, to sublime the iodine onto the watch glass.

4. Replacement Reactions of the Free Halogens and Halide Salts. To 2 ml each of 0.1 *F* KBr and 0.1 *F* KI, add a little chlorine water (a saturated solution of chlorine gas in water). Now, to each of these samples, add 1 ml of carbon tetrachloride, agitate the test tubes a moment, and observe the colors of the free halogen dissolved in the carbon tetrachloride.

In a similar fashion, test the reactivity of 2 ml each of 0.1 *F* NaCl and 0.1 *F* KI, with a saturated solution of bromine in water. Use carbon tetrachloride as before in each case, to help you decide whether a reaction has occurred. Likewise, test the reactivity of 2 ml each of 0.1 *F* NaCl and 0.1 *F* KBr by the addition of 1 ml of 0.1 *F* I_2 solution.

Summarize these results by comparing the reactivity of the free halogen elements in relation to their positions in the periodic table, group VII.

5. The Hydrogen Halides. (a) *Hydrogen Fluoride.* Etch a glass plate as follows. Coat the glass square on one side with a thin, evenly distributed film of paraffin, by warming the glass, and melting small bits of paraffin on the surface. When this is cool, write or sketch on the paraffined surface, using a pin or other pointed object. Now place 3 g of calcium fluoride (CaF_2) in a lead dish, moisten this with a few drops of concentrated sulfuric acid, and stir it with a match stick to make a paste. Place the glass square on the lead dish so as to expose the writing to the fumes. Leave this until the close of the period, or longer (at least an hour). Then remove the glass square, warm it and wipe off the paraffin. Wash out the lead dish.

(b) *Hydrogen Chloride.* Place 2 to 3 g of sodium chloride and 1 to 2 ml of concentrated H_2SO_4 in a dry wide mouth bottle, and connect this, as in Figure 14-2, to absorb excess HCl into water. (Sodium hydroxide is not necessary.) Let this stand a few minutes to complete the reaction. You can tell when the bottle is filled with the gas by the fog which results when your moist breath is blown across the mouth of the bottle. Also test the gas around the bottle top with moist blue litmus. Note the odor and color of the gas. Invert the bottle of hydrogen chloride into a 400-ml beaker two-thirds filled with water, removing the glass square as you do so.

(c) *The Relative Ease of Oxidation of the Hydrogen Halides.* To a very few crystals of potassium bromide, and of potassium iodide, in each of two 15-ml test tubes, add a few drops of concentrated H_2SO_4. Test the evolved gases with moist, blue litmus. Also, blow your breath across the mouth of the tubes. Warm the tubes slightly to obtain more definite evidence of the nature of the colored products which are formed. Note any characteristic odors.

Both hydrogen bromide and hydrogen iodide are colorless. They are quite similar to hydrogen chloride. Some of the free halogens are formed also, because concentrated H_2SO_4, in addition to being an acid, is a good oxidizing agent. Typical equations for these oxidation processes are

$$2\,KBr + 3\,H_2SO_4 \longrightarrow 2\,KHSO_4 + Br_2 + H_2SO_3 + H_2O,$$

$$8\,KI + 9\,H_2SO_4 \longrightarrow 8\,KHSO_4 + 4\,I_2 + H_2S + 4\,H_2O.$$

Judging by the amounts of the free halogen formed in each case, compare the relative ease of oxidation of HCl, HBr, and HI, and relate this to the position of the elements in group VII.

REPORT: Exp. 14

Group Relationships in the Periodic Table

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Metals of Groups I, II, and III

Write equations for the reactions with water of:

Sodium_____

Potassium_____

Calcium_____

What specific identification of the products formed in the above reactions did you observe?

Compare the relative activity of sodium and of potassium with water. What would you predict as to the reactivity with water of caesium? Of lithium?

Judging by the relative activity of calcium and of magnesium with water, what would you predict as to the behavior of strontium or barium with water?

Write equations for the reactions with dilute hydrochloric acid of:

Magnesium_____

Calcium_____

Aluminum_____

Predict the behavior of scandium metal with dilute hydrochloric acid. What would be the formula of its chloride?

Summarize the comparative reactivity of the metals of group I, of group II, and of group III with water and with dilute acids. What would you predict as to the relative ease of oxidation of these metals on exposure to the air?

2. The Behavior of Chlorine

Summarize your observations, and write the equations for the reactions of chlorine with:

	Observations	*Equations*
Antimony:		
Iron:		
Phosphorus:		
Methane, CH_4:		

Hydrogen gas also reacts readily with chlorine.
Write the equation:

3. The Formation of Bromine and Iodine

Describe the results of warming (1) a mixture of potassium bromide, manganese dioxide, and sulfuric acid (2) a mixture of potassium iodide, manganese dioxide, and sulfuric acid. Note the properties of the products formed in each case.

What is the function of the manganese dioxide, in the above reactions?

Complete and balance the equation for the above reaction of KBr (The reaction of KI is similar):

$2\ KBr + ____H_2SO_4 + MnO_2 \longrightarrow ____KHSO_4 + MnSO_4 + _____ + _____$.

4. Replacement Reactions of the Halogens and Halide Salts

Describe the results, and write the equations for the reactions, if any, of solutions of Cl_2, Br_2, or I_2, with solutions of NaCl, KBr, or KI, respectively:

	Observations	*Equations*
Cl_2 and KBr		
Cl_2 and KI		
Br_2 and NaCl		
Br_2 and KI		
I_2 and NaCl		
I_2 and KBr		

Comment on the relative activity of the halogen elements in relation to their positions in group VII of the periodic table.

5. The Hydrogen Halides

(a) *Hydrogen Fluoride.* Describe all your observations in connection with the preparation of hydrogen fluoride, and its use in etching glass.

Equation for the preparation of HF:_____

Complete the representative equation below for the etching of glass, of which calcium silicate is an important constituent:

$$CaSiO_3 + ____HF \longrightarrow CaF_2 + _____ + _____.$$

(b) *Hydrogen Chloride.* Describe all your observations of the properties of hydrogen chloride gas:

Equation for the preparation of HCl:_____

(c) *The Relative Ease of Oxidation of the Hydrogen Halides.* As evidenced by the behavior of the halide salts with concentrated sulfuric acid, comment on the relative amounts of HF, HCl, HBr, and HI formed, as compared with the corresponding oxidation products F_2, Cl_2, Br_2, and I_2. Correlate this with the position of the elements in the periodic table.

Application of Principles

1. Name, and give the location in the periodic table, of (a) the most electropositive element, and (b) the most electronegative element.

2. Write the formulas (not equations) of the new substances, if any, which you predict would be formed when:

(a) Francium metal is added to water . . . . . _____

(b) Beryllium is treated with HCl solution . . . . . _____

(c) Lithium metal and astatine are mixed . . . . . _____

(d) Rubidium bromide and iodine solutions are mixed . . . . . _____

(e) Fluorine gas is treated with calcium chloride . . . . . _____

(f) The gaseous product from (e) is bubbled into strontium bromide solution . . _____

(g) Caesium bromide, manganese dioxide, and concentrated sulfuric acid are mixed _____

(h) Sodium astatide is treated with concentrated sulfuric acid . . . . . _____

(i) Caesium metal is exposed to dry air . . . . . _____

The Periodic Classification of the Elements — C

College Chemistry, Chapters 5, 6

A Study Assignment
Review of Fundamental Concepts

One of the most useful generalizations of inorganic chemistry is the **Periodic Law**, which states that the properties of the elements are periodic functions of their atomic numbers. The relationship can best be seen by arranging the elements in a certain way; this arrangement is called the **Periodic Table.** In order that you may appreciate more fully the kinds of information which are summarized by the periodic table, the following study assignment has been provided. The student should review carefully Chapters 5, 6 and 9 of the text, which discuss the organization of the periodic table and contain numerous tables which summarize important properties of the elements by groups.

Special attention should be given to the characteristic properties of one of the common elements of each group and the relationship between its properties and those of the other congeners in the group. The increase in the metallic nature of the elements in Groups I and II from top to bottom, and the increase in the nonmetallic nature of the elements in Groups V, VI and VII from bottom to top are examples of vertical trends of importance.

Horizontal trends which should be noted include the regular change in maximum oxidation number and the decreased basicity or increased acidity of the hydroxides of the elements, as one proceeds from left to right across the second and third periods.

The student should also know the location in the periodic table of the different types of elements, such as: the noble gases, the light active metals, the nonmetals, the transition metals, the metalloids, the naturally radioactive metals and the rare earth metals.

Before beginning this exercise, the student must realize that although the periodic table does simplify the task of learning what kinds of properties might be expected of the various types of elements, it also has its limitations. In order to obtain a broad knowledge of chemistry, a great number of specific facts must also be learned many of which cannot be completely coordinated by the periodic table or other unifying theories at this time.

Directions

In the exercise which follows, the student is expected to identify various elements and their location in the table from the description of characteristic properties and interrelationships within groups. Each group has been assigned a capital letter which is carried through in the fictitious symbols used for all the elements in a particular group. The subscript letters a, b, c, d, e and f are used to distinguish the individual members within the group but they have not been assigned in alphabetical or any other special order. For instance, after reading the paragraph describing the family of elements whose symbols all begin with the capital letter C, you will soon decide that the elements Ca, Cb, Cc, Cd, Ce, Cf are noble gases. By referring to Table 5-2 in the text you will be able to determine the order in which they should be placed into Group O of the blank periodic table provided in the report sheet.

The less familiar elements in the second and third rows of transition elements as well as most of the rare-earth metals have been omitted but a representative group of about fifty-seven elements has been included in the discussion. Identify each of them and locate them in their proper place in the blank periodic table on the report sheet.

Discussion of the Properties of the Elements

The element X occupies a unique place in the periodic table in that, strictly speaking, it belongs to no other group. It forms binary compounds with nonmetals in which its oxidation state is +1. It also forms binary compounds with metals in which its oxidation state is −1. It is the lightest of all

gaseous elements. More compounds of this element are known than of any other element.

The group of elements whose symbols all contain the capital letter C possesses electronic structures with extraordinary stability. They do not react to form chemical compounds readily. They are all gases at room temperature. The element Ce ranks as the second least dense of all gases and has the lowest melting point of all elements. It can only be solidified under pressure. Cb is naturally radioactive and is a member of the Uranium-Radium series of radioactive metals. Ca, because of its inertness and comparatively greater abundance, is used as the gas in incandescent light bulbs to cut down the rate of evaporation of the filaments. When an electric discharge is passed through a tube containing Cf at low pressure, a brilliant red light is emitted. Cb, Cd, and Cc occur in very much smaller amounts than the other members of this family. Cd has a melting point and boiling point which are intermediate to those of Cb and Cc.

The elements to which the symbol D has been given are classified as active metals. They each decompose water readily with the evolution of hydrogen and the formation of hydroxides which are strong bases. They form ionic compounds with nonmetals in which they show an electrovalence of +1. Da is the most abundant of the group with Db ranking second in occurrence. The other four elements are much more rare and of lesser importance. Dc is the least dense of these metals and ranks along with Df at the top of the electromotive force series. De has been obtained in only very small quantities, is radioactive, and has been assigned an official name rather recently. Db has a metallic radius less than that of Dd and Df but greater than that of Dc and Da. Dd has a greater density than Db but is less dense than Df.

In the group to which the symbol G has been assigned the oxidation states possible may vary from −3 in the hydrides to +5 in certain oxides. Ge and Ga are distinctly nonmetallic in nature but as one proceeds down the group the metallic properties increase. Gc is sometimes classified as a metalloid since it possesses properties which are intermediate to those of the nonmetals above it and those of the more metallic Gb and Gd below it. Ge is a relatively unreactive element at ordinary temperatures and makes up about four-fifths by volume of the gases in the atmosphere. The strong ternary acid, $HGeO_3$, is an illustration of a compound of Ge in its highest oxidation state. The element Ga forms the oxide Ga_2O_5 when it is burned in air. This oxide reacts with water to produce the triprotic acid H_3GaO_4, which is a moderately strong acid. The element Ga exists in several allotropic forms in the solid state. It exists as a tetratomic molecule Ga_4 in the vapor state. Gd has physical properties which are mainly metallic, its chief use being as a component of low melting alloys. Its oxide Gd_2O_3 is the anhydride of the predominately basic but slightly soluble hydroxide $Gd(OH)_3$. Gb has a density, boiling point, and melting point which are intermediate with respect to those of its neighboring congeners Gc and Gd.

The six elements to which the letter R has been assigned form compounds of the following types: oxides RO, hydroxides $R(OH)_2$, carbonates RCO_3 and sulfates RSO_4. The metals of this family are less active than the alkali metals but are sufficiently active to necessitate their preparation by the electrolytic reduction of their fused chlorides. Rb and Rf react rather slowly with water at moderate temperatures, but as one proceeds down the group the metals react quite readily to displace hydrogen and form the hydroxides of the metals. Rd is the most abundant element of the group and is also the least dense. Rc is a naturally radioactive element, a member of the Uranium 238 series. Rb has the lowest melting point of the group and is of strategic importance as one of the constituents of light weight alloys. Ra is located in the second long period of eighteen elements. Its chemistry is closely parallel to that of Rd and Re, the three elements composing one of Dobereiner's triads. The density and metallic radius of Ra is intermediate to those of Rd and Re. Due to the low solubility of the sulfate of Re, the Re^{++} ion is used to test for the presence of sulfate ion in aqueous solutions. $ReSO_4$ may be swallowed without poisonous effects and is used in obtaining X-ray photographs of the alimentary tract. Rf is used for making windows for X-ray tubes since X-rays readily penetrate elements of low atomic number.

The family of elements to which the letter M has been assigned have as a member the element Ma which is the most electronegative and one of the most reactive of all the elements. The triad Mc,

Md, and Mb are closely related to each other in properties. They form gaseous binary compounds with hydrogen of the type HM, each of which is very soluble in water producing strong acids. Mc, Md, and Mb exist in the gaseous, liquid, and solid states, respectively, at room temperature. The strength of the elements as oxidizing agents increases in the order Mb, Md, Mc, to Ma, the latter element being the lowest one on the electromotive force series. The maximum oxidation number for this group is +7 and is illustrated by the ternary acids $HMcO_4$ and H_5MbO_6. Me is the least well known of this group and has just recently been given a name on the basis of its isolation from radioactive sources.

Element Ec is a nonmetal which shows oxidation states ranging from +4 to −4. Most of the chemical substances which constitute living matter contain this element. One of the allotropic forms of Ec is the hardest substance known. By contrast, element Eb is the important constituent of a large number of minerals which make up most of the rocks in the inorganic realm of nature, and ranks as the second most abundant element in the earth's crust. Ea is usually classified as a metalloid, and as one proceeds down the group the metallic character increases even more. Ed and Ee are quite dense, and their hydroxides in the bivalent states are predominately basic in nature. Different isotopes of Ee are the end products of the various radioactive series. Ea is the least well-known of this group and was not known at the time of Mendeleef's attempt at a periodic classification. However, he was able to predict its properties quite accurately on the basis of its location in the table.

The element Bd is the most abundant element in the earth's crust and is the most electronegative member of its group. Bc forms compounds in which its oxidation state varies from −2 to +6. The acid H_2BcO_4 is produced in greater quantities commercially than any other inorganic chemical. Although the group is classified as nonmetallic, there is an increase in the metallic nature with increasing atomic weight. For example, Bc is a nonconductor, of electricity; one of the allotropic modifications of Be has a small but measurable conductivity; while Bb is classified as a semiconductor. The hydrides H_2Bc, H_2Be, and H_2Bb, are gases. Ba is a radioactive element, a member of the Uranium-Radium series, and is the parent element of the end product of this series.

The element Aa is the most abundant metallic element of the earth's crust. Its oxide, Aa_2O_3, is the hardest of all naturally occurring substances except the diamond. Its hydroxide, $Aa(OH)_3$, is insoluble in water but is soluble in strong acids and also in strong bases. Ab is usually classified as a metalloid but resembles the nonmetallic elements in that its hydroxide H_3AbO_3 is weakly acidic. Pyrex glass contains about 12% of the oxide Ab_2O_3. The elements Ac, Ad, and Ae, are located in subgroup IIIb, and there is an increase in metallic character in the order given. The principal oxidation number of these metals is +3, but Ae also forms some compounds in which it exhibits a +1 oxidation state. Ac has an unusually low melting point for a metal, melting just slightly above room temperature.

Elements F, K, L, N, P, Q, J, W, and H are classified as transition metals and are discussed briefly in Chapter 24. Element K shows a maximum oxidation state of +4, but also exhibits a fairly stable +3 and a less stable +2 state. K ranks as the seventh most abundant metal, and its oxide KO_2 has considerable commercial importance as a white pigment in paints. Element N shows oxidation states of +2, +3, +4 and +5. Element P exhibits the principal oxidation states +2, +3 and +6 and got its name from the fact that its compounds are colored. L is a silver gray metal which is one of the most active of the transition metals, displacing hydrogen even from water at room temperature. It is located just below aluminum in the electromotive force series. L shows a maximum oxidation state of +7. Elements F, Q, and W are members of a subgroup which, for historical reasons, is still singly numbered. The element F is greatly strengthened when alloyed with small amounts of carbon and moderate amounts of other transition elements. W has a slightly larger atomic weight than Q even though its atomic number is one less than Q. Element H only forms one series of compounds in which it is bipositive. It is a relatively low melting metal whose main industrial use is to coat iron to protect it from rusting. It is located above hydrogen in the electromotive force series. J shows oxidation states of +1 and +2, and is the first element in the subgroup

known as the noble metals because of their relative inertness.

Elements S and Z are members of the Actinide series of rare earths. Z is the parent member of a radioactive series of elements bearing its name. One of the isotopes of Z and the artificially produced element S undergo nuclear fission when exposed to slow neutrons.

REPORT: Assignment C

The Periodic Classification of the Elements

*Name*_____

*Date*_____

*Section*_____

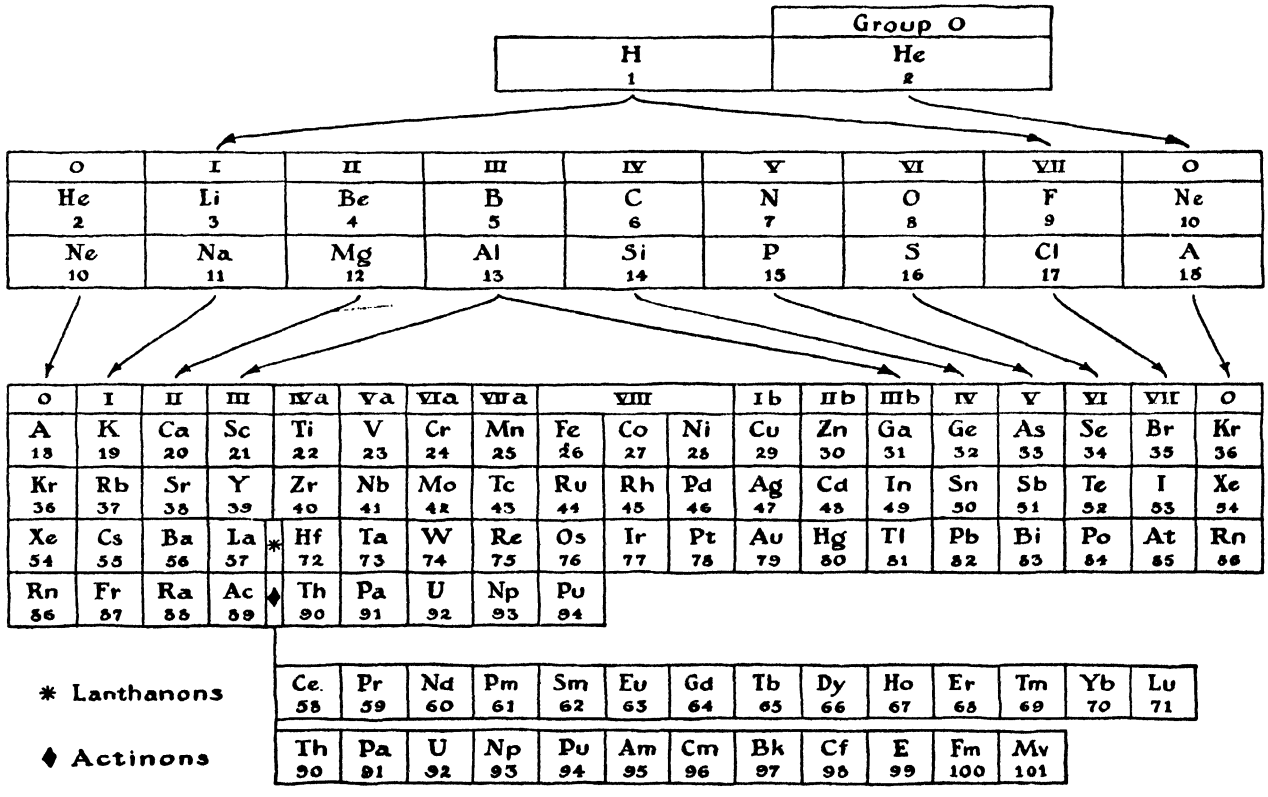
*Locker Number*_____

By means of a periodic table, it is possible to organize the 101 known elements into seven horizontal rows or periods and into eighteen vertical groups or subgroups of elements. The periods consist of one very short period of two elements, two short periods of eight elements each, two long periods of eighteen elements each, one very long period of thirty-two elements and another very long period which is incomplete. The latter two periods are compressed into the table by writing the fourteen rare-earth metals and the uranium metals below the chart. For a further description of the table, see *College Chemistry*, Chapter 5.

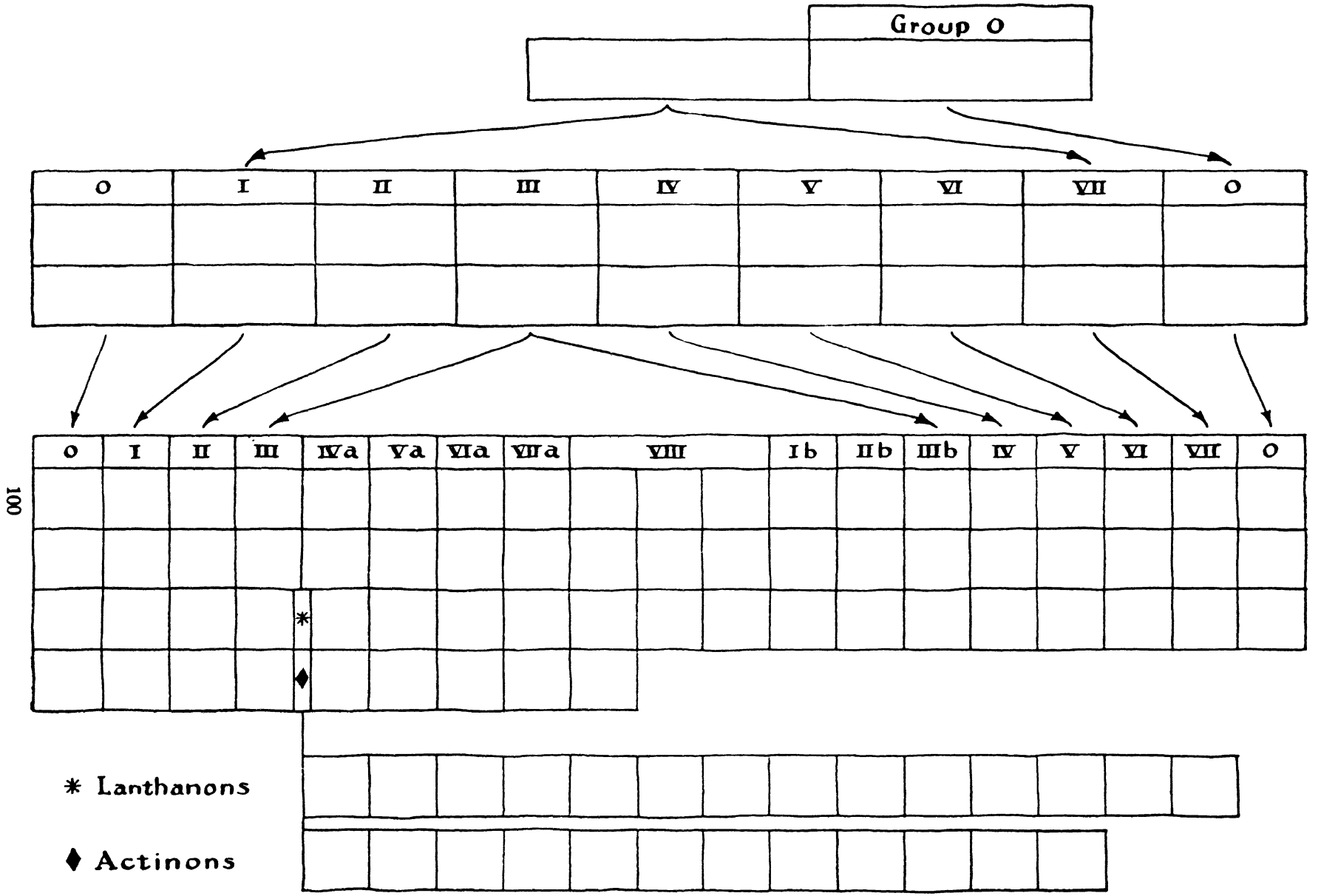
The increase of the maximum oxidation number of the elements from left to right across the table should be noted. Take the second period for example: Na^{+}, Mg^{+2}, Al^{+3}, Si^{+4}, P^{+5}, S^{+6}, Cl^{+7}. Another horizontal trend is the decrease in basicity and increase in acidity of the hydroxides of the elements from Group I to Group VII. For example: NaOH is a strong base; $Mg(OH)_2$ is basic; $Al(OH)_3$ is amphoteric; the hydroxide of silicon, $SiO(OH)_2$, is a weak acid usually written H_2SiO_3; $PO(OH)_3$ is a moderately strong acid (H_3PO_4); $SO_2(OH)_2$ is a strong acid (H_2SO_4); and $ClO_3(OH)$ is a strong acid ($HClO_4$).

The increase of the metallic nature of the elements in Groups I and II from top to bottom, and the increase in the nonmetallic nature of the elements in Groups V-Va, VI-VIa and VII-VIIa from bottom to top are examples of some of the vertical trends which should be noted.

Other trends in chemical and physical properties should be noted by referring to the numerous tables in Chapters 5 and 6 of *College Chemistry*, Second Edition.



THE PERIODIC SYSTEM OF THE ELEMENTS



THE PERIODIC SYSTEM OF THE ELEMENTS

The Equivalent Weight of a Metal. Ionic Valence — 15

College Chemistry, Chapters 6, 10

Review of Fundamental Concepts

Equivalent Weight

The term equivalent weight, as the adjective "equivalent" implies, is used to designate the relative amounts of substances which are chemically equivalent, that is, which just react with, or replace, one another in chemical reactions. We define *the equivalent weight of a substance* in a given reaction as that weight of it, in grams, which reacts with or replaces one gram-atomic weight (1.008 g) of hydrogen. Thus at each point of the connecting lines in Figure 15-1 below, we have indicated the amounts of several elements which are equivalent to one another.

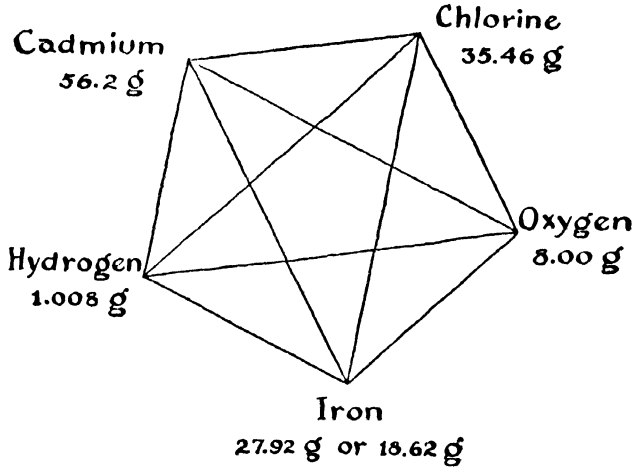


FIG. 15-1. Some equivalent weights of several elements.

56.2 g of cadmium, or 27.92 g of iron, is required by reaction with excess hydrochloric acid, to liberate 1.008 g of hydrogen. These are therefore the respective equivalent weights of cadmium and iron in these reactions. Likewise, in hydrochloric acid, 1.008 g of hydrogen is combined with 35.46 g of chlorine, which is therefore one equivalent of this element. This amount of chlorine, 35.46 g, is likewise the weight which is combined with 56.2 g of cadmium in cadmium chloride, and with 27.92 g of iron in ferrous chloride. Iron also forms another compound, ferric chloride, by direct reaction with chlorine, in which 35.46 g of chlorine is combined with 18.62 g of iron. The latter is therefore the equivalent weight of iron in this compound. The student can deduce other possible equivalent relationships from the diagram.

Equivalent Weight and Ionic Valence

The equivalent weights of certain elements, e.g. sodium, potassium, chlorine, and bromine, are found to be equal to their atomic weights. One gram-atomic weight of sodium or potassium may replace one gram-atomic weight of hydrogen, while one gram-atomic weight of the nonmetallic elements chlorine or bromine may unite with one gram-atomic weight of hydrogen. This means that these elements have a *valence* of one, (+1 for the two metals, and −1 for the two nonmetals)[1]. The equivalent weights of some other elements are simple fractional parts of their atomic weights. For example, the gram-atomic weight of cadmium is 112.41 g, while its equivalent weight is 56.2 g. Its valence is therefore two (+2) in its compounds. The valence, then, indicates the number of gram equivalent weights in one gram-atomic weight of an element.

$$\text{Ionic valence} = \frac{\text{gram-atomic weight}}{\text{gram equivalent weight.}}$$

The valence of an element is often stated as indicating the number of atoms of hydrogen an atom of the element unites with or replaces in forming a given compound. The valence of an element in a compound must always be a small *whole* number, as +1, +3, +4, or −2. The valence of all uncombined elements is always zero. (See Table XVI, Table of Ionic Valences, Appendix II.)

Some elements, such as iron in the previous examples, can have more than one equivalent weight, and correspondingly, will have *more than one possible valence.* In ferrous chloride ($FeCl_2$) where the equivalent weight of iron, 27.92 g, is one half of its atomic weight, 55.85 g, its valence is +2, while in ferric chloride ($FeCl_3$) where the equivalent weight of iron is one third of 55.85, namely 18.62, the valence of iron is +3.

[1] We are using the term valence here in the sense of "ionic valence," in which metallic ions, or cations, carry a positive (+) charge, and the nonmetallic ions, or anions, carry a negative (−) charge. Review Experiment 8, on valence.

Determination of the Equivalent Weight of a Metal

The equivalent weight of an active metal, when it reacts with an acid, is easily determined. A typical example of such a reaction is:

$$Cd + 2\,HCl = CdCl_2 + H_2.$$

A weighed sample of the metal is allowed to react with the acid, and the hydrogen that is produced is collected. Its volume is measured at the laboratory temperature and pressure, and calculated to the volume at standard conditions.

If we recall that the standard molal volume of a gas, as hydrogen, H_2, is 22.4 liters, then the volume of one gram-atom of hydrogen (1 H) at standard conditions, is 11.2 liters, or 11,200 milliliters. For convenience in calculations, then, we may restate our definition thus: *The equivalent weight of an active metal is that weight of it which will replace in an acid, 11,200 ml of hydrogen gas at standard conditions.*

Experimental Procedure

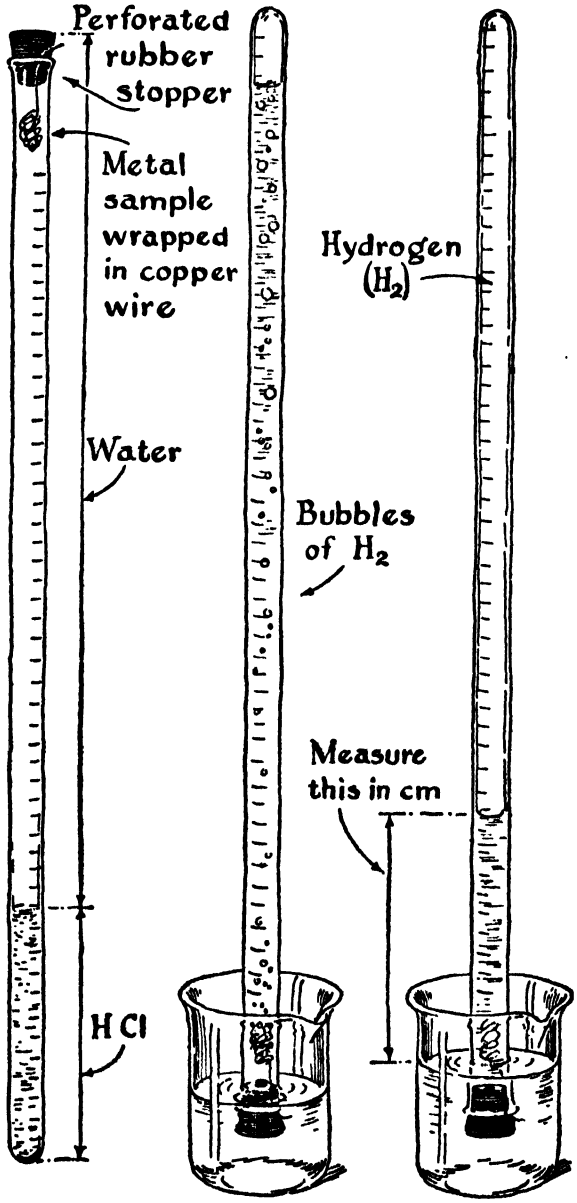


FIG. 15-2. To illustrate the method of handling a gas-measuring tube.

Special supplies: Analytical weights, 100-ml gas-measuring tube, 100° C thermometer. Pieces of Al, Mg, Zn, cut to size.

First heat 100 to 150 ml of tap water to boiling to remove dissolved air, and cool it under the water faucet to room temperature. Obtain a sample of the metal to be used (aluminum, zinc, or magnesium) which previously has been cut to such a size that not over 100 ml of hydrogen gas will be liberated. (Weights which will liberate about 80 to 95 ml of hydrogen are: 0.24 g Zn, 0.065 g Al, and 0.085 g Mg.) Clean the metal, if the surface is corroded, with emery cloth, and weigh it carefully to 0.001 g.[1] Wrap the piece of metal with a 20-cm length of fine copper wire in all directions in such a way as to form a little cage enclosing the metal. Leave 5 to 8 cm of the wire unwrapped, as a handle. (If a ribbon or wire form of the metal has been used, coil it rather tightly, and wrap the copper wire around the entire coil.)

Clean a 100-ml gas-measuring tube,[2] and put into it the required amount of concentrated HCl solution. Because of differences in the activity of the metals, it is necessary to vary the amount of acid accordingly. For magnesium use about 5 ml, and for aluminum or zinc use about 30 to 35 ml of concentrated HCl. Next slowly and carefully fill the entire tube to the very top with the cooled, boiled water, so as to avoid undue mixing with the acid.

[1] To the Instructor: Samples in wire or ribbon form may be cut to exact length to give a known weight, threaded through a small card, and individually issued to students by code number. The corrected volume of hydrogen obtained may then be reported by the student before he is given the weight, as a check on his calculations and data.

[2] If gas-measuring tubes are not available, you may, with slightly less precision, use a 100-ml graduated cylinder and a funnel (with the stem broken off) inverted in a beaker of water, as in Fig. 15-3. The graduated cylinder is filled with water. Add conc HCl, a little at a time, as needed, through another funnel, to the bottom of the beaker, where it will react with the metal encased in copper wire.

Insert the metal about two inches into the tube, leaving the end of the copper wire outside, and clamp it there by inserting a one or two-hole rubber stopper so that no air is entrapped in the tube. When all is ready, cover the end of the tube with your finger and invert it into a beaker partly filled with water. The acid, being more dense than water, stays down until inverted, and then quickly sinks and diffuses down the tube and reacts with the metal. The hydrogen liberated displaces the liquid from the tube. (Caution: If the reaction becomes too rapid, small hydrogen bubbles will escape from the bottom of the tube along with acid solution as it is expelled. In this case repeat the experiment, using less acid. If the reaction is too slow, use more acid.)

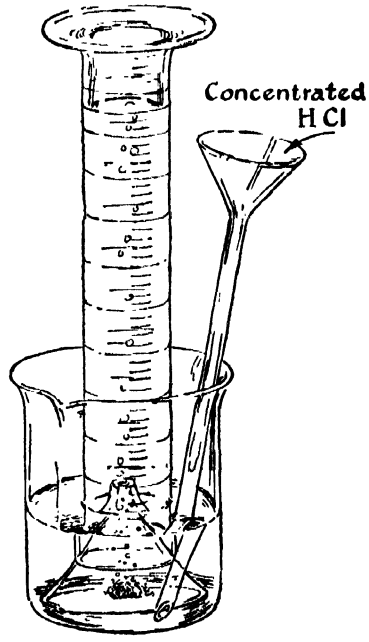


FIG. 15-3. A simple apparatus for the measurement of the volume of hydrogen gas evolved. See footnote 2, p. 102.

When the metal has completely dissolved, let the apparatus stand for a few minutes to allow it to cool to room temperature since heat is generated by the reaction. Any hydrogen bubbles adhering to the sides of the tube or copper wire may be freed by tapping the tube. If it is convenient, move the tube up or down so that the water in the tube is at the same level as the water in the beaker, but avoid warming the gas by contact of your hands with the tube. If this is not practical, measure the distance between the two water levels, using a metric rule, and recalculate this to its equivalent pressure in millimeters of mercury. Read and record the volume of gas in the tube. Take the temperature of the gas by holding a thermometer close beside the tube. Obtain the barometer reading for the day.

Calculate the weight of metal needed to liberate one gram-atom of hydrogen (11,200 ml at standard conditions). This is its equivalent weight. From this, calculate its valence.

Alternate Procedure:[1] Set up the apparatus as sketched in Figure 15-4. The exit tube C from the test tube must not extend below the rubber stopper (so that gas will not be trapped in the test tube). The longer glass tube should extend very nearly to the bottom of the test tube, and may best terminate in a capillary tip bent over toward the wall of the tube. The flask E, 500 or 1000 ml capacity, is filled with water, and the flask F is partially filled. The siphon tube D, extending to the bottom of both flasks, is likewise filled with water.

Place the carefully weighed sample of metal in the 15-cm test tube as indicated. It is well to have a fine copper wire wrapped in all directions about the metal, as a cage, and support this above the lower end of the glass tube, simply by leaving an extra length of the copper wire pointed downward. With the stopper in flask E loosened to permit air to escape, pour water into the funnel to completely fill the test tube and tubes B and C, and close clamp B. If flask E is not completely filled with water, raise flask F so that water siphons back into it, then push in the stopper in E tightly.

When all air bubbles have been thus removed from the apparatus, release clamps B and D just enough to permit the water level in the funnel to fall just to the stem top, *but no further*, then close the clamp B. Now empty and drain, but do not dry, flask F, leaving tube D filled with water. Replace the tube in the flask, leaving the clamp open. When all is ready, carefully measure 25.0 ml of conc HCl and place it in the funnel. Then release clamp B momentarily to permit a little acid to flow into the test tube and react with the metal at a

[1] This will give more experience with laboratory apparatus and techniques. It permits the use of larger samples, and other metals which react less rapidly with acid may be used, since the test tube may be warmed with a Bunsen burner to increase the rate, or the acid concentration may be increased during the experiment. The metals may be issued as unknowns. Maximum weights for a 500-ml flask E are about: Zn 1.10 g, Mg 0.40 g, Al 0.30 g, Fe 0.95 g.

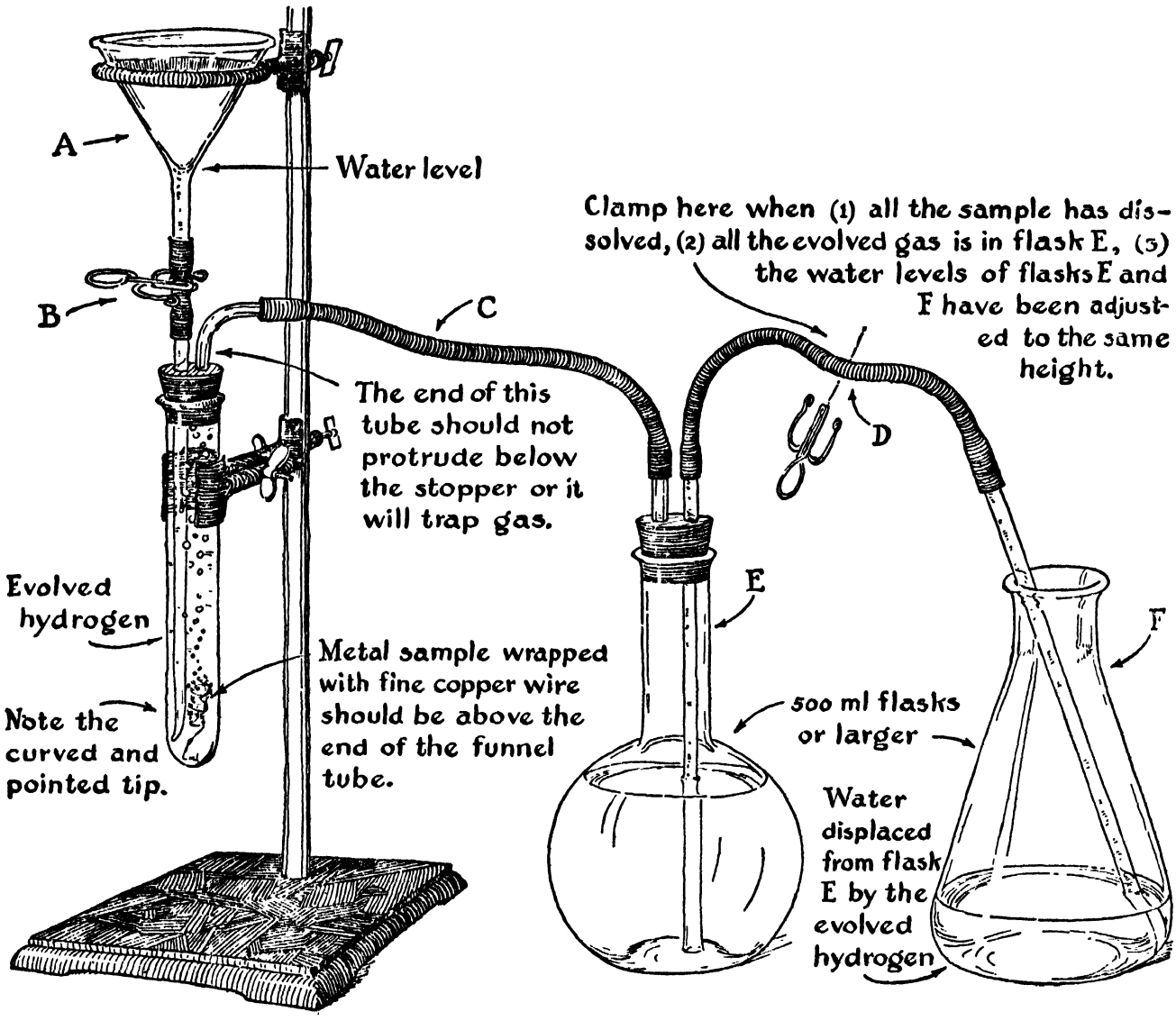


FIG. 15-4. An alternate apparatus for the determination of the equivalent weight of a metal.

moderate rate. Water will siphon from E to F in amount equivalent to the volume of hydrogen generated, which collects in E. When the metal has all dissolved and the apparatus has stood ten minutes to attain temperature equilibrium, release clamp B enough to permit the acid level to fall to the funnel stem, *but no further*. Carefully measure 25.0 ml of water, add to the funnel, and again release the clamp to let the level fall exactly to the funnel stem, then close the clamp tightly. All gas should now be displaced from the test tube and connecting tubes into flask E. If not, repeat the addition of a measured amount of water.

Adjust the levels in flasks E and F by raising or lowering one of them until they are even (do not warm the gas in E with your hands on the flask); then close clamp D tightly. Obtain the temperature of the hydrogen by removing the stopper enough to place a thermometer in flask E. Measure the volume of the water in flask F by pouring it into a 500-ml graduated cylinder. This volume minus the volumes of acid and water added to the funnel will be the volume of hydrogen generated. Obtain the barometer reading. Record all data on the report sheet, and calculate the equivalent weight of the metal.

REPORT: Exp. 15

The Equivalent Weight of a Metal

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Data	*1*	*2*
Weight of metal	g	g
Volume of hydrogen	ml	ml
Temperature of hydrogen	°C	°C
Barometric reading (uncorrected at .... °C)	mm	mm
Difference in water level inside and outside tube	mm	mm
Aqueous vapor pressure at temperature of hydrogen	mm	mm
Atomic weight of metal used		

	Calculations	*1*	*2*
Barometric pressure (corrected for scale expansion)		mm	mm
Mercury equivalent of difference of water levels		mm	mm
Pressure of H_2 after correction for difference in H_2O levels and for vapor pressure		mm	mm
Temperature, absolute		°K	°K
Volume of dry hydrogen at standard conditions		ml	ml
Equivalent weight of metal (from data)		g	g
Valence of the metal			
Theoretical equivalent weight of metal		g	g
Percentage error			

Problems

1. A certain metal has an equivalent weight of 68.7 g in a given reaction. Its valence is two in the compound formed. What is its atomic weight?

2. The equivalent weight of a certain metal is found to be 29.68 g. Its atomic weight is 118.70 g. What is the valence of the metal?

3. An element of gram atomic weight 58.69 g forms a compound in which its valence is +3. What is its equivalent weight? In another compound it manifests a valence of +2. What is its equivalent weight in this case?

4. 0.373 g of a certain metal replaces 250.0 ml of hydrogen, when collected over water at 25°C and 743 mm mercury pressure. What is the equivalent weight of the metal?

5. How many gram atomic weights of hydrogen under standard conditions would be liberated from hydrochloric acid reacting with one gram atomic weight of each of the following metals: Al, Mg, Ca, K, Zn, Na?

6. Calculate the weight of calcium which should be used with a 100-ml gas measuring tube, in order to liberate a convenient amount of hydrogen by reaction with an acid in an equivalent weight determination. Calculate on the basis of 85.0 ml of H_2 at standard conditions.

Answers

1_____g

2_____

3a_____g

b_____g

4_____g

5. G at of H_2 from:

Al _____

Mg_____

Ca _____

K _____

Zn _____

Na _____

6_____g

Ionic and Covalent Compounds. Ionic Reactions 16

College Chemistry, Chapters 10, 11

Review of Fundamental Concepts

Two Types of Chemical Bonds

When an active metal reacts with an active nonmetallic element, the metal becomes positively charged by the loss of one or more electrons to the nonmetal, which in turn becomes negatively charged. Each element tends to assume its most stable electronic configuration, with its outer electron energy level saturated—as in the noble gases. If we represent this outer level of electrons by dots, we may write, for example,

$$Na\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow Na^+ :\ddot{\underset{\cdot\cdot}{Cl}}:^-.$$

Such electrically charged atoms, or radicals, are called **ions.** The bonding force between such ions, which is due primarily to the attraction of unlike electrical charges, results in the formation of an **ionic bond.**

On the other hand, when two elements of more similar electropositive or electronegative character react, they do so by the formation of a stable electron pair, which is mutually attracted to both of the atomic nuclei, as in the examples

$$H\cdot + \cdot H \longrightarrow H:H, \text{ or } H_2,$$

and

$$2\,H\cdot + \cdot\ddot{\underset{\cdot}{O}}: \longrightarrow H:\ddot{\underset{H}{O}}:, \text{ or } H_2O.$$

Such a bond is called a **covalent bond.** In the second example, since oxygen is somewhat more electronegative than hydrogen, the bond is somewhat *polar*, or *partially ionic*, in character.

Electrolytes

Acids, bases, and salts either possess ionic bonds, or bonds which are quite polar, so that when these substances dissolve in water, the ions separate as independently moving particles, according to "ionization equations," such as

$$NaOH \longrightarrow Na^+ + OH^-,$$

and

$$K_2SO_4 \longrightarrow 2\,K^+ + SO_4^{--}.$$

In the case of solid salts, the ions are already present as the structural units in the crystal, so that when the salt is melted and this crystal structure broken down, the ions are free to move independently. The ionization of acids in water solution is discussed in a later paragraph.

Acids, bases, and salts are called **electrolytes,** because their water solutions conduct the electric current. Solutions of covalent compounds such as sugar ($C_{12}H_{22}O_{11}$), are **nonelectrolytes.**

The strong or active acids, bases, and most salts, ionize completely in dilute solution. In solutions of weak or slightly active acids and bases, a large part of the dissolved substance is present in molecular form, so that, although the total concentration may be high, the concentration of ions is low. This accounts for their slight activity. Relatively insoluble salts, although regarded as strong electrolytes in that all of the substance which is dissolved is present in ionic form, will likewise supply only a low concentration of ions to a solution.

Ions and Electrical Conductivity

Electricity, as carried by a metal wire, consists of a stream of electrons, which move along the wire from atom to atom. Electricity passing through a solution consists of a stream of negative ions moving toward the anode (positive electrode), and a stream of positive ions moving toward the cathode (negative electrode). In electrical conduction through solutions, a chemical change occurs at each electrode. Electrons are taken from the cathode, and electrons are deposited on the anode, by the ions undergoing the change.

These statements are illustrated by Figure 16-1. In this example, carbon electrodes dip into a rather concentrated solution of cupric chloride ($CuCl_2$), which contains cupric ions (Cu^{++}) and chloride ions (Cl^-). The positively charged cupric ions are attracted to the negative cathode and plate out as copper metal,

$$Cu^{++} + 2\,e^- \longrightarrow Cu.$$

Each of the substances, copper (Cu) and cupric ion (Cu^{++}), has its own distinctive properties. Cu

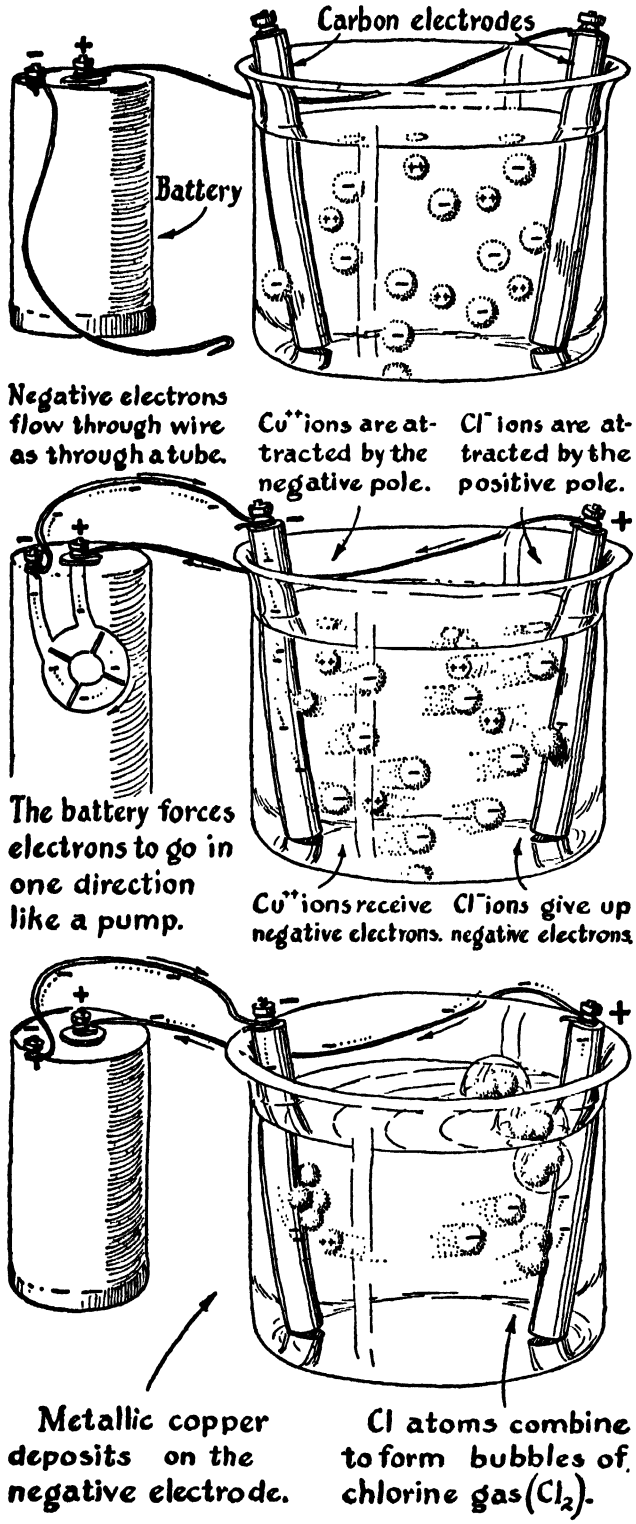


FIG. 16-1. The ionization and electrical conductivity of a rather concentrated cupric chloride solution. There are twice as many Cl^- ions (valence −1) as Cu^{++} ions (valence +2).

is reddish brown in color and can exist alone; Cu^{++} is blue and is always mixed with an equivalent amount of some negatively charged ion. Cu and Cu^{++} are *different substances*, differing in composition by two electrons.

Likewise, the negatively charged chloride ion, which is colorless and odorless, is attracted to the positive anode and gives up an electron to it, forming a neutral chlorine atom.[1] Two of these unite to form the greenish yellow, very corrosive, chlorine gas,

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^-.$$

Again, note that Cl^- and Cl_2 are *different substances.*

Ions as Individual Substances

Consider the common acids, with formulas HCl, HBr, HNO_3, and H_2SO_4. As pure substances they are each distinctive, with individual characteristics. But now place them in water and the solution possesses a list of common properties—the sour taste, the ability to dissolve active metals or to neutralize bases, and the ability to turn litmus red. These are the properties of hydrogen ion, written simply as H^+. But, also, the solutions are different, possessing respectively the properties of chloride ion (Cl^-), bromide ion (Br^-), nitrate ion (NO_3^-), and sulfate ion (SO_4^{--}). Any solution of an electrolyte is, thus, a mixture of at least two substances.

The Hydration of Ions

Since the hydrogen ion, as well as many others, is hydrated (combined with water), it is often written H_3O^+, called hydronium ion. (See Fig. 16-2.) According to the older viewpoint, using the simple formula, H^+, we write for the ionization of hydrochloric acid,

$$HCl \longrightarrow H^+ + Cl^-.$$

Using the hydrated formula, we write

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-.$$

The latter equation emphasizes the role of the solvent water in the ionization. The water molecule has a greater affinity for the simple hydrogen ion

[1] If a quite dilute solution of $CuCl_2$ were used, we should find that, with such a low concentration of chloride ions, the electrode reaction would be different. Water molecules would then be decomposed to supply the electrons needed, thus,

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-.$$

or proton (H^+) than has the chloride ion (Cl^-). Hence, the reaction takes place and two charged particles (ions) are produced. If hydrogen chloride gas is dissolved in some other solvent such as one of the many organic liquids, which are quite nonpolar, we find that the proton (H^+) is not attracted away from the chloride ion (Cl^-) by the solvent. As a result, hydrogen chloride is not an acid in such solvents.

Most ions are hydrated more or less in water solution. Thus, cupric ion attracts four molecules of water, $Cu(H_2O)_4^{++}$, and aluminum ion may attract six, $Al(H_2O)_6^{+++}$. These water molecules are held by covalent bonds. In this manual, for the sake of simplicity, we shall continue to use the simple unhydrated formula for most situations. You should recognize that whenever the formula H^+ is written, the more precise H_3O^+ is implied.

Ionic Equations

Previously, we have written the equation for a neutralization reaction, for example, with molecular formulas, as if actual molecules were the reacting particles,

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O.$$

Since electrical conductivity data and the chemical behavior of acids, bases, and salts indicate that their solutions consist of individual ions, it will be more nearly in accord with the facts to write the equation in terms of the principal substances (ions or molecules) actually present before, and after, the reaction. So we write

$$Na^+ + OH^- + H^+ + NO_3^- \longrightarrow Na^+ + NO_3^- + H_2O.$$

This is called a *total ionic equation.*

It is to be noted in this equation, that neither the Na^+ nor the NO_3^- have reacted—both are present as separate particles after, as well as before, the reaction. They may, therefore, be omitted, and the equation, which is now called a *net ionic equation*, becomes

$$OH^- + H^+ \longrightarrow H_2O.$$

Such an equation focuses attention on the essential changes—the disappearance of acid properties due to H^+, and of basic properties due to OH^-. The water formed is so slightly ionized that the concentration of these ions is too low to show their characteristic properties.

Ionic reactions occur whenever ions unite to form weakly ionized or insoluble substances. In the neutralization of nitric acid by sodium hydroxide, the net ionic equation shows that the only action occurring is the union of hydrogen ion and hydroxide ion to form water. The tendency for these ions to unite is the factor which causes the reaction to proceed. A similar reaction occurs when the ions of a weak acid or of a weak base unite as, for example,

$$NH_4^+ + OH^- \longrightarrow NH_4OH.$$

In the formation of the weak base ammonium hydroxide, the reaction is not as nearly complete as it is in the formation of water, for ammonium hydroxide has a far greater tendency to ionize than has water. A typical example of ions uniting to form an insoluble substance is expressed by the equation

$$Ca^{++} + CO_3^{--} \longrightarrow CaCO_3(s).$$

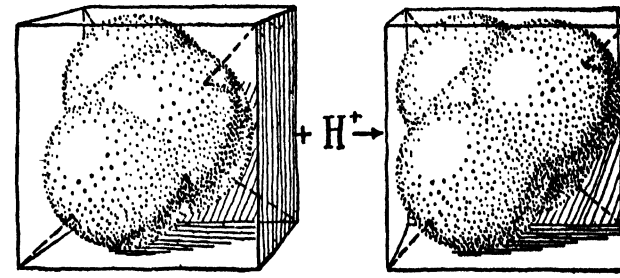
(The (s) indicates that $CaCO_3$ is a solid.) It makes no difference in the reaction whether calcium ion (Ca^{++}) is obtained from calcium chloride, calcium nitrate, or any other soluble calcium salt. Carbonate ion (CO_3^{--}) could be obtained equally well from sodium carbonate, ammonium carbonate, or any other soluble, well ionized carbonate. The chemical change, as recorded by the net ionic equation, is the same in each case.

It is also possible to change weakly ionized substances into substances which ionize to an even lesser extent. When ammonium hydroxide (NH_4OH) is neutralized by hydrochloric acid (HCl), the total ionic equation is

$$NH_4OH + H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O.$$

The net ionic equation is

$$NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O.$$



$$\begin{matrix} H \\ H \end{matrix}\!\!:\ddot{O}: + H^+ \longrightarrow \left[\begin{matrix} H \\ H \end{matrix}\!\!:\ddot{O}:H\right]^+$$

$$H_2O + H^+ \longrightarrow H_3O^+$$

FIG. 16-2. The formation of the hydronium ion by the attraction of a simple hydrogen ion, or proton (H^+), to an unshared pair of electrons on the oxygen atom of a water molecule.

Since ammonium hydroxide ionizes to a much greater extent than water, this reaction will proceed. It, however, will not be as complete as a neutralization in which the acid and base are both strong.

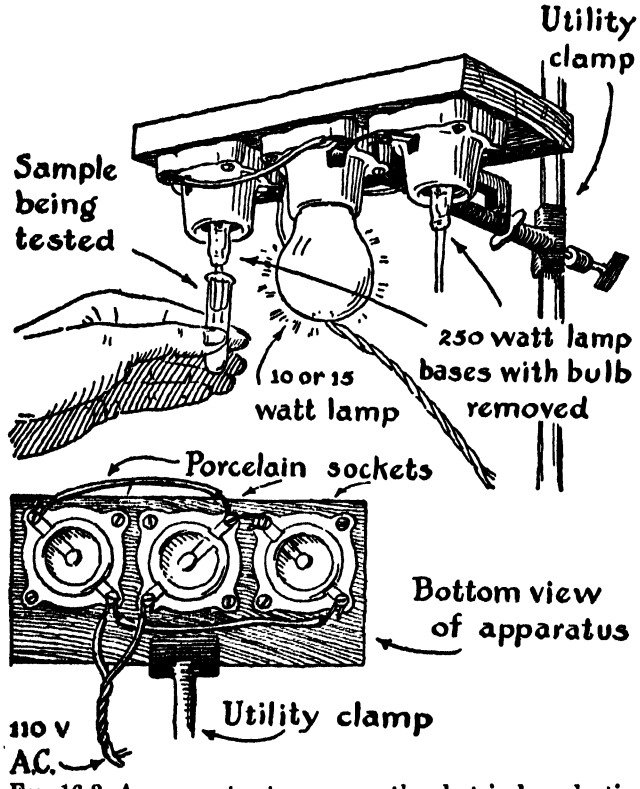


FIG. 16-3. An apparatus to compare the electrical conductivities of various solutions.

Again, the poorly ionized carbonic acid (H_2CO_3) contains fewer carbonate ions (CO_3^{--}) in solution than does a saturated solution of the relatively insoluble calcium carbonate ($CaCO_3$), so the reaction

$$CaCO_3(s) + 2\,H^+ \longrightarrow Ca^{++} + H_2CO_3$$

will take place. Furthermore, the carbonic acid is not stable, but breaks down into water and carbon dioxide.

Unless there is a tendency for the ions in a solution to unite, no reaction occurs. Thus, if a solution of ammonium nitrate, NH_4NO_3, (containing NH_4^+ and NO_3^-), and one of sodium chloride, NaCl, (containing Na^+ and Cl^-), are mixed, no reaction will occur; simply a mixture of the four kinds of ions will remain. The possible products, ammonium chloride, NH_4Cl, and sodium nitrate, $NaNO_3$, are soluble, highly ionized salts; they, therefore, do not form.

To summarize the technique of writing net ionic equations, note that this does not mean that *all* substances should *always* be written as ions. Poorly ionized, or slightly soluble substances, should be written as the un-ionized molecule.

The Experimental Method

By the measurement of the relative electrical conductivities of various pure substances, and their solutions, we shall obtain evidence concerning the presence and relative concentration of ions in these examples. We shall also trace the course of a number of reactions by comparing the electrical conductivities of the reactants with those of the products formed. We shall interpret these results in terms of the net ionic equation for the reaction.

Figure 16-3 shows a simple device for the comparison of electrical conductivities. In this, the filament support wires from two 250-watt light bulbs, with the glass bulbs removed, are screwed into porcelain bases. These are connected in parallel with one another, and in series with a 10 or 15-watt light bulb, and with the 110-volt alternating current. Thus, we may compare the separate conductivities of two different solutions, tested one at a time, or we may test the combined conductivities of both solutions.

Experimental Procedure

Special supplies: conductivity apparatus.

Chemicals: 17 *F* $HC_2H_3O_2$, 6 *F* $HC_2H_3O_2$, 0.1 *F* $HC_2H_3O_2$, C_2H_5OH, 0.1 *F* NH_4OH, 0.1 *F* $Ba(OH)_2$, C_6H_6, $CaCO_3$ (marble chips), 0.1 *F* $Cu(C_2H_3O_2)_2$, 0.1 *F* $CuSO_4$, $C_3H_5(OH)_3$, HCl in benzene, 0.1 *F* HCl, $KClO_3$, 0.1 *F* KNO_3, NaCl, 0.1 *F* NaCl, 0.1 *F* NaOH, $C_{12}H_{22}O_{11}$, 0.1 *F* H_2SO_4, mossy Zn.

Obtain an electrical conductivity apparatus of the type available in your laboratory, and determine the relative conductivities of the pure substances and solutions listed below. When testing solutions, use only 5 to 10 ml in a 10-cm test tube, a crucible, or a 50-ml beaker held at an angle. *Do not waste solutions by using unnecessarily large amounts.* Dip the conductivity wires in the solution to a uniform depth of about 1 cm each time, and have them at a uniform distance apart. Between each measurement, rinse the electrodes and

dry them with a piece of filter paper. **Caution: Disconnect the apparatus from the socket if the electrodes must be touched; keep your hands dry when using the apparatus.**

1. Electrolytes and Nonelectrolytes. By the above procedure, test the following, and classify each as a good, poor, or nonconductor of electricity.

(a) *Pure Substances:* (Save these for the next paragraph.) Water (distilled), alcohol 95% (C_2H_5OH), benzene (C_6H_6), glycerine ($C_3H_5(OH)_3$), glacial or 17 *F* acetic acid ($HC_2H_3O_2$), solid sugar ($C_{12}H_{22}O_{11}$), solid sodium chloride (NaCl), solid potassium chlorate ($KClO_3$).

(b) *Solutions:* To each of the above, except the distilled water and the benzene, which is insoluble, add about 5 ml of distilled water, mix to effect solution, and again test these with the conductivity apparatus.

(c) *Fused Salt:* Melt a little $KClO_3$ in a porcelain crucible, and test it, while molten, with the conductivity apparatus. Wash the electrodes *thoroughly* afterwards.

(d) *The Effect of the Solvent.* After drying the electrodes, test a solution of HCl gas (not hydrochloric acid solution in water) dissolved in benzene or toluene. (This is already prepared for your use.) Compare the conductivity with that of aqueous HCl as tested in the next paragraph.

(e) *A Comparison of Strong and Weak Acids and Bases.* Determine the relative conductivity of 5 to 10 ml each of 0.1 *F* HCl, 0.1 *F* $HC_2H_3O_2$, 0.1 *F* NaOH, and 0.1 *F* NH_4OH. Write equations to show the relative extent of ionization of each of the above substances. In doing this, use forward and reverse arrows. Vary the length of the arrow to indicate the desired tendency. Thus, $\longrightarrow$ means that the ionization is practically complete; $\rightleftharpoons$ means that the ionization takes place to only a moderate extent; and $\leftrightharpoons$ means that the ionization is quite weak.

Also, compare the above results of conductivity measurements with the physical and chemical properties of strong and weak acids, as follows:

1. Taste solutions of 0.1 *F* HCl and 0.1 *F* $HC_2H_3O_2$.

2. Compare the relative rates of reaction of 0.1 *F* HCl, 0.1 *F* $HC_2H_3O_2$, and HCl in benzene, on (a) marble chips ($CaCO_3$)—judge by the rate of evolution of CO_2 gas, and (b) mossy zinc—judge by the rate of evolution of H_2 gas.

2. Some Typical Ionic Reactions. Interpret the electricial conductivities of each of the following examples in terms of the solubilities and the extent of ionization of the substances involved.

(a) *A Mixture of Two Soluble Salts.* Determine the conductivities of 10-ml portions of 0.1 *F* NaCl, of 0.1 *F* KNO_3, and of their mixture. If the apparatus of Figure 16-3 is used, you can place the 0.1 *F* NaCl in contact with one electrode and the 0.1 *F* KNO_3 in contact with the other. Determine the total conductivity of the two solutions, separately, then mix them. Divide the mixture into the two containers and place these in contact with the electrodes. Note whether there is any change in the conductivity of the mixture as compared to that of the separate solutions. To what extent has a reaction taken place?

(b) *A Strong Acid with a Strong Base, to Form a Soluble Salt.* Prepare 50 ml each of 0.01 *F* HCl and 0.01 *F* NaOH by diluting 5 ml of the 0.1 *F* solutions of each to 50 ml with distilled water, and mixing these well. Test the conductivities of these separate 0.01 *F* solutions, and of a mixture of equal volumes of them, as in paragraph (a). In preparing the mixture, add a drop of phenolphthalein and carefully adjust the relative amounts to equivalence. How do you account for the slight decrease in the conductivity of the mixture as compared to that of the separate solutions? Write the total and the net ionic equations for the reaction.

(c) *A Weak Acid with a Weak Base, to Form a Soluble Salt.* In a similar manner, mix equal volumes of the 0.1 *F* $HC_2H_3O_2$ and the 0.1 *F* NH_4OH solutions, and compare the brilliance of the light with that of either the acid or the base solution alone. Explain the effect by writing the total and the net ionic equations for the reaction.

(d) *A Strong Acid with a Strong Base, to Form an Insoluble Salt.* As in paragraph (a), determine the conductivities of 0.1 *F* H_2SO_4 and of 0.1 *F* $Ba(OH)_2$ solutions. Are these highly ionized? While the electrodes are dipping in the H_2SO_4 solution, add a drop of phenolphthalein and then add the $Ba(OH)_2$ solution gradually, with stirring, until the exact equivalence point is reached as indicated by the change in color of the phenolphthalein. (With care, you can adjust the relative amounts of acid and

base so that the light ceases to glow.) Explain, and write the total and net ionic equations for the reaction.

(e) *A Salt of a Strong Acid, with a Weak Acid, to Form an Insoluble Salt.* First determine the conductivity of 0.1 *F* $CuSO_4$ solution, and of a solution made by bubbling H_2S gas[1] through 10 ml of distilled water, to saturate it. This gives an approximately 0.1 *F* H_2S solution. Then pass H_2S gas directly into the 0.1 *F* $CuSO_4$ solution for two or three minutes in order to precipitate the cupric sulfide, CuS, as completely as possible. Test the conductivity of the solution. Does the presence of the solid CuS materially contribute to the conductivity of the mixture? Why or why not? Write the total and the net ionic equations for the reaction, and explain any difference in conductivity in terms of the ions present.

(f) *A Salt of a Weak Acid, with a Weak Acid, to Form an Insoluble Salt.* Determine the conductivity of 0.1 *F* $Cu(C_2H_3O_2)_2$ solution, then saturate about 5 to 10 ml of this solution with H_2S gas to precipitate the cupric sulfide completely, and again determine the conductivity of the solution. Write the total and the net ionic equations for the reaction. Explain the difference in conductivity in terms of the ions present.

[1] Consult your instructor as to the method of obtaining H_2S gas in your laboratory. A cylinder of the compressed gas, or a Kipp generator charged with ferrous sulfide sticks and 6 *F* HCl, is frequently used. A commercial preparation of sulfur and a paraffin hydrocarbon, with asbestos added, is available from the Henga Co., 1833 Chestnut St., Philadelphia, Pa., or from various laboratory supply houses. On heating this substance in a test tube, H_2S gas is liberated. See also Figure F-4, Page 292.

REPORT: Exp. 16

Ionic and Covalent Compounds. Ionic Reactions

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Review Questions

The substance present in all acids which accounts for their common properties is: _____

Four ways (composition or properties) in which this substance differs from hydrogen molecules are:

(1)_____

(2)_____

(3)_____

(4)_____

What is the difference in composition between (a) a chloride ion and a chlorine atom? (b) a sodium ion and a sodium atom?

1. Electrolytes and Nonelectrolytes. Indicate after each substance whether it is relatively a good, poor, or nonconductor of electricity:

Distilled water_____	Glycerine_____	Solid NaCl_____
Alcohol_____	Glacial acetic acid_____	Solid $KClO_3$_____
Benzene_____	Solid sugar_____	Fused $KClO_3$_____

On the basis of your conductivity data of solutions, write beside the substances shown to be electrolytes, the formulas of any ions present in the solution, and beside the nonelectrolytes, the formulas of the molecular species in solution.

Sugar_____	Glycerine_____	Ammonium hydroxide_____
Sodium chloride_____	Sodium hydroxide_____	Acetic acid_____
Alcohol_____	Potassium chlorate_____	HCl in water_____
		HCl in benzene_____

Can you suggest a reason for the difference in the behavior of HCl dissolved in water, and in benzene?

How do you explain the difference in the conductivity of solid $KClO_3$ and of fused $KClO_3$?

List the relative electrical conductivities of the acids and bases tested, and write the ionization equations for each, indicating the relative extent of ionization by the relative length of forward and reverse arrows:

	Conductivity	*Equation*
0.1 *F* HCl		
0.1 *F* $HC_2H_3O_2$		
0.1 *F* NaOH		
0.1 *F* NH_4OH		

Compare 0.1 *F* HCl and 0.1 *F* $HC_2H_3O_2$ as to (1) taste, (2) reactivity with $CaCO_3$, and with zinc:

2. Some Typical Ionic Reactions. (a) *A Mixture of Two Soluble Salts.* The relative conductivities of the salt solutions tested are as follows:

0.1 *F* NaCl _____ 0.1 *F* KNO_3 _____ Mixture _____

The substances present before the solutions are mixed are (use ionic formula if ionized, molecular formula if un-ionized): _____

The substances present after the solutions are mixed are: _____

Comment on the extent to which any chemical reaction has actually occurred: . . . . . _____

(b) *A Strong Acid with a Strong Base, to Form a Soluble Salt.* The relative conductivities of the solutions tested are as follows:

0.01 *F* HCl _____ 0.01 *F* NaOH _____ Mixture _____

The total ionic equation for the reaction is: _____

The net ionic equation is: _____

Interpret any change in conductivity of the solutions, before and after mixing, with the above equations:

(c) *A Weak Acid and a Weak Base, to Form a Soluble Salt.* The relative conductivities of the solutions tested are as follows:

0.1 *F* $HC_2H_3O_2$ _____ 0.1 *F* NH_4OH _____ Mixture _____

The total ionic equation for the reaction is: _____

The net ionic equation is: _____

Interpret any change in conductivity of the solutions, before and after mixing, with the above equations:

(d) *A Strong Acid with a Strong Base, to Form an Insoluble Salt.* The relative conductivities of the solutions tested are as follows:

0.1 *F* H_2SO_4_____ 0.1 *F* $Ba(OH)_2$_____ Mixture_____

The solid substance formed by the reaction is: _____

The total ionic equation for the reaction is: _____

The net ionic equation is: _____

Interpret any change in conductivity of the solutions, before and after mixing, in accord with the above equations:

(e) *A Salt of a Strong Acid, with a Weak Acid, to Form an Insoluble Salt.* The relative conductivities of the solutions tested are as follows:

0.1 *F* $CuSO_4$_____ 0.1 *F* H_2S_____ Mixture_____

The total ionic equation for the reaction is: _____

The net ionic equation is: _____

Interpret any change in conductivity of the solution, before and after passing in H_2S gas, in accord with the above equations:

(f) *A Salt of a Weak Acid, with a Weak Acid, to Form an Insoluble Salt.* The relative conductivities of the solutions tested are as follows:

0.1 *F* $Cu(C_2H_3O_2)_2$_____ Mixture with H_2S_____

The total ionic equation for the reaction is: _____

The net ionic equation is: _____

Interpret any change in conductivity of the solution, before and after passing in H_2S gas, in accord with the above equations:

Interpretation of Data

1. Underline the formulas of the following substances which the experiment would lead you to believe would have many properties in common. (Other than similar electrical conductivity.)

A. NaCl, HNO_3, C_2H_5OH, H_2SO_4.
B. HNO_3, KNO_3, Na_2SO_4, $CuCl_2$.

2. Underline the formulas of the substances whose aqueous solutions are good conductors of electricity:

$NH_4C_2H_3O_2$, NH_4OH, $NaOH$, $C_3H_5(OH)_3$, $HC_2H_3O_2$

3. Underline the formula of a substance which ionizes completely in solution, but for which it is impossible to prepare a solution with a high concentration of its ions:

$BaSO_4$, Na_2SO_4, $BaCl_2$, NH_4OH, C_2H_5OH

4. Underline the formula of each substance which is very soluble in water, but whose water solution cannot contain a high concentration of its ions:

$BaSO_4$, Na_2SO_4, $BaCl_2$, NH_4OH, C_2H_5OH

5. From data obtained from this experiment or from Tables X and XI in Appendix II, write, after the formula of each substance listed below, the formula or formulas of the principal substances found in the solution, and the molecular formula with a small (*s*) after it if the substance is insoluble. Four of the items are answered as examples.

$HC_2H_3O_2$ — *$HC_2H_3O_2$*	Sugar — *$C_{12}H_{22}O_{11}$*	$BaSO_4$ — *$BaSO_4(s)$*
NaCl — *Na^+, Cl^-*	NH_4OH	Na_2CO_3
Na_3PO_4	K_2SO_4	H_2CO_3
Glycerine	$PbSO_4$	$CaCO_3$
$Mg(OH)_2$	HCN	$Ba(OH)_2$

Application of Principles

Using information when needed from Tables X and XI in Appendix II, write in the space at the right the formulas of the principal ions or molecules found in the mixture when the substances listed at the left are allowed to react. If a solid molecular substance is produced, underline the formula. Assume that water is present so that soluble, strong electrolytes will be represented by ions, not molecules. Also assume that equivalent amounts are used. *Note:* Use coefficients preceding formulas *only* when expressing definite amounts of substances, but not when just writing the formulas.

(1) $Ba(OH)_2$ and HCl — *Example: Ba^{++}, Cl^-, H_2O*

(2) $BaCl_2$ and Na_2CO_3

(3) NaCl and $AgNO_3$

(4) $NaC_2H_3O_2$ and NaCl

(5) $Fe(NO_3)_3$ and KOH

(6) $ZnSO_4$ and $K_4Fe(CN)_6$

(7) $Cu(C_2H_3O_2)_2$ and H_2S

(8) Mg and H_2SO_4

(9) NaOH and $HC_2H_3O_2$

(10) CuS and KNO_3

(11) KOH and HNO_3

(12) Zn and $CuSO_4$

(13) NH_4Cl and $Ba(OH)_2$

(14) NH_4OH and HNO_3

(15) NH_4Cl and $CuSO_4$

(16) $CaCO_3$ and HNO_3

Oxidation-Reduction 17

College Chemistry, Chapter 12

Review of Fundamental Concepts

Two Fundamental Types of Chemical Reactions

Chemical processes may be divided into two general types.

(1) The simpler of these types involves all those reactions in which there is no change in valence of any of the atoms taking part in the reaction. Such reactions include: The union of two ions to form a precipitate or slightly ionized substance, the solution of soluble substances to form the ions, and the formation of complex ions. Complex ions may be formed by the union of two kinds of ions or by the union of ions with neutral molecules. Familiar examples of these are the following:

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4,$$
$$H^+ + OH^- \longrightarrow H_2O,$$
$$Na_2SO_4(\text{solid}) \longrightarrow 2\,Na^+ + SO_4^{--},$$
$$Ag^+ + 2\,NH_3 \longrightarrow Ag(NH_3)_2^+.$$

(2) On the other hand, many reactions which we have studied involve changes in valence, or electrical charge, and are classed as *oxidation-reduction processes.* These may involve such simple types as the replacement of one element in a compound by another, the direct union of two elements, and the decomposition of a compound into its elements. Other types are more complex in nature, as illustrated by the last of the following examples.

Reaction	*Element Oxidized*	*Element Reduced*
$Cu + 2\,Ag^+ \longrightarrow 2\,Ag + Cu^{++}$	copper	silver
$2\,H_2 + O_2 \longrightarrow 2\,H_2O$	hydrogen	oxygen
$2\,HgO \longrightarrow 2\,Hg + O_2$	oxygen	mercury
$2\,Fe^{+++} + Sn^{++} \longrightarrow 2\,Fe^{++} + Sn^{++++}$	tin	iron
$16\,H^+ + 10\,Cl^- + 2\,MnO_4^- \longrightarrow 2\,Mn^{++} + 5\,Cl_2 + 8\,H_2O$	chlorine	manganese

Note that in each case the element which is oxidized either increases in positive valence (copper, hydrogen, tin), or decreases in negative valence (oxygen, chlorine). The substance which is reduced (silver, oxygen, mercury, iron, manganese) undergoes the reverse change, decreasing in positive valence or increasing in negative valence. A graphical interpretation of these facts is given by Figure 17-1.

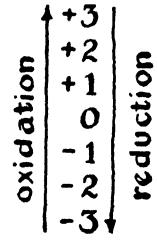


FIG. 17-1. A change in oxidation number involves oxidation and reduction.

Oxidation-Reduction and Electron Transfer

According to the modern view of atomic structure, when an element or simple ion undergoes a change in its ionic valence (that is, its electrical charge) it does so by gaining or losing electrons. *An oxidation process always involves a loss of electrons.* Correspondingly, *a reduction process always involves a gain of electrons.* In any chemical reaction where there is such a transfer of electrons, both oxidation and reduction must occur simultaneously. These processes may be written as separate "half-reactions." In the reaction of metallic copper with silver ion, the copper is oxidized to cupric ion with the resultant loss of two electrons:

$$Cu \longrightarrow Cu^{++} + 2\,e^- \text{ (oxidation—loss of electrons)}$$

At the same time, silver ions gain the electrons lost by the copper:

$$2\,Ag^+ + 2\,e^- \longrightarrow 2\,Ag \text{ (reduction—gain of electrons).}$$

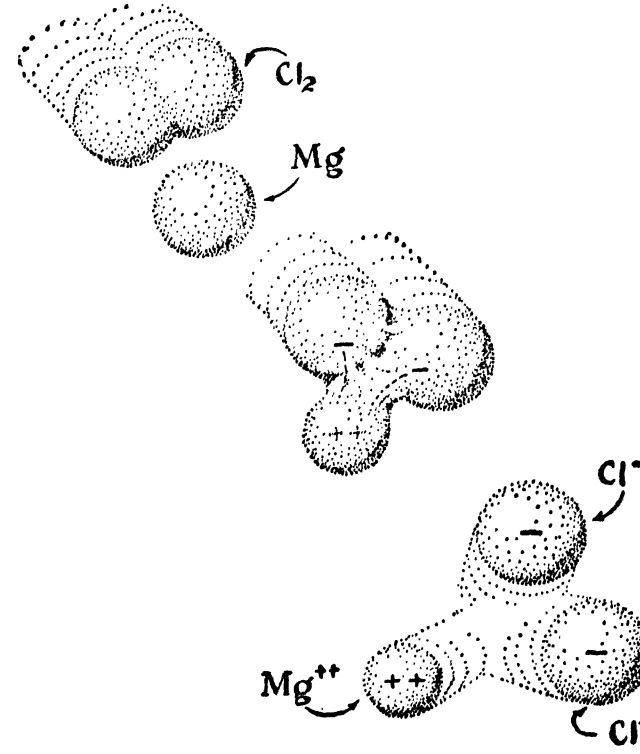


FIG. 17-2. Oxidation-reduction and electron transfer. When chlorine, Cl_2, reacts with magnesium metal, two electrons are transferred from one magnesium atom to two chlorine atoms.

As another example, we may refer again to the last of the examples of oxidation-reduction given earlier in this section, namely, the rather complicated case of the reaction of Cl^- in acid solution with MnO_4^-. Here the 10 Cl^- are oxidized to 5 Cl_2,

$$10\ Cl^- \longrightarrow 5\ Cl_2 + 10\ e^- \text{ (oxidation—loss of electrons),}$$

and the 2 MnO_4^- are reduced to 2 Mn^{++},

$$2\ MnO_4^- + 16\ H^+ + 10\ e^- \longrightarrow 2\ Mn^{++} + 8\ H_2O \text{ (reduction—gain of electrons).}$$

It is necessary to use 16 H^+ to react with the combined oxygen, giving 8 H_2O. The total charges on the ions used are, 2 (−) for the 2 MnO_4^- and 16 (+) for the 16 H^+, or a net of 14 (+) charges on the left. On the right side of this reduction process, we have 4 (+) for the 2 Mn^{++}. It is, therefore, necessary to write in 10 e^- on the left, in order to make this "half-reaction" balance electrically. We see, then, that the 10 Cl^- lose the same number of electrons that the 2 MnO_4^- gain. These quantities are, therefore, *equivalent* from the standpoint of oxidation-reduction. Note that we have arrived at these equivalent quantities from the number of electrons lost and gained in the half-reaction processes, and have not found it necessary to make any assumptions as to the valence of individual atoms in the ions or molecules.

The Oxidation State of an Element

In the calculation of the valence change in oxidation-reduction reactions, it frequently is an advantage to ascribe a definite **oxidation number or oxidation state** to each element in the compound. In binary compounds of metals with nonmetals, this oxidation number is the same as the ionic valence of the elements concerned. Thus, we have an oxidation number of +2 for iron in Fe^{++}, or $FeCl_2$, and of +1 for silver and −2 for oxygen in silver oxide, Ag_2O. In ammonia, NH_3, in which the bonds are quite covalent in type, the nitrogen is the more electronegative element, so we assign the oxidation number of −3 to nitrogen, and +1 to hydrogen.[1] Any element in its free state, as zinc metal, Zn, or hydrogen gas, H_2, has an oxidation number of zero.

In compounds of three or more elements, the elements hydrogen, oxygen, and the alkali and alkaline earth metals, etc., are assigned their usual oxidation numbers. A third element in the compound is then given such an oxidation number as will make the algebraic sum of the charges of all the elements in the neutral molecule add up to zero. Thus, in H_2SO_4 we have two positive charges due to the two hydrogen atoms, and eight negative charges due to the four oxygen atoms. The sulfur must then have a charge or oxidation state of +6. Similarly, the oxidation state of N in HNO_3 is +5, of P in H_3PO_4 is +5 and of Cr in $K_2Cr_2O_7$, is +6. Note in the last case that the sum of +2 (due to potassium) and −14 (due to oxygen) gives a total of −12, which is balanced by the opposite charges due to *two* Cr atoms, so the oxidation state of Cr is +6.

The charge of an ion must be considered in the calculation of the oxidation state of a given element in the ion. Thus, in MnO_4^-, there are eight negative charges due to oxygen. The oxidation state of Mn must therefore be +7, if the ion as a whole is to have a charge of −1. Likewise, in sulfite ion (SO_3^{--}), we have six negative charges due to oxygen, so the oxidation state of sulfur must be +4, to account for the total ionic charge of −2.

The assignment of a particular charge to an individual element in a compound or ion is quite arbitrary, since it is only in the extremely polar valence bonds that we are justified in assuming a complete transfer of an electron from one atom to another. In many cases, particularly those involving carbon atoms, the bonding electron pair is shared by both atoms, so that the valence bond is more or less non-polar. However, in many cases, the assignment of a definite charge or valence number to an element serves as a useful device in the classification of the different oxidation states of an element.

The Relative Strength of Oxidizing and Reducing Agents

The strength of an oxidizing agent depends on its tendency to gain additional electrons. Likewise, the less attraction a substance has for electrons which it already possesses, the stronger reducing agent it will be. Thus, silver ion is a stronger oxidizing agent than cupric ion because the reaction

$$2\ Ag^+ + Cu \longrightarrow Cu^{++} + 2\ Ag$$

takes place as indicated, but not in the reverse direction. That is, silver ion has a strong enough attraction for electrons to take them away

[1] See Figure 11-11 in *College Chemistry*, on the electronegativity scale of the elements.

from copper atoms. It is possible to arrange the various oxidizing and reducing agents as "oxidation-reduction couples" in a series according to their relative tendencies to gain or lose electrons. (See Table XIII, Appendix II, Oxidation-Reduction Potentials.)

Preliminary Exercise

Before performing the experiment, complete the preliminary exercise in the report sheet, showing the substances oxidized and reduced in the several equations given, and the change in oxidation state of each.

Experimental Procedure

Chemicals: metal strips (about 5 mm x 15 mm) of Cu, Pb, Fe, Ag, Sn, Zn; saturated Br_2 water, CCl_4, saturated Cl_2 water, Cu turnings, 0.1 *F* $Cu(NO_3)_2$, 0.1 *F* I_2, Fe filings, 0.1 *F* $FeCl_3$, 0.1 *F* $Pb(NO_3)_2$, 0.1 *F* $Hg_2(NO_3)_2$, 0.1 *F* KBr, 0.1 *F* $K_4Fe(CN)_6$, 0.1 *F* $K_3Fe(CN)_6$, 0.1 *F* KI, $KMnO_4$ cryst., 0.1 *F* $AgNO_3$, 0.1 *F* $SnCl_2$, 0.1 *F* $Zn(NO_3)_2$.

In this experiment, we shall determine qualitatively in the laboratory the relative position of a limited number of oxidation-reduction couples in the potential series. We shall start with only three metals and their ions, and in subsequent sections gradually include more couples until we have considered thirteen in all.

1. A Simple Potential Series for the Metals. (a) Place a small strip of copper in 3 ml of 0.1 *F* zinc nitrate solution, and a small strip of zinc in 3 ml of 0.1 *F* cupric nitrate solution. Which is the stronger reducing agent, copper or zinc? Now try a small strip of lead (sandpaper it if necessary) in cupric nitrate and also in zinc nitrate solutions. Try also copper and zinc strips in lead nitrate solution. Write equations wherever reactions occur. Compare the strength of lead as a reducing agent with that of copper and of zinc. Prepare a table by arranging the symbols of these three metals in a vertical column, placing the strongest reducing agent at the top, and the weakest at the bottom. To the right of each metal, make a dash, followed by the symbol for the oxidized form of the metal, thus $Me-Me^{++}$. You now have a brief "oxidation-reduction potential series." Which is the stronger oxidizing agent, lead ion or cupric ion? Why do the lead pipes used in draining laboratory sinks frequently corrode and develop leaks? Be specific in your answers.

2. Other Metals in the Potential Series. Now expand your series to include the couples, H_2-H^+, $Sn-Sn^{++}$, $Fe-Fe^{++}$, $Ag-Ag^+$, and $Hg-Hg_2^{++}$. To do this, try various combinations of the sandpapered metal strips with 3-ml portions of the nitrates or chlorides of other metals. *Try only* the combinations necessary for you to determine the position of each $Me-Me^{++}$ couple in the series. Use only ferr*ous*, not ferr*ic*, salts. Try only mercur*ous*, not mercur*ic*, nitrate on silver and copper metals. Free mercury need not be used. In cases of doubt as to reaction, rub the metal surface with your finger to note any deposit formed. You may not be able to determine the relative position of iron and zinc, since such electropositive metals do not plate out readily in water solution. Zinc is the stronger reducing agent. Likewise, tin and lead are so nearly the same that it is difficult to get a replacement. Tin is a slightly stronger reducing agent than lead. In determining the position of the H_2-H^+ couple, use hydrochloric acid. Nitric acid cannot be used here because nitrate ion in acid solution is a much stronger oxidizing agent than hydrogen ion and the results therefore would be confusing. Write the net ionic equations for all cases in which you obtained a reaction. Arrange your potential series, including these couples with the three from the preceding paragraph, first on scratch paper. When you have decided on the right order, enter them on the report sheet. Name the strongest oxidizing agent and the strongest reducing agent thus far included in your series.

3. The Oxidizing Power of the Halogens. Review the results of the replacement reactions of the free halogens and halide ions, as carried out in Experiment 14, paragraph (4). If you did not do this, carry out that procedure now. Re-write the equations for all reactions which occurred, and interpret the results by arranging the halogens and their ions in a potential series. Again place the strongest *reducing* agent (Is this the free element or the ion?) at the *top* and at the *left* side of the couple. The strongest oxidizing agent will be at the bottom, on the right.

4. The Ferrous Ion—Ferric Ion Couple. Determine whether ferric ion is a stronger or a weaker oxidizing agent than iodine or bromine, by adding 1 ml of 0.1 *F* $FeCl_3$ to 2 ml each of 0.1 *F* KBr and

of 0.1 *F* KI. Add a little carbon tetrachloride and shake to note the formation of any free halogen. The presence of any ferrous ion in the solution may be tested by adding a little potassium ferricyanide solution, which gives the deep blue ferrous ferricyanide $Fe_3(Fe(CN)_6)_2$ precipitate. Write equations for any cases in which the ferric ion is reduced; note that it does not go to metallic iron. Place the $Fe^{++}-Fe^{+++}$ couple in its proper place in your potential series of the halogens.

5. The Manganous Ion—Permanganate Ion Couple. Try the action of a little potassium permanganate (add several small crystals of the solid) in 3 ml of 6 *F* HCl. Warm, and note the odor. (See previous discussion for this equation.) Place the $Mn^{++}-MnO_4^-$ couple in your potential series.

6. The Reaction of the Halogens with Metals. Are the halogens strong enough oxidizing agents to oxidize the metals to the corresponding metal ions? To decide this, add bromine water to a little fine iron filings in a test tube. Try also the action of fine copper turnings with bromine water. Shake each mixture a few minutes, decant the solutions into clean test tubes, boil a moment to remove all free bromine, and test for the presence of bromide ion by adding a few drops of silver nitrate solution. To test for the presence of ferric ion and also of cupric ion, add a little potassium ferrocyanide reagent to each solution. Ferric ion gives a deep blue ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ precipitate, while cupric ion gives the maroon cupric ferrocyanide $Cu_2[Fe(CN)_6]$. It is also possible to oxidize silver or mercury metals by means of the halogens. It should be noted, however, that when a metal such as silver is reacted on by a halogen, a precipitate, as AgI, is formed, which keeps the Ag^+ at a low concentration. Under these conditions (low Ag^+ concentration), silver metal is a stronger reducing agent than when it is in the presence of 1 *F* Ag^+. Why? As a matter of fact the $Ag-Ag^+$ and the $Hg-Hg_2^{++}$ couples are below the I^--I_2 and the $Fe^{++}-Fe^{+++}$ couples but above the Br^--Br_2 couple.

7. Summary. You should now be able to combine the two separate potential series you have developed into one general oxidation-reduction potential series, which shows the relative tendencies of the various elements and ions studied to lose electrons. Note that each couple is written so that the change reading from left to right represents the loss of electrons. Along the left side of your list, write "Reducing Agents," and along the right side write "Oxidizing Agents." Which end of the left column represents the strongest (S) reducing agents? Which the weakest (W)? Label these positions with an S and W. Which end of the right column represents the strongest oxidizing agent? Which the weakest? Label these with an S and W.

Such a table as this may be expanded to include many more oxidation-reduction couples, and is useful in predicting the course of many reactions. (Table XIII, App. II.) Any reducing agent (on the left) will have the possibility of reacting with any oxidizing agent (on the right) which is stronger than it is, that is, which is lower down in the series. In some cases, while there is a definite tendency for a reaction to take place, the *rate* of the reaction is extremely slow. Again, the *concentration* of the ions in a solution has a definite effect on the tendency for reaction. This factor will be considered in Experiment 19.

REPORT: Exp. 17

Oxidation-Reduction

Name _____

Date _____

Section _____

Locker Number _____

Preliminary Exercise

As a review, in the following equations for familiar reactions, underline once the reducing agent, and twice the oxidizing agent. Indicate at the right the number of electrons gained or lost *per atom* for each element concerned. If there is no change, simply write in "no valence change."

Reactions	*Element Oxidized*	*Electrons Lost Per Atom*	*Element Reduced*	*Electrons Gained Per Atom*
$Fe + S \longrightarrow FeS$				
$2\ Fe + 3\ Cl_2 \longrightarrow 2\ FeCl_3$				
$2\ Al + 3\ H_2SO_4 \longrightarrow 3\ H_2 + Al_2(SO_4)_3$				
$Hg^{++} + H_2S \longrightarrow HgS + 2\ H^+$				
$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2$				
$3\ Ca^{++} + 2\ PO_4^{---} \longrightarrow Ca_3(PO_4)_2$				
$PbO + 2\ H^+ \longrightarrow Pb^{++} + H_2O$				
$PbO + H_2 \longrightarrow Pb + H_2O$				
$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$				
$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$				
$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$				
$4\ Zn + 5\ H_2SO_4 \longrightarrow H_2S + 4\ ZnSO_4 + 4\ H_2O$				

1. A Simple Potential Series for the Metals. Write net ionic equations for any reactions taking place between the metals and metal ions listed below (indicate any cases of no action).

copper and zinc ion _____

zinc and cupric ion _____

lead and cupric ion _____

lead and zinc ion _____

copper and lead ion _____

zinc and lead ion _____

Which metal is the stronger reducing agent, copper or zinc? . . . . . _____

lead or copper? . . . . . _____

lead or zinc? . . . . . _____

1

Construct an oxidation-reduction potential series for lead, copper, and zinc and their ions in the space at the right, following the directions in the experimental procedure.

Which is the strongest oxidizing agent, lead ion, cupric ion, or zinc ion?

_____

Discuss a frequent cause of corrosion of lead plumbing in chemistry laboratory table drain pipes:

2. Other Metals in the Potential Series. Write net ionic equations for the reactions performed in deciding on the relative position of iron, tin, silver, mercury, and hydrogen, and their ions in the potential series (this time omit listing cases where no action occurs):

2

Construct a potential series for lead, copper, zinc, iron, tin, silver, mercury, and hydrogen in the space at the right, in accordance with your experimental results.

The strongest oxidizing agent in this series is . . . . . _____

The strongest reducing agent in this series is . . . . . _____

3. The Oxidizing Power of the Halogens. The net ionic equation for the laboratory method of preparing chlorine from HCl, with MnO_2, is:

_____

In this reaction the oxidizing agent is . . . . . _____

and the reducing agent is . . . . . _____

Write net ionic equations for the reactions of the free halogens with the halide ions, in accordance with your experimental data:

chlorine and bromide ion, _____

chlorine and iodide ion, _____

bromine and iodide ion, _____

iodine and bromide ion, _____

Construct a potential series for the three common halogens and their ions in the space at the right, arranging it as directed in the experimental procedure. 3

The strongest oxidizing agent in this series is . _____

The strongest reducing agent in this series is . _____

If fluorine were included in the series, the F^-—F_2 couple would be located . . . . . _____

4. The Ferrous Ion-Ferric Ion Couple. Write net ionic equations for the reaction of Fe^{+++} with the halide ions, in accordance with your experimental results.

Ferric ion with iodide ion, _____

Ferric ion with bromide ion, _____

The Fe^{++}—Fe^{+++} couple should therefore be placed between the _____ couple and the _____ couple.

5. The Manganous Ion-Permanganate Ion Couple. Note your observed result on mixing MnO_4^- with Cl^- in acid solution: 5

_____

The equation for this reaction is given in the preceding discussion. Rewrite it here:

_____

In this reaction, the oxidizing agent is _____, the reducing agent is _____.

Construct a potential series, including the three halogens, the Fe^{++}—Fe^{+++} couple, and the Mn^{++}—MnO_4^- couple, in the space at the right, in accordance with your observations.

6. The Reaction of the Halogens with Metals: Write net ionic equations showing the results of your experiments on the reaction of bromine water with iron and with copper. 7

_____

_____

7. Summary. Construct an oxidation-reduction potential series for all thirteen couples studied in this experiment. Write "Oxidizing agents" and "Reducing agents" along the proper sides of the table. Indicate the position of the strongest and weakest oxidizing agents and reducing agents by placing (S) and (W) beside the formulas for these substances.

Application of Principles

(Refer to Table XIII, Appendix II, to answer the following.)

1. After each of the following, write an O if it may be used as an oxidizing agent, an R if it may be used as a reducing agent, and both O and R if it may be used as either, depending on the substance with which it reacts. Also write the formula of the reduced form, the oxidized form, or both, as the case may be.

Al ( )( )_____ Br_2 ( )( )_____ H_2S ( )( )_____

MnO_2 ( )( )_____ Mg ( )( )_____ Fe^{++} ( )( )_____

H^+ ( )( )_____ HCl ( )( )_____ H_2O_2 ( )( )_____

2. Indicate the following as true (+) or false (−) statements:

(a) Manganese metal can dissolve in dilute HCl . . . . . ( )

(b) An acid solution of stannous nitrate is a stable solution . . . . . ( )

(c) Sn metal will reduce Sn^{++++} to Sn^{++} . . . . . ( )

(d) H_2O_2 in acid solution can oxidize Br^- to Br_2 . . . . . ( )

(e) Ag metal will dissolve in HNO_3, liberating H_2 gas . . . . . ( )

(f) Gold may be dissolved by 1 *F* HNO_3 . . . . . ( )

(g) Oxygen from the air can oxidize Fe^{++} to Fe^{+++} . . . . . ( )

3. Name a substance which can

(a) reduce Fe^{+++} to Fe^{++}, but cannot reduce Sn^{++++} to Sn^{++} . . . . . _____

(b) oxidize Al to Al^{+++}, but cannot oxidize Ag to Ag^+ . . . . . _____

(c) reduce Sn^{++} to Sn, but cannot reduce Co^{++} to Co . . . . . _____

(d) oxidize Fe to Fe^{++}, but cannot oxidize Fe^{++} to Fe^{+++} . . . . . _____

Conclusions

Write a thoughtful and reasonably complete list of the most important principles and viewpoints you have gained from this experiment:

Common Oxidizing and Reducing Agents. The Balancing of Oxidation-Reduction Equations

D

College Chemistry, Chapter 12

A Study Assignment

Charts of Oxidation States for Common Reagents

Much useful information about the behavior of oxidizing and reducing agents, under various conditions, can be summarized in the form of charts. Such charts for some common elements are presented below, and are repeated again in later experiments when these elements are studied in greater detail. These charts, and the comment given with them, will help you to predict the probable changes in oxidation state which will occur in a particular reaction. Note that the oxidation state is given just before each formula in the chart. Let us illustrate by commenting briefly on the charts for sulfur and oxygen compounds.

It should be obvious from the chart on *sulfur compounds* that, since H_2S represents the lowest possible oxidation state, it can act *only* as a reducing agent in oxidation-reduction processes, in which case it can be oxidized to free sulfur, or to some higher state, as a sulfate, depending on the conditions and on the strength of the oxidizing agent. Sulfuric acid (H_2SO_4), representing the highest oxidation state, can act *only* as an oxidizing agent, its reduction products being any of the lower states of sulfur. On the other hand, since sulfurous acid (H_2SO_3) represents an intermediate state of sulfur, it may act either as a reducing agent with substances which can take on electrons, as chlorate ion (ClO_3^-), or as an oxidizing agent with substances which can lose electrons, such as a metal like zinc.

Hydrogen peroxide and the peroxides are important oxidizing agents, both commercially and in the laboratory. Note, according to the chart, that when hydrogen peroxide acts as an oxidizing agent it is *reduced to water*, or in basic solution to hydroxide ion. It is *oxidized to free oxygen* only when it is acting as a reducing agent, in the presence of stronger oxidizing agents. The instability of hydrogen peroxide, especially in the presence of certain catalysts, is due to this ability of one molecule to oxidize another molecule of the same substance (auto-oxidation-reduction). The half-reactions corresponding to these statements are:

$$2\,H^+ + H_2O_2 + 2\,e^- \longrightarrow 2\,H_2O \quad \text{(reduction)}$$
$$H_2O_2 \longrightarrow 2\,H^+ + O_2 - 2\,e^- \quad \text{(oxidation)}$$
$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 \quad \text{(auto-oxidation-reduction)}$$

Sulfur compounds:

↑	+6	SO_3, H_2SO_4, SO_4^{--}	Concentrated acid is a strong oxidizing agent.
	+4	SO_2, H_2SO_3, SO_3^{--}	Active either as oxidizing or reducing agent.
o	ave +2	$S_2O_3^{--}$	Thiosulfate ion. Decomposes to S and H_2SO_3 in acid solution. Oxidized to $S_4O_6^{--}$ (tetrathionate ion) by free I_2.
r	0	S	
↓	−2	H_2S, S^{--}	Strong reducing agent, usually oxidized to S.

Oxygen compounds, peroxides:

↑	0	O_2	
o r	−1	H_2O_2, HO_2^-	Active as an oxidizing or as a reducing agent.
↓	−2	H_2O, OH^-	

Chlorine compounds:

↑	+7	(Cl_2O_7), $HClO_4$, ClO_4^-	Cl_2O_7 is unstable. $HClO_4$ is a very strong oxidizing agent. Reduced to Cl^-.
	+5	$HClO_3$, ClO_3^-	Strong oxidizing agent. Reduced to Cl^-.
	+4	ClO_2	Unstable, explosive.
o r	+3	$HClO_2$, ClO_2^-	
	+1	Cl_2O, $HClO$, ClO^-	Good oxidizing agent. Reduced to Cl^-.
	0	Cl_2	Good oxidizing agent. Reduced to Cl^-.
↓	−1	Cl^-	

Nitrogen compounds:

+5	N_2O_5, HNO_3, NO_3^-	Strong oxidizing agent, usually reduced to NO_2 in concentrated acid, or to NO in dilute acid. With strong reducing agent may go to NH_3.
+4	NO_2, (N_2O_4)	A heavy brown gas.
+3	(N_2O_3, HNO_2), NO_2^-	N_2O_3 and HNO_2 are unstable; nitrites are fairly stable. Active as oxidizing or as reducing agent.
+2	NO	Oxidized by the air to NO_2.
+1	N_2O	Supports combustion quite vigorously.
0	N_2	
−3	NH_3, NH_4OH, NH_4^+	

Chromium compounds:

	Acidic	*Basic*	
+6	$Cr_2O_7^{--}$	CrO_4^{--}	Strong oxidizing agents. Bichromate ion is orange, chromate ion is yellow.
+3	Cr^{+++}	$Cr(OH)_4^-$	Amphoteric. Chromic ion is green to violet. Chromic hydroxide complex ion is green.
+2	Cr^{++}		An uncommon ion, because it is such a strong reducing agent that it reduces water to hydrogen gas.
0	Cr		The metal.

Manganese compounds:

+7	MnO_4^-	Permanganate ion, purple. Strong oxidizing agent, reduced to Mn^{++} in acid solution, or to MnO_2 (sometimes to MnO_4^{--}) in neutral or basic solution.
+6	MnO_4^{--}	Manganate ion, green. Easily reduced to manganese dioxide.
+4	MnO_2, $MnO(OH)_2$	Brown as precipitated from solution.
+3	Mn^{+++}, $Mn(OH)_3$	Mn^{+++} is unstable, gives Mn^{++} and MnO_2.
+2	Mn^{++}	Colorless in solution, pale pink as solid manganous salts. $Mn(OH)_2$ is oxidized by air to $Mn(OH)_3$.
0	Mn	The metal.

Some common reducing agents:

a) The metals—oxidized to their positive ions, as:

Sn—oxidized to Sn^{++}

Zn—oxidized to Zn^{++}

b) Ions in which the metal has another higher oxidation state, as:

Sn^{++}—oxidized to Sn^{++++}
Fe^{++}—oxidized to Fe^{+++}
Hg_2^{++}—oxidized to Hg^{++}

c) Carbon and organic compounds—may be oxidized to other organic compounds, or to CO_2 and H_2O, as:

C (coke, much used in industry)—oxidized to CO or to CO_2
C_2H_5OH (alcohol)—may be oxidized to $HC_2H_3O_2$ (acetic acid)
Thus: $C_2H_5OH + H_2O \longrightarrow HC_2H_3O_2 + 4\,H^+ + 4\,e^-$
HCHO (formaldehyde)—oxidized to $HCHO_2$ (formic acid)
Thus: $HCHO + H_2O \longrightarrow HCHO_2 + 2\,H^+ + 2\,e^-$.

The Balancing of Oxidation-Reduction Equations

Since the fundamental event in an oxidation-reduction reaction consists in a transfer of electrons, it is obvious that in balancing the equation for such a reaction one must take such relative amounts of the reactants that the electrons supplied by the oxidation process are all used by the reduction process. There are several techniques for doing this, differing in the mechanics of the operation, but all involving the same principle.

The Half-Reaction Method

Separate half-reactions, or electron reactions, are first written for the oxidation and for the reduction processes. In developing these, one may first determine the number of electrons required from the change in oxidation number, then insert H^+ (or OH^- if the solution is basic) to balance the charges, and finally add H_2O to balance the atoms. For an example of this technique, study the oxidation of $FeSO_4$ by $KClO_3$ as given in your text, *College Chemistry*, Chapter 12.

The reverse process is sometimes used. By this technique, first balance the atoms in the half-reaction by inserting H^+ and H_2O as needed, and then insert as many electrons as needed to balance

the charges. Study the following examples.

Example 1. Let us consider the oxidation of sodium sulfite (Na_2SO_3) by potassium dichromate ($K_2Cr_2O_7$) in an acid solution. Reference to the charts of oxidation states for sulfur compounds and for chromium compounds will indicate that the sulfite ion would be oxidized to sulfate ion, and that the dichromate ion would be reduced to chromic ion (Cr^{+++}), as would be evidenced by the green color of the solution. We may write first a partial equation including only the sulfite ion (SO_3^{--}) and its oxidation product,

Step (1) $$SO_3^{--} \longrightarrow SO_4^{--}$$

We need another oxygen atom on the left, which will be supplied by water, and then we write the hydrogen as 2 H^+ on the right. (Note that we keep the oxygen with a valence of -2 and the hydrogen with a valence of $+1$ on both sides of the equation, since they are not the substances oxidized and reduced.) Our partial equation then becomes

Step (2) $$H_2O + SO_3^{--} \longrightarrow SO_4^{--} + 2\,H^+$$

We still need to balance the charges so that they are the same on both sides of the equation. To do this we add two electrons on the right side of the equation,

Step (3) $$H_2O + SO_3^{--} \longrightarrow SO_4^{--} + 2\,H^+ + 2\,e^- \quad \text{(a)}$$

which completes the oxidation half-reaction, and emphasizes the fact that an oxidation process involves the loss of electrons.

The reduction of dichromate ion to chromic ion may be expressed similarly. The several steps are:

Step (1) $$Cr_2O_7^{--} \longrightarrow 2\,Cr^{+++}$$

then balance the hydrogen and oxygen by inserting 14 H^+ to react with the seven oxygen atoms to form 7 H_2O,

Step (2) $$Cr_2O_7^{--} + 14\,H^+ \longrightarrow 2\,Cr^{+++} + 7\,H_2O$$

Finally, balance the charges. As above written, we have 12 positive charges on the left and 6 positive charges on the right, or a net charge of 6+ on the left. We, therefore, need 6 electrons on the left side to complete the reduction half-reaction,

Step (3) $$Cr_2O_7^{--} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{+++} + 7\,H_2O \quad \text{(b)}$$

This emphasizes the fact that a reduction involves the gain of electrons. Note that the requirement of 6 electrons corresponds with the change in oxidation state of chromium from +6 to +3, so that the two chromium atoms decrease by a total of 6 charges. However it was not necessary to assume these oxidation states in order to balance the reduction half-reaction properly.

Finally, we may combine (a) and (b) in such a way as to balance the electrons gained against those lost, since free electrons never appear in the final equation. To do this, we multiply (a) by 3, and add algebraically to (b),

Balanced equation:

$$3\,H_2O + 3\,SO_3^{--} \longrightarrow 3\,SO_4^{--} + 6\,H^+ + 6\,e^- \quad \text{(a)} \times 3$$
$$Cr_2O_7^{--} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{+++} + 7\,H_2O \quad \text{(b)}$$
$$Cr_2O_7^{--} + 3\,SO_3^{--} + 8\,H^+ \longrightarrow 2\,Cr^{+++} + 3\,SO_4^{--} + 4\,H_2O$$

You should always check your results to see that the equation balances *both* as to atoms and as to charges.

Example 2. The spontaneous decomposition of *aqua regia* results from the slow oxidation of chloride ion by nitrate ion in a strongly acid solution. This time we shall give only the completed half-reactions involved. See if you can develop them, on a piece of scratch paper, by either or both of the above techniques. For the half-reactions we have

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \quad \text{(oxidation)} \quad \text{(a)}$$
$$4\,H^+ + NO_3^- + 3\,e^- \longrightarrow NO + 2\,H_2O \quad \text{(reduction)} \quad \text{(b)}$$

Now multiply (a) by 3 and (b) by 2 to give the same number of electrons in each case, and then add:

Balanced equation:

$$6\,Cl^- \longrightarrow 3\,Cl_2 + 6\,e^- \quad \text{(a)} \times 3$$
$$8\,H^+ + 2\,NO_3^- + 6\,e^- \longrightarrow 2\,NO + 4\,H_2O \quad \text{(b)} \times 2$$
$$8\,H^+ + 2\,NO_3^- + 6\,Cl^- \longrightarrow 2\,NO + 3\,Cl_2 + 4\,H_2O^1$$

Example 3. A case in basic solution. If the same reaction studied in Example 1 is carried out in basic solution, we proceed as follows. Write the reducing agent and its oxidized form as before:

Step (1) $$SO_3^{--} \longrightarrow SO_4^{--}$$

But now the reaction must be balanced in terms of H_2O and OH^- (since H^+ is not available), so we add 2 OH^- on the left (twice as much as the re-

[1] Nitric oxide, NO, will combine with free chlorine, Cl_2, to give nitrosyl chloride, so the final equation may be written to include 2 NOCl + 2 Cl_2, instead of 2 NO + 3 Cl_2.

quired oxygen) and then water on the right to balance the atoms:[1]

Step (2) $2\ OH^- + SO_3^{--} \longrightarrow SO_4^{--} + H_2O$

Finally add electrons to balance the charges, as before:

Step (3) $2\ OH^- + SO_3^{--} \longrightarrow SO_4^{--} + H_2O + 2\ e^-$ (a)

For the reduction of the dichromate ion, note, in the chart on chromium compounds, that in basic solution this will be present as chromate ion, CrO_4^{--}, and when reduced to the trivalent state will be present in basic solution as the hydroxide complex ion, $Cr(OH_4)^-$. We therefore write:

Step (1) $CrO_4^{--} \longrightarrow Cr(OH)_4^-$

The oxygen now balances, but there are four extra hydrogen atoms on the right; so, by adding 4 OH^- on the right to react with these, and 4 H_2O on the left, we have achieved a balance of atoms:

Step (2) $4\ H_2O + CrO_4^{--} \longrightarrow Cr(OH)_4^- + 4\ OH^-$

Finally, add electrons to balance the charges:

Step (3) $3\ e^- + 4\ H_2O + CrO_4^{--} \longrightarrow Cr(OH)_4^- + 4\ OH^-$ (b)

We may now combine the oxidation half-reaction (a) with the reduction half-reaction (b) so as to eliminate electrons.

Balanced equation:

$6\ OH^- + 3\ SO_3^{--} \longrightarrow 3\ SO_4^{--} + 3\ H_2O + 6\ e^-$ (a) × 3
$6\ e^- + 8\ H_2O + 2\ CrO_4^{--} \longrightarrow 2\ Cr(OH)_4^- + 8\ OH^-$ (b) × 2
$3SO_3^{--} + 2CrO_4^{--} + 5H_2O \longrightarrow 3SO_4^{--} + 2Cr(OH)_4^- + 2OH^-$

The Oxidation Number Method

This technique differs from the preceding one principally in that both the oxidizing and the reducing agents, and their respective products, are written as a single preliminary equation. The relative amounts of each are then computed from the changes in oxidation numbers. The total charge on each side of the equation is then balanced by the addition of H^+ (or OH^- in a basic solution), and the atoms are balanced by the addition of H_2O. Study the following example.

Example 1. Let us consider again the oxidation of sodium sulfite by potassium dichromate in an acid solution:

Step (1) Write down the principal substances used and produced:

$$SO_3^{--} + Cr_2O_7^{--} \longrightarrow SO_4^{--} + Cr^{+++}$$

Step (2) Note the change in oxidation number, i.e., the number of electrons lost and gained. These may be indicated by brackets, thus:

$$\underset{+4}{SO_3^{--}} + \underset{+6}{Cr_2O_7^{--}} \longrightarrow \underset{+6}{SO_4^{--}} + \underset{+3}{Cr^{+++}}$$

loses 2 e^-; gains 3 e^- per Cr

Step (3) Take such amounts of oxidizing and of reducing agents as will make the number of electrons lost equal those gained. In this case, since each S loses 2 e^- and each Cr gains 3 e^-, we need 3 S to 2 Cr, or

$$3\ SO_3^{--} + Cr_2O_7^{--} \longrightarrow 3\ SO_4^{--} + 2\ Cr^{+++}$$

Step (4) Note the total charges on each side of the equation, in this case 8 negative charges on the left and 0 charges on the right. Then add H^+ so as to balance the charges, and insert H_2O to balance the atoms. In this case we need 8 H^+ on the left and 4 H_2O on the right. The final equation is then:

Balanced equation:

$$3\ SO_3^{--} + Cr_2O_7^{--} + 8\ H^+ \longrightarrow 3\ SO_4^{--} + 2\ Cr^{+++} + 4\ H_2O$$

Example 2. If this same reaction were being carried out in basic solution, the chromium would be present as chromate ion (CrO_4^{--}) before the reaction and as chromic hydroxide complex ion ($Cr(OH)_4^-$) afterward. (See the chart for chromium compounds.) The steps in balancing the equations are:

Step (1) $SO_3^{--} + CrO_4^{--} \longrightarrow SO_4^{--} + Cr(OH)_4^-$

Step (2) $\underset{+4}{SO_3^{--}} + \underset{+6}{CrO_4^{--}} \longrightarrow \underset{+6}{SO_4^{--}} + \underset{+3}{Cr(OH)_4^-}$

loses 2 e^-; gains 3 e^-

Step (3) $3\ SO_3^{--} + 2\ CrO_4^{--} \longrightarrow 3\ SO_4^{--} + 2\ Cr(OH)_4^-$

Step (4) Since we have 10 negative charges on the left and 8 negative charges on the right, we need 2 OH^- on the right, and 5 H_2O on the left:

Balanced equation:

$$3\ SO_3^{--} + 2\ CrO_4^{--} + 5\ H_2O \longrightarrow 3\ SO_4^{--} + 2\ Cr(OH)_4^- + 2\ OH^-.$$

[1] For cases in which it is easy to assign definite oxidation states, it may be simpler for you to note, as in this case, that sulfur changes from oxidation state +4 in SO_3^{--} to +6 in SO_4^{--}, and therefore 2 e^- are needed on the right. Finally, then you can balance the charges by adding 2 OH^- on the left and H_2O on the right to balance the atoms.

REPORT: Study Assignment D

Common Oxidizing and Reducing Agents

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

Application of Principles

I. What is the change in oxidation number (give number of electrons gained or lost, *per atom;* e.g., 3 e^- gained) when:

$Cl_2 \longrightarrow NaClO$ . . _____ $H_2SO_3 \longrightarrow S$ . . . _____ $H_2O_2 \longrightarrow H_2O$ . . . _____

$Cr_2O_7^{--} \longrightarrow CrO_4^{--}$. _____ $KMnO_4 \longrightarrow MnO_2$. _____ $NH_3 \longrightarrow NH_4^+$ . . _____

II. Give the formula of a product (derived from the first-named substance) which may be formed when:

1. HNO_2 is treated with an oxidizing agent . . . . . _____
2. HNO_2 is treated with a reducing agent . . . . . _____
3. H_2S is treated with H_2SO_3 . . . . . _____
4. Hot, conc H_2SO_4 reacts with carbon . . . . . _____
5. H_2O_2 is treated with $FeSO_4$ and H_2SO_4 . . . . . _____
6. H_2O_2 is treated with $KMnO_4$ and H_2SO_4 . . . . . _____
7. MnO_2 is treated with conc HCl . . . . . _____

III. Write the half-reaction equation for the oxidation of:

1. Cl^- to ClO^- (acid) . . . . . _____
2. NO_2^- to NO_3^- (acid) . . . . . _____
3. SO_3^{--} to SO_4^{--} (basic) . . . . . _____
4. Cr^{+++} to $Cr_2O_7^{--}$ (acid) . . . . . _____
5. C_2H_5OH to CH_3CHO (acid) . . . . . _____

IV. Write the half-reaction equation for the reduction of:

1. NO_3^- to NH_4^+ (acid) . . . . . _____
2. SO_3^{--} to S (acid) . . . . . _____
3. MnO_4^- to MnO_2 (basic) . . . . . _____
4. ClO_4^- to Cl_2 (acid) . . . . . _____
5. SO_3^{--} to S^{--} (basic) . . . . . _____

V. Using the method you prefer, write balanced net ionic equations for the reactions of the following substances. (Show your method in each case.)

1. Cl_2 gas is bubbled into H_2S solution, forming a yellow precipitate.

2. Al metal is used to reduce $FeCl_3$ to $FeCl_2$.

3. H_2S gas is passed into concentrated HNO_3, giving a brown gas.

4. Bleaching solution, NaClO, is added to an acid solution of $FeSO_4$.

5. SO_2 gas is bubbled into an acid solution of $KMnO_4$.

6. SO_3^{--} is added to a basic solution of $KMnO_4$.

7. Ag metal is dissolved by dilute HNO_3.

8. Sn^{++} is added to an acidified $Cr_2O_7^{--}$ solution, turning it green.

9. H_2O_2 and NaOH are added to Mn^{++} solution, giving a brown precipitate.

The Preparation and Properties of Some Oxygen Compounds of the Halogens — 18

College Chemistry, Chapter 13

Review of Fundamental Concepts

Halogen compounds:

↑ oxidizing power ↓	+7	(Cl_2O_7),	$HClO_4$,	ClO_4^-	Cl_2O_7 is unstable. $HClO_4$ is a very strong oxidizing agent. Reduced to Cl^-.
	+5		$HClO_3$,	ClO_3^-	Strong oxidizing agent. Reduced to Cl^-.
	+4	ClO_2			Unstable, explosive.
	+3		$HClO_2$,	ClO_2^-	
	+1	Cl_2O,	HClO,	ClO^-	Good oxidizing agent. Reduced to Cl^-.
	0	Cl_2			Good oxidizing agent. Reduced to Cl^-.
	−1	Cl^-			

The oxygen compounds of the halogen elements —chlorine, bromine and iodine—are important substances whose preparation and properties furnish further interesting illustrations of the principles of oxidation-reduction. Due to its great electronegativity (see text), fluorine exists only in the oxidation states −1 and 0. The other halogens, however, are capable of existence in a range of oxidation states extending from −1 to +7. The student should acquaint himself with the names and formulas of the oxides, acids, and anions of the halogens in each of the oxidation states.

In this experiment, we shall follow the element chlorine through changes in its oxidation state from −1 to 0 to +1 to +5 by a series of successive reactions. We shall also perform some experiments which illustrate the ability of a lighter halogen to increase the oxidation number of a heavier halogen while the lighter halogen is undergoing a decrease in its oxidation number. This is in consequence of increasing electronegativity of the halogens in the order I, Br, Cl, F.

Experimental Procedure

Chemicals: MnO_2, KOH, CCl_4, starch iodide paper, solutions of 0.1 *F* KI, 0.1 *F* KBr.

1. Preparation of Chlorine, Potassium Chlorate and Sodium Hypochlorite. Before beginning the experiment, turn to the report sheet and write the equations for the reactions which you are to observe; namely, the oxidation of chloride ion in an acid solution by MnO_2; the reaction of chlorine with cold sodium hydroxide solution; the reaction of an excess of chlorine with a hot solution of potassium hydroxide.

Set up the apparatus as illustrated. After you have obtained the instructor's approval on the arrangement of the apparatus, place the following chemicals in their respective containers. Into the Erlenmeyer flask, put approximately 0.1 gram-formula weights (gfw) of MnO_2. Place a loose plug of cotton in the bulb B of the drying tube, which serves to catch any spray from the chlorine generator. Dissolve about 0.06 gfw of solid KOH in 15 ml of water and put this solution into the 15-cm test tube in a beaker, C. Dilute 5 ml of the 6 *F* NaOH stock solution with 20 ml of distilled water and place this solution in test tube D, which is surrounded by an ice bath. Heat the water bath in C almost to boiling. Add about 75 ml of 6 *F* HCl through the thistle tube and warm flask A gently until chlorine gas is being produced. Keep the water in C almost at the boiling point by heating it intermittently. Use the same burner to heat flask A gently from time to time, but do not let the reaction mixture boil.

After the air has been displaced from the apparatus, note how the chlorine gas-bubbles decrease in size as they are absorbed by reaction with the basic solutions. Continue the heating until the chlorine gas is no longer appreciably absorbed in the cold NaOH solution. Allow the system to cool, and when flask A is cool enough to be handled, disconnect the drying tube and replace it with a right-angled tube which is long enough to dip into a beaker of cold water. Allow the generator to remain this way until the end of the period, when it should be completely cooled and the contents may

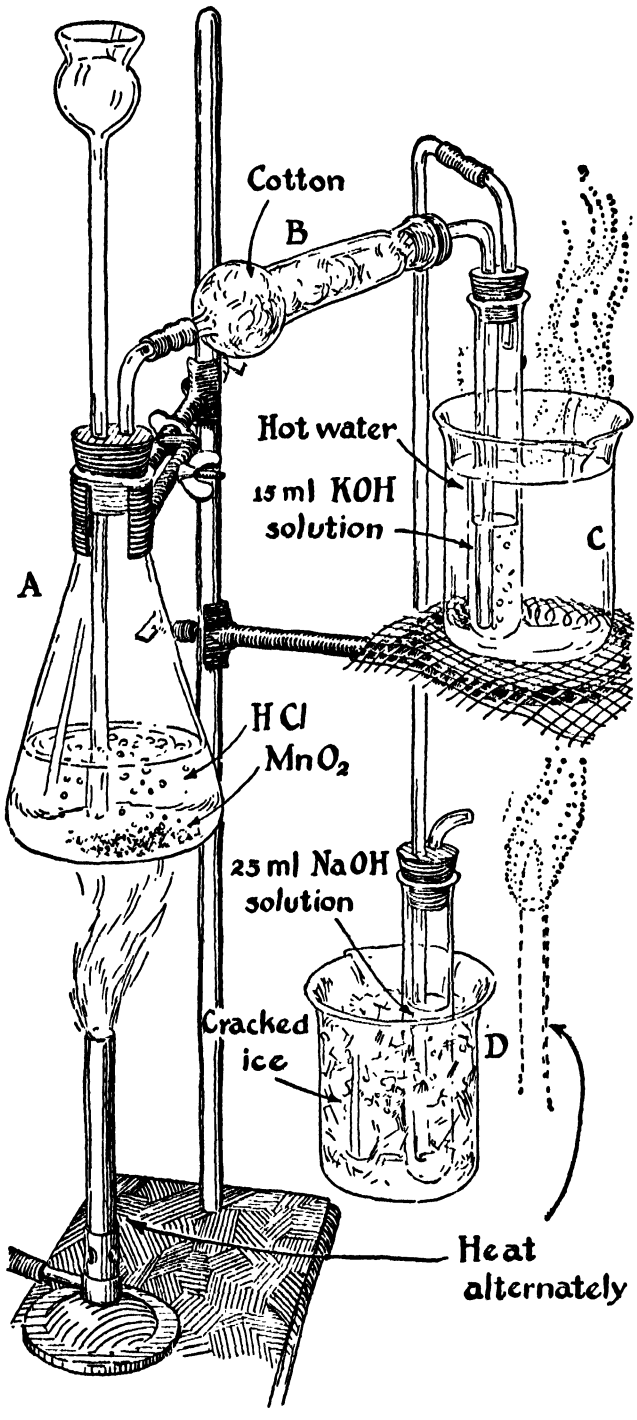


FIG. 18-1. The preparation of chlorine, potassium chlorate and sodium hypochlorite.

be washed down the sink with water. This should prevent any appreciable amount of chlorine from escaping into the laboratory.

2. The Crystallization of Potassium Chlorate. Transfer the solution in the test tube in C to a small beaker and evaporate it to about half its volume. Cool this solution in the ice bath until a crop of crystals has formed. Separate the crystals from the supernatant solution by filtering. Rinse any crystals remaining in the beaker into the funnel with a few ml of ice water. Transfer the crystals to a small beaker and dissolve them in as small an amount of hot water as possible (5 to 10 ml should suffice). Cool the solution in the ice bath; separate the crystals by filtration and dry them between several thicknesses of filter paper. Refer to the solubility chart, Fig. 18-4 of the text, to determine the relative solubilities of KCl and $KClO_3$ in water at different temperatures.

While the $KClO_3$ crystals are drying, perform the following experiments with the NaOCl solution in the test tube at D.

3. The Chemical Properties of the Hypochlorite Ion. Test the bleaching properties of hypochlorite ion by putting several drops of the solution in D on pieces of red and blue litmus paper.

To test the oxidizing strength of the hypochlorite ion, put 3 ml of 0.1 *F* KI and 1 ml of CCl_4 in a 10-cm test tube and add one or two drops of the NaOCl solution. Shake the test tube and note the color of the CCl_4 layer. Write the equation for this reaction. Now add about 1 ml more of the NaOCl solution to the same test tube, shake it again and note any change in the CCl_4 layer. Write the equation for this reaction. Are these results in agreement with the general principle stated in the text?

Before beginning the next experiment, refer to Appendix II, Table XIII for the relative oxidation potentials of the ClO^- ion in basic and in acid solutions. Record these on the report sheet. Now repeat the experiment of the preceding paragraph using 0.1 *F* KBr in place of the KI solution. If no results are obtained with the basic solution, acidify with several drops of 3 *F* H_2SO_4. Write the equation for the reaction in the acid solution. (Sometimes the freshly prepared NaOCl solution contains some dissolved chlorine, which of course displaces Br_2 from the KBr solution, even when alkaline.)

The greater ease with which I^- is oxidized to I_2, and thence on to IO_3^- by the hypochlorite ion in alkaline solution may be utilized to differentiate

between the I^- and Br^- ions when they are present in the same solution. Put 1 ml each of 0.1 *F* KI and 0.1 *F* KBr and CCl_4 into a test tube. Add one or two drops of the alkaline NaOCl solution and shake the tube. Note the color of the CCl_4 layer. Now add 1 to 2 ml of NaOCl and shake the tube again until the color in the CCl_4 layer has disappeared. Then acidify the solution with several drops of 3 *F* H_2SO_4 and shake the test tube again. Note the color in the CCl_4 layer now. Explain the results in the report sheet.

4. The Chemical Properties of Potassium Chlorate. Test the dry crystals of $KClO_3$ prepared in 2, by heating about half of the crystals in a small Pyrex test tube. If the $KClO_3$ is kept just at its melting point, note that very little visible decomposition takes place. (See text for the reaction.) Now add a small amount of MnO_2 to the test tube and note any difference in the rate and type of decomposition which takes place. Write the equation for this reaction.

Treat a few crystals of $KClO_3$ with about 1 ml of 12 *F* HCl in a small test tube. Test for the product of this reaction with moistened starch-iodide paper. Write the equation for the reaction which occurs in the test tube and also for the one which takes place in the starch-iodide paper.

Dissolve the remainder of the $KClO_3$ in about 10 ml of water. Add 5 ml of this solution to a test tube containing 1 ml of 0.1 *F* KI and 1 ml CCl_4. Repeat this test, but acidify the second solution with 5 drops of 3 *F* H_2SO_4. Shake the test tubes and observe any signs of a reaction. Allow the tests to stand until the next period and then shake the test tubes and note any oxidation of iodide ion. Note the relative positions of the chlorate ion and the hypochlorite ion in the oxidation-reduction potential series in Appendix II. One may account for the difference in results noted in 3, with the hypochlorite ion, by relative rates of the reactions rather than by any significant difference in the oxidation potentials.

Fundamental Rules of Nomenclature of Inorganic Compounds

Optional drill for students who have not yet mastered the elementary rules of nomenclature.

In Experiment 8 the naming of binary compounds was discussed. Now, with the introduction of the variety of oxyhalogen compounds in Experiment 18, a more complete presentation of the rules of nomenclature is appropriate.

Binary Compounds

Rule 1. Binary, or two-element, ionic compounds are named by the following general system:

metal nonmetal (abbrev.) -ide

Thus NaCl is sodium chloride $MgBr_2$ is magnesium bromide
CaO is calcium oxide KOH is potassium hydroxide

If the metal has a variable valence, the suffix *ous* is used to denote the lower valence state and the suffix *ic* the higher valence state.

Thus $FeCl_2$ is ferrous chloride; $FeCl_3$ is ferric chloride.
Hg_2O is mercurous oxide; HgO is mercuric oxide.

Rule 2. Binary covalent compounds use the same ending, *ide*, but in case of variable valence the Greek prefixes *mono*, *di*, *tri*, etc. are used to denote the number of atoms of the more negative element.

Thus SO_2 is sulfur dioxide; SO_3 is sulfur trioxide.
NO_2 is nitrogen dioxide; N_2O_5 is nitrogen pentoxide.
CO is carbon monoxide; CCl_4 is carbon tetrachloride.

Rule 3. Binary acids are named by the following general system:

hydro nonmetal (abbrev.) -ic acid

Thus HCl is hydrochloric acid.
H_2S is hydrosulfuric acid.
HI is hydroiodic acid.

Ternary Compounds

Most of the nonmetals form compounds with oxygen and hydrogen which are acidic in nature. These are called oxyacids; examples are H_3BO_3, H_2CO_3, HNO_3, H_2SO_4, and $HClO_3$. Some transition metals in their higher oxidation states also form hydroxides which are oxyacids—e.g., H_2CrO_4 and H_2MnO_4. In many cases there may be a series of oxyacids, each one containing the same nonmetal in a different oxidation state—e.g., HClO, $HClO_2$, $HClO_3$, $HClO_4$. In order to distinguish between these acids and their respective salts, the following system of suffixes and prefixes has been devised:

Oxidation state of Cl	*Acid*	*Name*
+1	$HClO$	*hypo*chlor*ous* acid
+3	$HClO_2$	chlor*ous* acid
+5	$HClO_3$	chlor*ic* acid
+7	$HClO_4$	*per*chlor*ic* acid

	Salt	*Name*
+1	$NaClO$	sodium *hypo*chlor*ite*
+3	$NaClO_2$	sodium chlor*ite*
+5	$NaClO_3$	sodium chlor*ate*
+7	$NaClO_4$	sodium *per*chlor*ate*

Rule 4. Oxyacids with suffix *ic* form salts with suffix *ate*. Oxyacids with suffix *ous* form salts with suffix *ite*. Oxyacids with prefix *hypo* and suffix *ous* form salts with prefix *hypo*[1] and suffix *ite*. Oxyacids with prefix *per* and suffix *ic* form salts with prefix *per* and suffix *ate*.

Rule 5. In a series of oxyacids, the *ic* acid is the one in which the nonmetal has the oxidation number corresponding to its group number in the periodic table, with the exception of the halogens, whose *ic* acids have the oxidation state +5.

Examples of *ic* acids are:

Group	III	IV	V	VI	VII
	H_3BO_3	H_2CO_3	HNO_3		
		H_4SiO_4	H_3PO_4	H_2SO_4	$HClO_3$
			H_3AsO_4	H_2SeO_4	$HBrO_3$
				H_6TeO_6	HIO_3

Some *ic* acids formed by metals are H_2SnO_3, H_2ZnO_2, HVO_3, H_2CrO_4, H_2MoO_4, and H_2MnO_4.

Rule 6. In some cases there may be several oxyacids of an element in the same oxidation state. The common acid of such a series is given the prefix *ortho*. The acid which contains one less water molecule in its formula is called the *meta* acid. The acid whose formula may be derived by removing one molecule of water from two molecules of the *ortho* acid usually has the prefix *pyro*. When no prefix appears, the *ortho*, or common, acid is assumed to be the one intended.

Examples: H_3PO_4 *ortho*phosphoric; HPO_3 *meta*phosphoric; $H_4P_2O_7$ *pyro*phosphoric; H_3BO_3 *ortho*boric; HBO_2 *meta*boric; H_4SiO_4 *ortho*silicic; H_2SiO_3 *meta*silicic; H_2SO_4 (*ortho*)sulfuric; $H_2S_2O_7$ *pyro*sulfuric

Rule 7. In forming salts of polyprotic acids such as H_2SO_4 or H_3PO_4, it is possible to replace one or more of the hydrogen atoms by metal ions. To differentiate between these salts, several systems of nomenclature are in use; in the illustrations below the first name given is usually preferred.

NaH_2PO_4 monosodium phosphate, primary sodium phosphate
Na_2HPO_4 disodium phosphate, secondary sodium phosphate
Na_3PO_4 trisodium phosphate, tertiary sodium phosphate
$NaHSO_4$ sodium acid sulfate, sodium hydrogen sulfate, sodium bisulfate
Na_2SO_4 sodium sulfate, normal sodium sulfate

Optional Drill on Nomenclature

To the student: When you answer the following, write *both* the formula of a substance and its corresponding name side by side, in a simple outline or chart form. This will be an aid to your understanding and memory.

1. Name the following binary compounds: Cl_2O, Hg_2O, HgO, $SnCl_2$, $SnCl_4$, FeS, Fe_2S_3, N_2O_4, SiF_4, PCl_3, PCl_5, MnO_2.

2. Write the formulas of the following: cuprous oxide, nitrogen trichloride, mercuric sulfide, carbon monoxide, silicon dioxide, ferrous hydroxide, phosphorus pentoxide, chlorine heptoxide, arsenious oxide, mercuric chloride.

3. In the first of four vertical columns copy the following formulas of acids: HF, H_2CO_3, HNO_2, HNO_3, H_2SO_3, H_2SO_4, $HBrO$, $HBrO_2$, $HBrO_3$, $HBrO_4$. In the second column write the name of each acid, paying attention to the correct prefixes and suffixes. In the third and fourth columns write, respectively, the formula of the corresponding sodium salt, and its correct name.

4. Write the names of the following ortho, meta, or pyro acids and salts: H_3AsO_3, H_3AsO_4, $HAsO_2$, $HAsO_3$, $Pb_3(AsO_4)_2$, Na_3AsO_3, $KAsO_3$, $Ca(AsO_2)_2$.

5. Write the formulas of the following: ferrous sulfate, ferric sulfate, ferric phosphate, ferrous phosphate, potassium sulfite, potassium hydrogen sulfite, magnesium hydrogen sulfite.

6. Name these: Na_2S, $Ba(HS)_2$, $BaSO_3$, $AgHSO_4$, KH_2PO_4, K_2HPO_4, $Mg_2P_2O_7$, $Pb(OH)Cl$, $NaIO$, $KBrO_3$, $KClO_2$, $Ba(ClO)_2$.

[1] The prefix *hypo* is from the Greek meaning under or less than, and the prefix *per* is Greek for above or more than.

REPORT: Exp. 18

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

The Preparation and Properties of Some Oxygen Compounds of the Halogens

Preliminary Exercise:

Fill in the following chart with the names and formulas of the oxygen acids of chlorine, bromine, and iodine. Do the same for the anions corresponding to these acids.

OXYGEN ACIDS OF HALOGENS

Formula	*Name*

ANIONS OF THE OXYGEN ACIDS

Formula	*Name*

1. The Preparation of Chlorine, Potassium Chlorate, Sodium Hypochlorite.

Equation for the reaction of MnO_2 with 6 *F* HCl:_____

Equation for reaction of Cl_2 and cold NaOH solution:_____

Auto-oxidation-reduction of hypochlorite ion in hot KOH solution:_____

_____

2. Crystallization of $KClO_3$.

Compare the solubility of KCl and $KClO_3$ in water at 0° C. and at 100° C._____

_____

_____

On the basis of the above data explain the reasons for the steps involved in the crystallization and recrystallization of $KClO_3$.

_____

_____

_____

3. Properties of the Hypochlorite Ion.

Result of bleaching test on litmus paper:_____

What is main commercial use of NaOCl?_____

_____

How is NaOCl made on a commercial scale?

Balanced equation for reaction of basic solution of OCl^- (few drops) on 0.1 *F* KI solution

Equation for reaction of excess OCl^- on I_2 produced above:

Equation for reaction of OCl^- in acid solution on 0.1 *F* KBr solution:

Explain the basis of the test by which both I^- and Br^- may be determined by the use of the OCl^-:

Properties of Potassium Chlorate.

Equation for reaction which takes place if $KClO_3$ is kept just at its melting point:

Equation for decomposition of $KClO_3$ in presence of MnO_2:

How do you account for the decomposition taking place at a lower temperature in the presence of MnO_2?

Equation for reaction of $KClO_3$ and 12 *F* HCl:

Equation for reaction of product of previous reaction with starch-iodide paper:

Reaction of solution of $KClO_3$ on 0.1 *F* KI:

Record the relative oxidation-reduction potentials for the various couples involved in this experiment:

How do you account for the difference in the results with ClO_3^- and ClO^- as oxidizing agents?

How do the electronegativities of the halogens affect the relative stabilities of the various oxidation levels of these elements?

The Production of an Electric Current By Means of Oxidation-Reduction Reactions

19

College Chemistry, Chapter 12

Review of Fundamental Concepts

The Nature of Electrical Cells

We have observed that whenever an oxidation-reduction reaction occurs, there is a transfer of electrons from the substance oxidized to the substance reduced. Thus, when zinc is oxidized by cupric ion, the zinc atom loses two electrons and the cupric ion gains two electrons. We may express this as two separate half-reactions:

$$Zn \longrightarrow Zn^{++} + 2\,e^- \qquad \text{(oxidation)}$$
$$Cu^{++} + 2\,e^- \longrightarrow Cu \qquad \text{(reduction)}$$

The sum of these two half-reactions of course gives the total equation for the process

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu.$$

This total equation does not contain any free electrons for, obviously, the electrons lost by the zinc are all gained by the cupric ion. An *electrical cell*, or battery, is simply a convenient mechanical device for carrying out an oxidation-reduction reaction in such a way as to transfer the electrons through a wire rather than by actual contact of the oxidizing agent with the reducing agent. The chemical reactions taking place at the separate poles of the battery are simply the half-reactions above described. The oxidation half-reaction takes place at the negative pole, since electrons are liberated there, and the reduction half-reaction takes place at the positive pole. See Figure 19-1.

Cell Voltage

The *volt* is the unit of electrical potential, or driving force. It furnishes a measure of the work done when a unit electrical charge is transferred from one substance to another. *The voltage of a cell*, sometimes called its electromotive force, *is thus a quantitative value expressing the tendency of the chemical reaction occurring in the cell to take place.* This voltage, of course, depends on the strength of the oxidizing and reducing agent used. In other words, if the oxidizing agent has a very great affinity for electrons as compared to the tendency of the reducing agent to hold these electrons, the electrical potential, or voltage, will be corrrespondingly large.

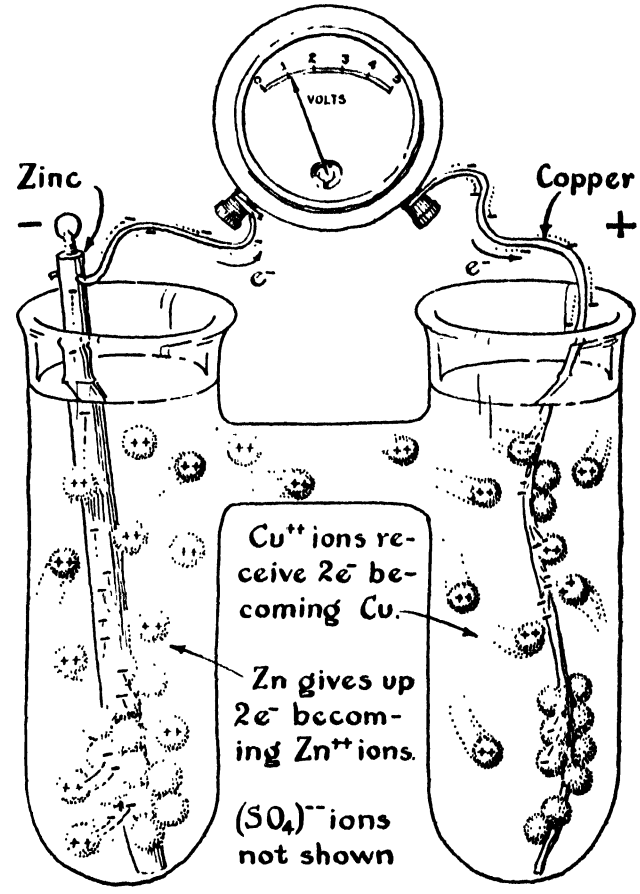


FIG. 19-1. A simple electric cell which transforms the energy liberated by a chemical reaction into electrical energy. The electrical current in the solution consists of sulfate ions (not shown) moving from right to left, as well as of the positive zinc and cupric ions moving to the right as shown.

Standard Electrode Potentials

The total voltage of the cell is a combination of the separate voltages due to the oxidation half-reaction and the reduction half-reaction involved. Since we cannot measure the voltage due to a single couple, it is customary to calculate the voltage of all oxidation-reduction couples in terms of the total voltage which would be given by a cell in which the couple under consideration is combined with the $H_2 - H^+$ couple. The $H_2 - H^+$ couple is arbitrarily assigned a potential of zero, so that the total voltage is then ascribed to the other

couple. For example, if a cell is measured involving the reaction of zinc in an acid, we have the half-reactions, with the potentials for each, as follows:

$Zn \longrightarrow Zn^{++} + 2\,e^-$	$E = +0.763$ volts
$2\,H^+ + 2\,e^- \longrightarrow H_2$	$E = 0$
$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$	$\Sigma E = +0.763$ volts

This value, + 0.762, is called the *standard electrode potential*[1] for the $Zn-Zn^{++}$ couple. See Figure 19-2. In all such data, the values refer to the voltages obtained when all substances in solution are at a concentration of one molar, all gases at one atmosphere pressure, and the temperature at a fixed, convenient value, usually 25° C. (See Table XIII, Appendix II.)

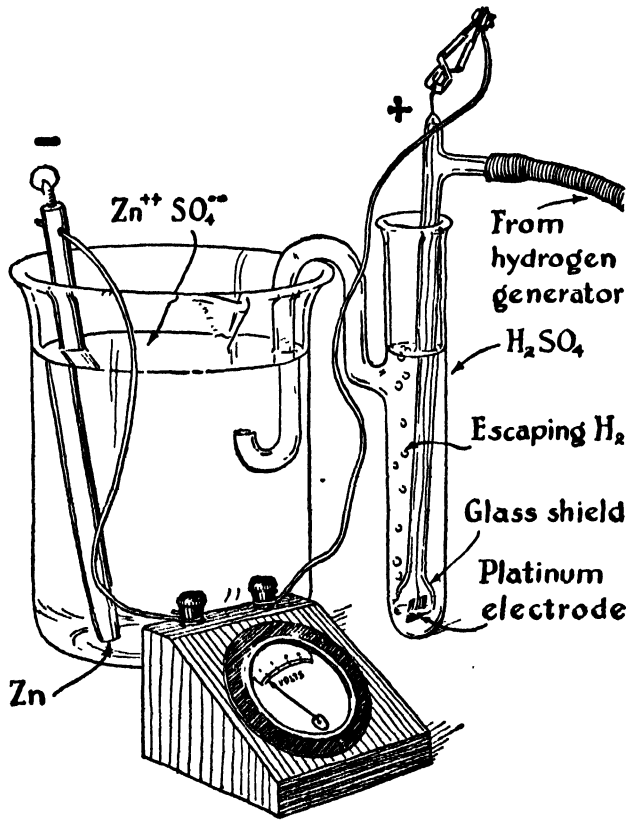


FIG. 19-2. Hydrogen gas, adsorbed on the platinum electrode, acts as a hydrogen electrode. When this is immersed in 1 *M* H^+, and coupled with zinc in 1 *M* Zn^{++}, the meter reads 0.762 volts.

To obtain the voltage for any given cell, we calculate the *algebraic difference* of the two oxidation-reduction couples concerned. For example, we may make a battery utilizing the strong reducing agent zinc, reacting with the strong oxidizing agent chlorine, according to the reaction

$$Zn + Cl_2 \longrightarrow Zn^{++} + 2\,Cl^-.$$

A zinc rod is placed in 1 *F* zinc chloride, and a platinum electrode in 1 *F* potassium chloride saturated with chlorine gas. A salt bridge connects the solutions. The platinum electrode is inactive, and serves merely to conduct electrons from the solution as chlorine is reduced to chloride ion. The two couples, with the corresponding half-reactions and voltages as given in Table XIII, are:

$Zn-Zn^{++}$, i.e. $Zn \longrightarrow Zn^{++} + 2\,e^-$	$E = +0.763$ volts
$Cl^- - Cl_2$, i.e. $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$	$E = -1.3595$
(subtracting) $Zn + Cl_2 \longrightarrow Zn^{++} + 2\,Cl^-$,	$\Sigma E = 2.122$ volts

Since the standard electrode potentials are always tabulated in the direction of loss of electrons, i.e., oxidation, it was necessary to *subtract* the second equation from the first in order to obtain the correct cell reaction. (We could have obtained the same result by reversing the second equation and also the sign of its voltage, thus, $Cl_2 + 2\,e^- \longrightarrow 2Cl^-$, E = +1.3595, and *adding*.)

Electrode Potentials and the Principle of Le Chatelier

We have observed that the tendency for a reaction to take place is measured by the voltage created when the reaction takes place in an electric cell. Thus, the electromotive force of 2.122 volts created by the cell in the preceding paragraph, for the reaction

$$Zn + Cl_2 \rightleftharpoons Zn^{++} + 2\,Cl^-$$

is indicative of the behavior of quite a strong reducing agent, Zn, with a strong oxidizing agent, Cl_2. There is also some tendency for the reverse reaction to occur. However, zinc ion (Zn^{++}) is quite a weak oxidizing agent, and chloride ion (Cl^-) is a weak reducing agent; hence this reverse tendency, as indicated by the short reverse arrow in the equation, is not very great. A reaction, in which the forward and the reverse processes have attained a balance, and are taking place at equal but opposing rates, is said to be in *chemical equilibrium.*

According to the principle expressed by *Le Chatelier's Theorem,* and in accord with observed fact, an increase in the concentration (or pressure)

[1] There is a lack of uniformity among authors regarding the sign of the potential. We shall follow the convention of calling the potential of couples of the active metals, that is, those above the H_2—H^+ couple, positive (+), and those below it negative (—).

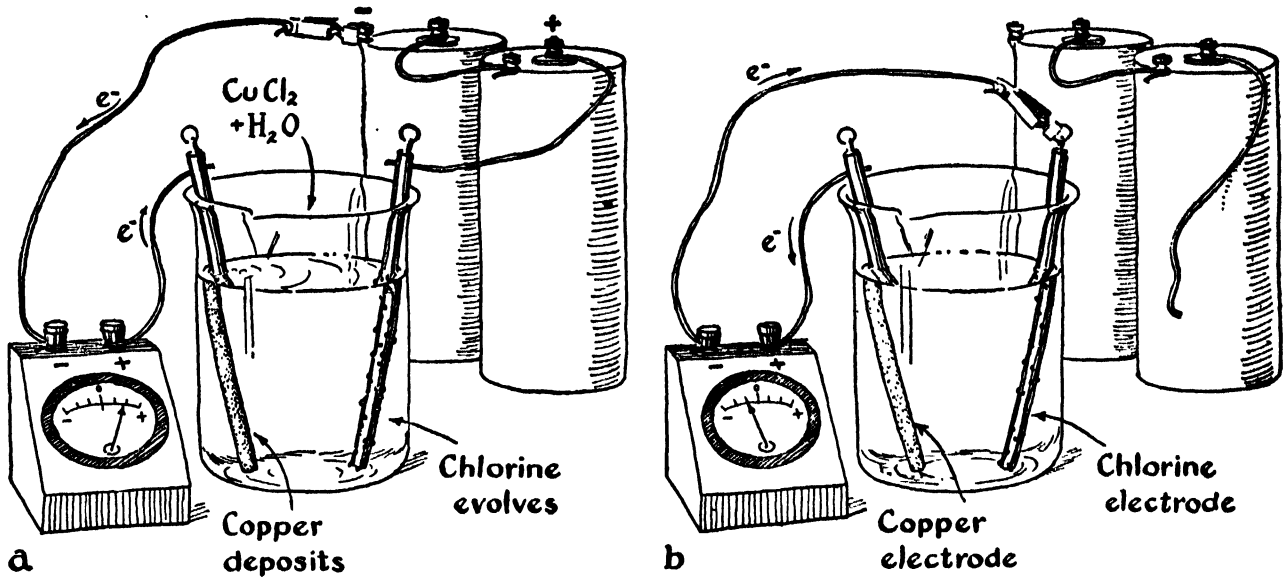


FIG. 19-3. Electrolysis and counter electromotive force. The products of electrolysis in (a) will create an electric cell which operates in the reverse direction, as in (b).

of chlorine gas (Cl_2) will increase the rate of reaction with zinc, and consequently will increase the voltage of the cell. Conversely, an increase in the concentration of zinc ion or of chloride ion will favor the reverse process and therefore decrease the voltage.[1]

Again, in the forward reaction of zinc with chlorine, heat is evolved. Therefore, if the cell is operated at a higher temperature, say 50° C, the voltage will be less, since this higher temperature will repress the evolution of heat, and the tendency for the forward reaction will be decreased.

[1]While the potential values in Table XIII are all calculated for 1 *M* concentration, or 1 atmosphere pressure in the case of gases, we may calculate the corresponding potential, E, for a given reaction, at other conditions from the equation

$$E = E^\circ - \frac{0.059}{n}(\log Q)$$

where E° is the standard electrode potential, n is the number of electrons gained by the oxidizing agent in the reaction equation, and Q is the product of the concentrations (molarity of solutes, gas pressure in atmosphere) of the products, divided by the product of the concentrations of the reacting substances.

Example: In the reaction above we found that for

$$Zn(s) + Cl_2(1atm) \rightleftarrows Zn^{++}(1M) + 2\ Cl^-(1M),\ E^\circ = 2.12 \text{ volt.}$$

To calculate the corresponding voltage, if the Cl_2 were at 4 atm pressure, and the Zn^{++} were 0.01 *M*, we would have

$$E = E^\circ - \frac{0.059}{2}\log\frac{0.01}{4} = 2.12 + 0.08 = 2.20 \text{ volt.}$$

Electrolysis

The electrolysis of a solution involves just the reverse process to that discussed thus far in this experiment. In this case, the electric current itself constitutes the oxidizing and the reducing agent. The negative electrode in the solution (the cathode), with its excess of electrons, is the reducing agent. The positive electrode (the anode) is, correspondingly, the oxidizing agent. Note, in Figure 19-3a, that at the negative electrode, the excess of electrons results in the electrode reaction

$$2\,e^- + Cu^{++} \longrightarrow Cu \quad \text{(reduction)}$$

At the positive electrode, the deficiency of electrons results in the removal of electrons from the chloride ions

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^- \quad \text{(oxidation)}$$

Study the electrode reactions in the commercial processes for the manufacture of sodium, sodium hydroxide, chlorine, aluminum, etc., as described in your text, *College Chemistry* Chapter 14.

In any process of electrolysis, the substances produced at the electrodes, together with their corresponding ions, constitute oxidation-reduction couples. These, in turn, act as an electric cell to set up a counter electromotive force. (See Fig. 19-3b.) It is necessary, therefore, in order for any

electrolysis to occur, to apply a greater voltage than this internal counter electromotive force.[1]

Faraday's Law

The amount of oxidation and reduction which takes place of course depends on the amount of electricity passed through the solution. The unit quantity of electricity is the *coulomb*. The unit of electric current is the *ampere*. There is a current of one ampere when one coulomb per second passes a given point in the circuit. That is:

$$\text{amperes} = \frac{\text{coulombs}}{\text{seconds}}.$$

The relationship between the quantity of electricity and the amount of chemical action produced by it, called *Faraday's Law*, states that a flow of 96,500 coulombs (one *Faraday*) of electricity will liberate one *chemical equivalent* of a substance. This is the amount of substance corresponding to the gain or loss of one "equivalent of electrons." Since there are 0.6023×10^{24} atoms (Avogadro's Number) in one gram-atom of an element, and since one electron is liberated when a silver atom becomes a silver ion (Ag^+), two electrons when a copper atom becomes a cupric ion (Cu^{++}), and so forth, we may say that one Faraday of electricity is equivalent to the transfer of 0.6023×10^{24} electrons.

Electrolytic Separation of Substances

In any process of electrolysis, the negative electrode (acting as a reducing agent) will react most easily and completely with the strongest oxidizing agent in contact with it. Thus, in a mixture of gold, silver, and copper salts, since auric ion is a stronger oxidizing agent than silver ion, and this in turn is stronger than cupric ion, we can plate out first gold, then silver, and finally copper, as the voltage is successively increased. As long as the voltage is kept below the reduction or decomposition potential for the remaining ions, *only* the more active one can plate out.[2]

Likewise, at the positive electrode (acting as an oxidizing agent), the most active reducing agent present will be liberated first. Thus, in a mixture of the halide ions, since iodide ion is the strongest reducing agent, then bromide ion, and finally chloride ion, the free halogen elements would be liberated, on electrolysis, in the same order—first iodine, next bromine, and then chlorine, as the voltage is successively increased. If the voltage is only slightly more than enough to liberate iodine, no bromine or chlorine will be produced.

In the commercial preparation of chlorine, it is necessary to use a concentrated chloride ion solution, because at low concentrations the chloride ion is a weaker reducing agent than the water present, in which case oxygen gas from the water, rather than chlorine gas, is liberated. At intermediate concentrations, or if the current density is too high to allow time for the chloride ion to migrate to the electrode, both oxygen and chlorine will be liberated.

Experimental Procedure

Special supplies: voltmeter (1000 ohms/volt) for class use; two dry cells connected in series, with 8-inch leads of bare copper wire to use as electrodes; 10-cm U-tube; electrode strips of Cu, Zn, Pb, and Sn, about 1×10 cm; very narrow strips or wire (1 mm $\times$ 8 cm) of Zn, Sn, and Cu, and also a few nails, for paragraph 5.

Chemicals: 1 *F* NH_4NO_3, 0.5 *F* $CuSO_4$, 0.5 *F* $Pb(NO_3)_2$, 0.1 *F* KI, 2 *F* Na_2S, 0.5 *F* $SnCl_2$, 0.5 *F* $ZnSO_4$.

1. A Simple Daniell Cell. Place a strip of sandpapered copper metal in a 100 or 150-ml beaker which contains about 35 ml of 0.5 *F* $CuSO_4$ solution. (Do not waste solution by using an excessive amount.) The metal electrode may be bent so as to lie across the bottom of the beaker and should extend above the top of the beaker. Prepare a similar "half-cell" with a strip of zinc metal in a 0.5 *F* $ZnSO_4$ solution. The solution should be at the same height in both beakers to avoid any siphoning action. Connect the two beakers by a "salt bridge" consisting of an inverted U-tube which is filled with zinc sulfate solution and which

[1] This discussion has not taken into account an empirical factor called the "overvoltage." This varies with the electrolysis reaction, the electrodes, and the conditions of electrolysis. It is frequently a polarization effect. To obtain any effective electrolysis, the applied voltage must be greater than the counter electromotive force plus the overvoltage.

[2] If a voltage sufficiently high to plate out copper is applied initially, and if the current density is too high to allow time for the more active ions to migrate to the electrode, those of lesser activity, such as Ag^+ and Cu^{++}, will also plate out with the gold.

has the ends plugged with cotton wet with the zinc sulfate solution. The voltage produced by this cell may then be measured by connecting the metal strips by means of copper wire to a high resistance voltmeter.[1] What constitutes the electric current in the wire? In the solution? Complete the diagram of this cell on the report sheet, labeling it as directed to show the various features and characteristics of the cell. Keep the cell for parts 2 and 3.

2. Standard Electrode Potentials. On the report sheet, rewrite the oxidation-reduction potential series for the couples studied in the last experiment and, at the right of each couple, list in another column its "standard electrode potential" as obtained from Table XIII, App. II, or from any handbook, text, or other reference source. Now calculate the potential which your Daniell cell should have, by algebraically subtracting (why do you subtract?) the voltage for the $Cu—Cu^{++}$ couple from that for the $Zn—Zn^{++}$ couple.[2]

For the experimental part of this section, set up cells similar to the Daniell cell, except use the $Pb—Pb^{++}$ couple. First connect it with the $Zn—Zn^{++}$ couple, and then with the $Cu—Cu^{++}$ couple, reading the voltages and noting the polarity in each case. For these cells, use a U-tube salt bridge of 0.5 *F* NH_4NO_3, to avoid forming insoluble salts. (Cells using other couples, such as the $Sn—Sn^{++}$ couple in combination with those already studied, may be tried, if you have time. The $Ag—Ag^{+}$ couple, which is too expensive for class use, may be demonstrated by the instructor.) Compare the voltage obtained in each case with the calculated values from the standard electrode potentials.

3. The Effect of Concentration. In order to see how changes in concentration affect the voltage, again set up the Daniell cell ($Zn—Zn^{++}$ with $Cu—Cu^{++}$). After reading the voltage, add an excess of sodium sulfide (about 10 ml of 2 *F* Na_2S) to the Cu^{++} half-cell, at the same time diluting the Zn^{++} solution with an equal volume of water. Mix, and read the voltage. If there is no material change, add a little more Na_2S. Explain the results. Will the presence of solid CuS affect the voltage?

4. The Electric Current as an Oxidizing and Reducing Agent. Dip the ends of the copper wires leading from two or more dry cells connected in series, into a small beaker containing 10 ml of 0.1 *F* KI solution and three drops of phenolphthalein. Explain the formation of the yellow color at one of the electrodes. Which one? Has this electrode acted as an oxidizing or a reducing agent? Write the equation for this half-reaction. The red color at the other electrode indicates the formation of what substance? What gas is being liberated? The reason for this is as follows. At this electrode (which one?), the most easily reduced substance will, of course, be the one to react. This is hydrogen ion from the water, not potassium ion, so instead of liberating potassium metal, the half-reaction here is

$$2\,e^- + 2\,H_2O \longrightarrow H_2 + 2\,OH^-.$$

As shown in the discussion, the products of the electrolysis will act as an electric cell, generating a counter electromotive force which tends to work against the applied voltage. From Table XIII, we see that the standard electrode potential for the $H_2—H_2O(10^{-7}\,M\ H^+)$ couple, corresponding to the reverse of the half-reaction above, is +0.414 volts. From this, subtract algebraically the standard potential for the $I^-—I_2$ couple, to get the minimum external voltage necessary to apply to cause any oxidation-reduction for this solution. Would a single Daniell cell be satisfactory to electrolyze a potassium iodide solution? (The student should remember that standard electrode potentials are based on solutions of definite concentration, one molar unless otherwise stated. Since these conditions are not maintained during the electrolysis, particularly with respect to the hydroxide ion around the hydrogen electrode, the calculated voltages are only a rough approximation.)

---

[1] An ordinary voltmeter which has about 250 ohm/volt will give a low reading because of the high internal resistance of cells constructed as suggested here. Voltmeters with a resistance of about 1000 ohm/volt, as the Weston Model 301, are quite satisfactory. These (one for each 10–15 students) may be located conveniently at a wall shelf for all to use.

A demonstration cell which has a low internal resistance and, therefore, gives a more accurate voltage measurement, may be made by placing the zinc strip and zinc sulfate solution in an unglazed porcelain cup which is supported in the cupric sulfate solution. Ionic contact thus is made through the porous porcelain, so that a salt bridge is unnecessary. This type of cell, using very small unglazed porcelain cups, may be used by the entire class, if desired.

[2] In these cells, we have used 0.5 *F* solutions, rather than 1 *F* on which the standard electrode potentials are based. This does not affect the equilibrium potential in these cases, since the concentrations of both product and reactant have been changed alike. See footnote 1, P. 139, and paragraph 3, this page.

5. The Corrosion of Metals.[1] This phenomenon is closely related to oxidation-reduction and its application in electric cells. Select three bright iron nails or other pieces of iron. Wrap around one of these a small narrow strip of tin, around another a copper wire, and around the third a small, narrow strip of zinc. Place the nails in separate test tubes and partially cover them with water. Let them stand over night or longer. Explain the results in terms of the action of an electric cell.

[1] This can be set up advantageously as a demonstration in the laboratory for all to observe.

Drill on Products of Electrolysis and on Cells

Note: Here is some supplementary drill material for you to work on after completion of your regular Report Sheets. This need not be handed in unless called for.

I. In each of the following cases, indicate, in the spaces provided at the right, *all* the substances (ions or molecules) which will be liberated *first* at each electrode when electrolysis takes place. Assume inert electrodes, such as carbon rods, and a low current density.

	At the Positive Electrode	*At the Negative Electrode*
1. Concentrated $CuCl_2$ solution		
2. Fused NaCl		
3. Concentrated NaCl solution		
4. Dilute NaCl or Na_2SO_4 solution		
5. Dilute H_2SO_4 solution		
6. A solution of $CuSO_4$ and $NiSO_4$		
7. A concentrated solution of $FeBr_2$ and $SnCl_2$		

II. In the commercial preparation of aluminum, purified Al_2O_3, obtained from bauxite, is dissolved in molten cryolite, Na_3AlF_6, and the mixture is electrolyzed with carbon electrodes. List all the ions present in the molten mixture, write equations for the electrode reactions, and account for the fact that the other ions present are *not* liberated as the free elements under these conditions.

III. Make simple diagrammatic sketches of the lead storage battery and of the dry cell (see your text for any needed information). Show all essential parts—electrolytes (a "dry cell" isn't dry) and electrodes, with the charge induced on each. Write equations for the half-reactions at each electrode, with the voltage for each (from Table XIII in Appendix II), and combine these to get the total cell reaction and total voltage. Compare with your common knowledge of this and with the value given in your text. (Use another paper for these sketches.)

REPORT: Exp. 19

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

The Production of an Electric Current by Means of Oxidation-Reduction Reactions

1. A Simple Daniell Cell. Complete the diagram at the right by writing in the formulas for the substances present in various parts of the cell. Indicate the charge at each electrode by (+) and (−) signs.

What constitutes an electric current in a wire?

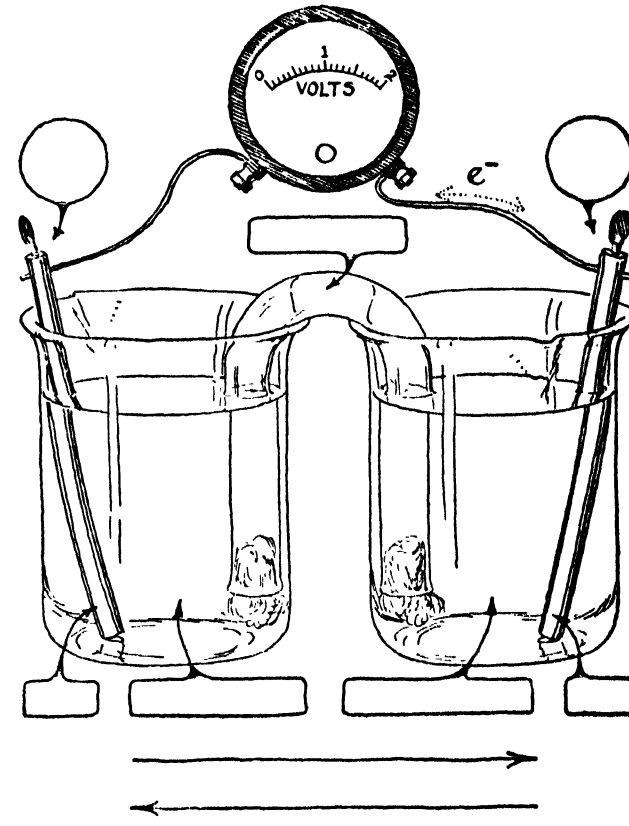
_____

Indicate the direction of these particles by an arrow placed on the wire.

What constitutes an electric current in a solution?

_____

Indicate the direction of the movement of these particles by placing their formulas on the proper arrow below the sketch.



The half-reaction taking place at the negative electrode is

_____

The half-reaction taking place at the positive electrode is

_____

The total cell reaction is

_____

_____

2. Standard Electrode Potentials. In the space at the right, rewrite the potential series for the couples studied in Experiment 17, page 123 and insert the standard electrode potential for each, as obtained from Table XIII, App. II.

Potential Series

Couple	*Volts*

Calculate the potential for your Daniell cell, as directed:

What voltage did you obtain experimentally for the Daniell cell?[1]

_____

[1] The values in Table XIII are obtained by measurements in a reversible manner, with very small currents, using a potentiometer, so that the internal resistance of the cells does not tend to decrease the voltage reading, as is the case when a voltmeter is used.

In the space below, write the equation for the cell reaction for each cell that you tried. Indicate which metal is the positive and which the negative electrode, and give the experimental and the calculated voltages in each case.

Cell Reaction	*Positive Pole*	*Negative Pole*	*Experimental Voltage*	*Calculated Voltage*

3. The Effect of Concentration. Write the net ionic equation for the reaction taking place when Na_2S is added to the copper sulfate solution:

Explain the effect of this addition of Na_2S on the cell voltage:

How would you adjust the concentrations of the Cu^{++} and of the Zn^{++} in the Daniell cell in order to get the maximum voltage possible for this cell?

4. The Electric Current as an Oxidizing and Reducing Agent. At the right sketch a diagram for the electrolysis of a potassium iodide solution, indicating the cathode, the anode, the direction the various ions move in the solution, and the products formed at each electrode. (Make a *neat sketch.*)

The yellow color at one electrode is due to the formation of

This appeared at which electrode?

Is this electrode the oxidizing agent or the reducing agent?_____

The equation for the half-reaction taking place at this electrode is:

_____

The equation for the half-reaction taking place at the other electrode, which liberates H_2 gas (see experiment directions), is:

_____

The net ionic equation for the electrolysis of a potassium iodide solution is therefore:

_____

Calculate the minimum external voltage needed to cause oxidation-reduction of a 1 *F* KI solution:

_____ volts

Would a single Daniell cell be satisfactory to bring about this oxidation-reduction? Explain. (See experiment directions.)

5. The Corrosion of Metals. The observed results on the rusting of iron in contact with other metals is indicated below:

Iron with copper _____

Iron with zinc _____

Iron with tin _____

Explanation of these results:

Why does a "tin" can (iron plated with tin) rust more easily than a galvanized pipe (iron plated with zinc) when exposed to weathering?

Why do we use cans of tin plate, rather than galvanized iron, for preserving fruit and other food products?

Application of Principles

1. At the right make a sketch for a cell using the Br^-—Br_2 and the Zn—Zn^{++} couples. Indicate the behavior of all parts of the cell, as you did for the Daniell cell.

2. Write the equations for the electrode reactions, and for the total cell reaction:

3. Calculate the potential to be expected if all ions are at 1 *M* concentration, and the solution is saturated with Br_2.

_____ volts

4. Heat is evolved when zinc reacts with bromine. Would the potential for this cell be greater or smaller if the cell were heated? Explain.

5. a) In commercial silver plating the article to be plated, e.g. a teaspoon, is connected to which electrode of the battery?

_____

b) Is this electrode the oxidizing or the reducing agent?

_____

c) To plate a surface of silver 0.1 mm thick on a knife (estimated 75 cm^2 surface) would require about 7.00 grams of silver. How long would it take to plate out this much silver, using a 0.400 ampere current?

_____minutes

d) How long would it take to plate out 4.00 grams of gold from an auric chloride solution on this same knife, using 0.400 ampere?

_____minutes

The Concentration of Solutions. The Fractional Crystallization of Salts

20

College Chemistry, Chapter 18

Review of Fundamental Concepts

Units of Concentration as Used in Chemistry

Since the concentration of the solutions we use is an important factor to be considered in this and in many succeeding experiments, we shall introduce a study of this concept at this time. It is, first of all, important to distinguish between units of quantity and units of concentration. The term concentration refers to the amount of dissolved substance in a given amount or volume of solution, that is

$$\text{concentration} = \frac{\text{amount of solute}}{\text{volume}}.$$

For example, if we dissolve 34.2 g of sugar ($C_{12}H_{22}O_{11}$) in enough water to make 100 ml of solution, we will have quite a concentrated solution which will taste distinctly sweet. But if we dissolve 34.2 g of sugar in enough water to make 10 liters of solution, we will have used the same *amount* of sugar, but the *concentration* will be much less than before, and the solution will hardly taste sweet at all.

In chemical practice, it simplifies calculations to express the concentration of solutions in terms of the fundamental chemical units of quantity, as follows:

Formality. A solution which contains one gram-formula weight of solute dissolved in water and diluted to a total volume of one liter (not added to one liter of water) is called a one formal solution, designated 1 *F*. One might dissolve a half formula weight in a half liter, or ten formula weights in ten liters, and likewise have a 1 *F* solution. The defining equation is

$$\text{Formality} = \frac{\text{formula weights of solute}}{\text{liters of solution}}, \text{ or } F = \frac{\text{gfw}}{\text{V(liters)}}.$$

Molarity. Likewise, a solution which contains one mole of substance per liter of solution is designated a one molar (1 *M*) solution. The defining equation is

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}, \text{ or } M = \frac{\text{moles}}{\text{V(liters)}}.$$

Note that the terms "formula weight" and "formality" are inclusive terms, and include "mole" and "molarity," respectively. While these latter terms are often used in the same sense as formula weight and formality, we shall restrict their use to cases where a definite molecular or ionic species is represented by the formula used. Thus, we speak of a 1 *F* (not 1 *M*) NaCl solution, since the formula NaCl does not represent a definite molecule which is present as such either in the solid crystal or in solution. Since the solution is regarded as completely ionized, we may speak of a 1 *F* NaCl solution as containing 1 *M* Na^+ and 1 *M* Cl^-.

Several examples will help you to understand the meaning of the above defining equations.

Example 1. What are the concentrations of the sugar solutions mentioned above, which contain 34.2 g $C_{12}H_{22}O_{11}$ in 100 ml and in 10 liters of solution, respectively?

Since the solution contains molecules of the composition $C_{12}H_{22}O_{11}$, we can designate this as molarity. Formality would be equally correct, but less specific. First we shall express 34.2 g as moles,

$$\frac{34.2\text{ g}}{342\text{ g/mole}} = 0.1\text{ mole}.$$

From the defining equation, we write

$$M = \frac{\text{moles}}{\text{V}} = \frac{0.1\text{ mole}}{0.1\text{ liter}} = 1\ M \text{ for the first solution,}$$

and

$$\frac{0.1\text{ mole}}{10\text{ liters}} = 0.01\ M \text{ for the second solution.}$$

Example 2. How many gram-formula weights are there, and what is the weight of H_2SO_4 in grams, in 250 ml of 0.300 *F* H_2SO_4?

Transposing the defining equation $F = \text{gfw/V}$, we have

$$\text{gfw} = F \times \text{V} = 0.300\,\frac{\text{gfw}}{\text{liter}} \times 0.250\text{ liter} = 0.075\text{ gfw } H_2SO_4.$$

And to express this quantity in grams, we write

$$0.075\text{ gfw} \times 98\,\frac{\text{g}}{\text{gfw}} = 7.35\text{ g } H_2SO_4.$$

Example 3. What volume of 0.300 *F* H_2SO_4 will be required to react with 4.00 g NaOH?

$$\frac{4.00 \text{ g NaOH}}{40.0 \text{ g/gfw}} = 0.100 \text{ gfw NaOH.}$$

By the equation for the reaction

$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,H_2O$$

it is evident that 2 gfw NaOH will require 1 gfw H_2SO_4, therefore 0.1 gfw NaOH will require 0.050 gfw H_2SO_4. From the defining equation $F = \text{gfw}/V$, we have by transposing,

$$V = \frac{\text{gfw}}{F} = \frac{0.050 \text{ gfw.}}{0.300 \text{ gfw/l}} = 0.167 \text{ l or } 167 \text{ ml of } 0.300\ F\ H_2SO_4.$$

Some Other Units of Concentration. Other ways in which the concentration of solutions may be designated are the following. **Percent by weight** refers to parts of solute per one hundred parts of solution. Thus, a 5% solution is one which contains 5 g of solute to every 95 g of solvent. Sometimes, as in tables of solubility data in the reference literature, the concentration is expressed as **grams of solute per 100 g of solvent.** Again, in cases where the relative number of molecules of solute and solvent are fundamental to the theory, concentration is expressed as **mole fraction,** or as **weight formality** or **weight molarity.** These two latter terms refer to the number of formula weights or moles, respectively, per 1000 g of solvent (rather than per liter of solution). **Normality** as a unit of concentration will be introduced in Experiment 27.

Saturated Solutions

A saturated solution is one in which an **equilibrium** exists between the rate at which molecules or ions in solution are depositing on the surface of the solid crystals and the rate at which molecules or ions are leaving the crystal surface and mixing with the solvent molecules in solution. At equilibrium these opposing rates are equal, so that the concentration of the solution remains constant. Any factor which disturbs this system, such as the evaporation of solvent or the cooling of the solution, may cause additional crystals to deposit.

When soluble salts dissolve in water, they are present as separate ions in solution (Exp. 16). Any given positive ion, or cation, may combine with any given negative ion, or anion, to form a crystalline salt whenever the concentration of ions in solution is great enough to exceed the solubility of the salt in question. Thus from a solution containing sodium ion (Na^+), potassium ion (K^+), chloride ion (Cl^-), and nitrate ion (NO_3^-), it is possible to form four crystalline salts, with the formulas NaCl, $NaNO_3$, KCl, and KNO_3. The particular salt which crystallizes out first will depend on the temperature and relative concentration of the several ions in the solution. The deposits of soluble salts which occur in nature, as those at Stassfurt, Germany, and those at Searles Lake in California, have been formed by such fractional crystallization from solution, as large bodies of salt-bearing water evaporated. The following discussion will help you to understand how such fractional crystallization may occur.

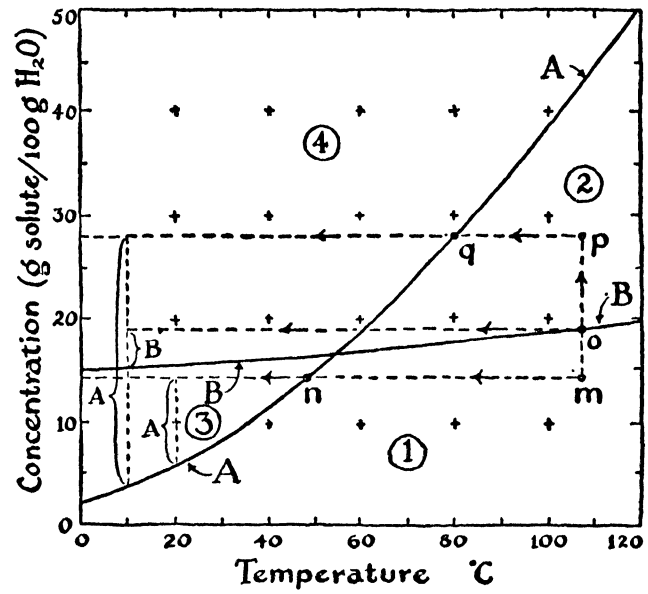


FIG. 20-1. The principles of fractional crystallization, as illustrated by the solubility curves for two substances A and B.

The Theory of Fractional Crystallization

Study the graph, Figure 20-1, which shows the saturated solution curves for two typical substances. The solubility of A increases rapidly with increasing temperature, while that of B increases only slightly. Note the different situations in different regions of the graph. In area (1), below both curves, the solution is unsaturated with respect to both A and B. In area (2) it is unsaturated with respect to A, saturated with respect to B, and contains excess solid B. What is the situation in area (3)? In area (4)?

Now suppose we start from a point *m*, at which

the solution will contain about 14 g each of A and B per 100 g of water, at the boiling point. Let us cool the solution. The point moves horizontally to the left. At *n* (about 50° C), the saturation point of A is reached and solid A begins to separate. When the solution has cooled to 20° C, approximately 7 grams of A per 100 grams of water will have crystallized.

Again start as before from point *m* but, instead of cooling the solution, evaporate it at the boiling point until half the water is removed. Now the point moves directly upward. At point *o*, solid B begins to separate, so that at point *p*, when half the water is evaporated, we have about 28 grams of A per 100 grams of water. We also have a saturated solution of B and about 8 grams of solid B. Now filter off the solid and cool the filtrate (moving to the left from both *p* and *o*, on the diagram). A little additional solid B will at once begin to separate and when the solution is cooled to about 80° C (point *q*), solid A will also separate. When the mixture is cooled to 10° C, we will have a large amount of A (about 24 grams per 100 grams of water) and only a small amount of B (about 4 grams) crystallized out. We have, thus, achieved quite a separation. How could this mixture of A and B be dissolved and recrystallized so as to obtain pure A?

Preliminary Exercise

Before the laboratory period, make a neat and accurate graph of the solubility, in grams per 100 grams of water, of each of the four salts given in Table 20-1 below, at temperatures from 0° C to 100° C. Arrange the temperature scale to extend well across the horizontal axis, with a suitable scale of concentration on the vertical axis. Make all four curves on the same graph paper, and draw a smooth curve through the points for each substance. Label each curve with the formula for the salt. From a study of the theory of fractional crystallization as given above, and from your graph, decide what effect temperature and concentration will have in determining which particular salt will crystallize out first under various conditions. (Answer the four questions in the report sheet bearing on this question.)

TABLE 20-1.

THE SOLUBILITY OF CERTAIN SALTS AT VARIOUS TEMPERATURES

(Solubility in grams of solute per 100 grams of water. Data from Seidell, *Solubilities of Inorganic and Organic Compounds*, Vol. 1, P. 747, 834, 1218, 1275. D. Van Nostrand Co., N. Y. 1940.)

	0° C	10° C	20° C	30° C	50° C	80° C	100° C
NaCl	35.7	35.7	35.8	36.1	36.8	38.0	39.2
$NaNO_3$	73.3	80.8	88	95	114	148	175
KCl	28.0	31.2	34.2	37.0	42.9	51.2	56.3
KNO_3	13.9	21.2	31.6	45.4	83.5	167	245

Experimental Procedure

Special supplies: Buechner funnel and filter flask to fit, with pressure tubing connection. Nichrome wire and 2 squares of cobalt glass for flame tests. Ice. Thermometer.

Chemicals: Chile saltpeter $NaNO_3$, crude KCl, $FeSO_4$, 0.1 *F* $AgNO_3$.

We shall utilize the same method for preparing potassium nitrate that is extensively used in chemical industry, namely by fractional crystallization from crude Chile saltpeter, $NaNO_3$, and crude potassium chloride, KCl. The sodium chloride obtained as a by-product will also be purified.

1. Preparation of Potassium Nitrate and Sodium Chloride. Calculate the weights of ¾ of a gram-formula weight each of crude $NaNO_3$ and KCl. (Do not use the reagent grade chemicals on the reagent shelf.) Place these weights of the $NaNO_3$ and KCl, together with 140 ml of tap water, in a 400-ml beaker, and heat the mixture almost to boiling to dissolve the salts. Filter while hot with the aid of vacuum, using either technique as illustrated in Figure 20-2, to remove any insoluble foreign matter. Transfer the hot filtrate to a 250-ml beaker and chill it, with stirring, to 5° C or lower, by immersing the beaker in an ice bath in some suitable container. Clean and rinse the funnel and filter flask. (Cool the funnel if it is still warm.) Quickly filter the cold KNO_3 crystals and press out all excess moisture with another filter paper laid over the crystals (Fig. 20-3). Set these crystals aside for later purification.

By reference to your graph, estimate the weight of KNO_3, which still remains dissolved in the filtrate. (Remember that 140 ml of water was used.)

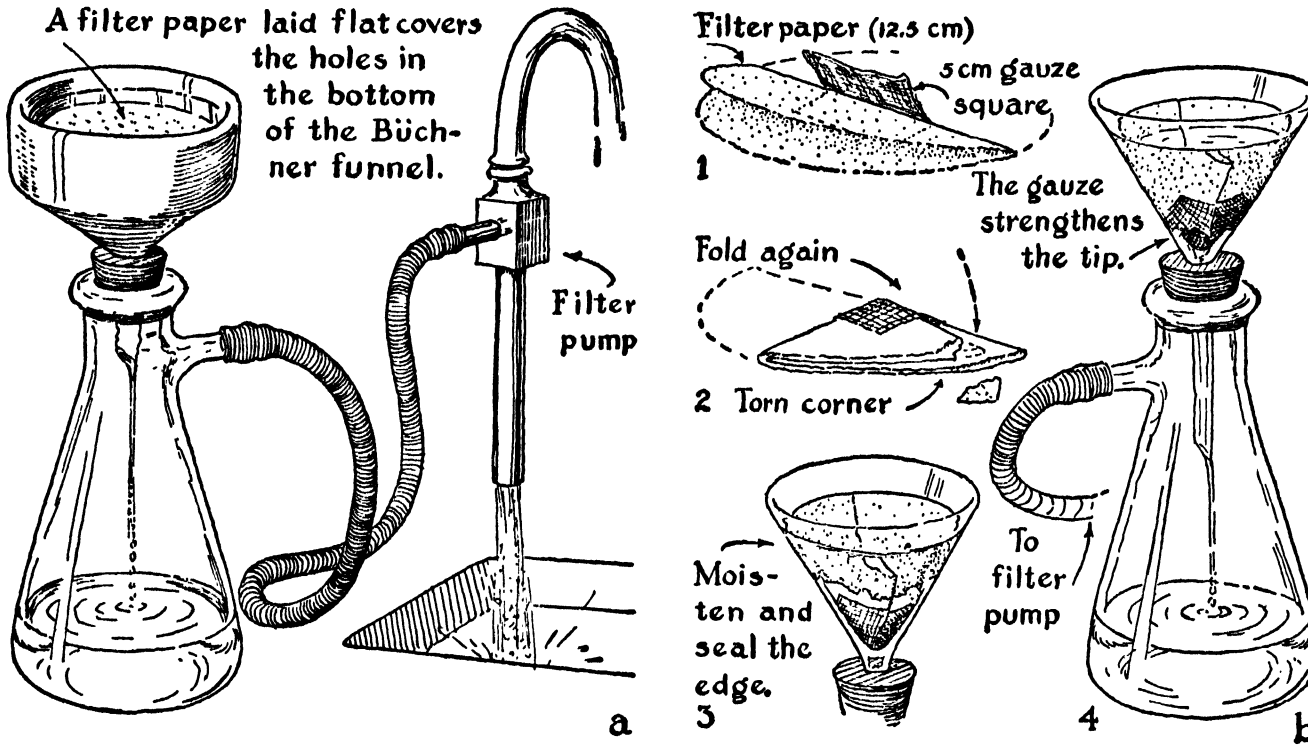


FIG. 20-2. Vacuum filtration technique: (a) using a Buechner funnel, (b) using an ordinary funnel with gauze folded in the filter paper to strengthen it.

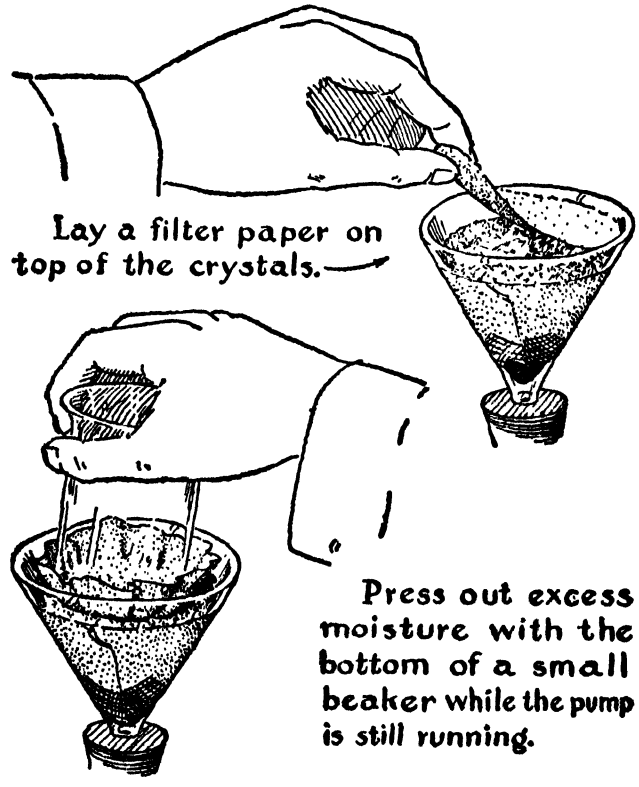


FIG. 20-3. Pressing out the excess moisture from the crystals.

To obtain a second crop of KNO_3 crystals, place the filtrate in a beaker and boil it down rapidly. What solid separates as the solution is concentrated? As the boiling continues, the mixture begins to bump violently. This may be minimized as follows. Seal one end of a 20-cm glass tube. Leave the other end open with sharp edges. Use this, open end down, to stir the mixture continuously (Fig. 20-4).

Continue the evaporation until the volume has been reduced to a half or a third of its original volume, as estimated by its height in the beaker, and until quite a large amount of salt has separated. Do not reduce the volume to less than a third of its original volume, however. Filter this mixture, while boiling hot, by vacuum filtration. Press out all the mother liquor you can and at once transfer the filtrate to a small beaker. Rinse the flask with a volume of water about one tenth of the volume of the filtrate (estimate it rather carefully), and add this to the filtrate. Why is this done? Save this crude NaCl for later purification, if time is available.

Heat the filtrate to redissolve any salts which

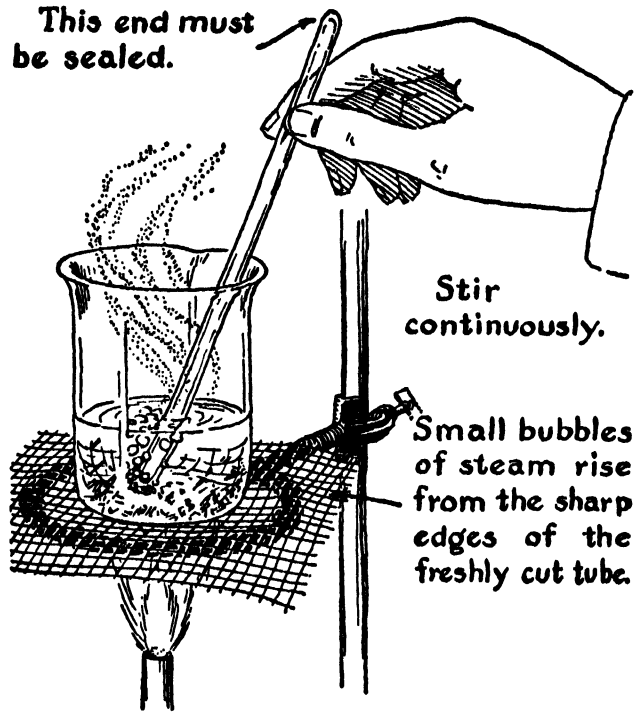
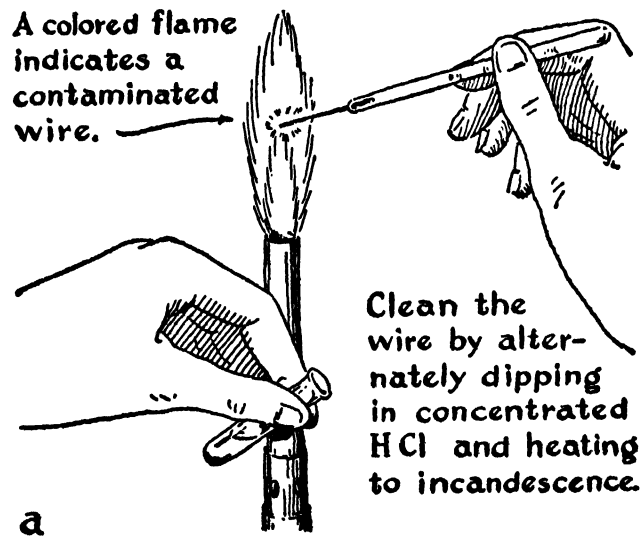


FIG. 20-4. The use of a closed tube to prevent excessive bumping as sodium chloride is crystallized by evaporation.

have separated and then chill the filtrate to 5° C or less by immersing the beaker in ice, as before, to obtain a second crop of KNO_3 crystals. Filter, and combine these crystals with the first batch. They may be weighed damp, and the dry weight estimated as about 90% of the damp weight. Or if you have time before recrystallizing, they may be spread out on a clean paper in your locker to air dry. Record the weight of the crude KNO_3 you have prepared.

2. Tests for Purity. Both of your crude salts will need to be purified by recrystallization. Before you do this, learn the following qualitative tests and use them to check on the purity of your salts as you recrysallize them.

Flame Tests for Sodium Ion and Potassium Ion. Obtain a nichrome wire and two pieces of cobalt glass. Clean the wire by alternately heating it intensely in the flame and dipping it in a little concentrated HCl in a small test tube. Continue this treatment until the wire does not impart a definite color to the flame. Then moisten a very small pinch of the salt to be tested and touch the nichrome wire to it. (Be sure the wire touches nothing else after it has been cleaned.) Place the wire in the edge of a low Bunsen flame to heat it to incandescence. A strong yellow flame indicates sodium, while a fainter violet flame, which does not last very long, indicates potassium. With a mixture of sodium and potassium, the intense yellow flame completely masks the fainter violet flame. The sodium flame may be screened out by placing two



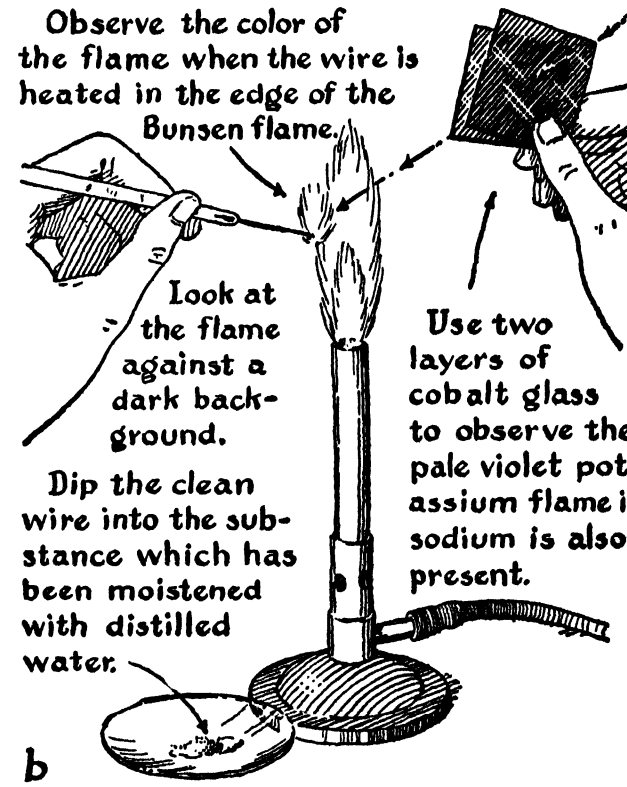


FIG. 20-5. The flame test for sodium and potassium: (a) Cleaning the wire, (b) Observing the flame colorations.

thicknesses of cobalt glass in front of the flame. The shorter wave-length potassium flame is transmitted, and may be seen through the glass; however, it lasts only a short time (see Fig. 20-5).

Test for Chloride Ion.[1] Dissolve a very small amount (0.01 g) of the salt to be tested in 2 ml of water, acidify with 2 drops of 6 *F* HNO_3, and then add a drop of 0.1 *F* $AgNO_3$. A milky precipitate of AgCl indicates the presence of chloride ion.

Test for Nitrate Ion.[1] Dissolve 0.01 g of the salt to be tested in 2 ml of water and add this to 2 ml of saturated $FeSO_4$ solution. (Since $FeSO_4$ solution is easily oxidized, prepare your own solution by adding a small amount of the solid to a little water in a test tube and mixing.) Incline the test tube containing your test sample and $FeSO_4$ at quite an angle and very gently add a little concentrated H_2SO_4 so that it runs down and underlies the other solution. A characteristic brown ring at the juncture of the two layers indicates the presence of a nitrate.

3. The Purification of Potassium Nitrate. Before recrystallizing, test a very small amount (half the size of a pea) for chloride ion. *Save this test*, as well as subsequent tests for Cl^-, so they may be compared and any increase in purity thus observed. To recrystallize your KNO_3, place the salt in a 150-ml beaker, add as many milliliters of distilled water as you have grams of dry KNO_3 crystals, and warm the mixture to completely dissolve the crystals. Cool the solution in an ice bath to 5° C or less, and filter the crystals while they are cold by vacuum filtration. Press down the crystals and suck out all the moisture you can. Again test the purity of your KNO_3 crystals by the chloride test. It will probably be necessary for you to recrystallize your KNO_3 a third time, or possibly a fourth time, before you get it reasonably pure, so that it fails to give a significant chloride test.

Test a small amount of the final salt also for nitrate ion, and by the flame test for potassium ion and for freedom from sodium ion. The sodium flame test is exceedingly sensitive, and responds to the slightest amount of impurity.

Air-dry the crystals by spreading them out on a watch glass, or clean paper. Weigh the crystals and compute the percent of pure KNO_3 recovered from the crude salt. Hand in your crystals, labeled with your name, the formula of the salt, and a note as to the extent of any impurities found, as your laboratory instructor may direct.

4. The Purification of Sodium Chloride. (Optional.) Test a small sample (size of half a pea) of your crude NaCl for K^+ and for NO_3^-. The salt may be recrystallized by first dissolving it in the minimum amount of boiling water (use about 3 ml of H_2O to each gram of salt), and then by boiling the solution rapidly to concentrate it to one third of its volume. The addition of concentrated HCl at this point (use a volume about one tenth that of the mixture) will cause some additional precipitation of NaCl, due to the increase in the Cl^- concentration. Filter the crystallized salt by vacuum filtration. The salt may be dried by heating it, with stirring, in an evaporating dish. A second crop of crystals of lesser purity can be obtained by further concentration of the filtrate. Test the recrystallized samples for purity.

[1] Both the chloride and the nitrate ion tests are discussed more fully in Experiment 39. See Figure 39-1 for an illustration of the brown ring test for nitrate ion.

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

REPORT: Exp. 20

Fractional Crystallization

Preliminary Exercise

The graph of salt solubilities you have made should be handed in with this report. Use this graph to help you answer the following:

a. If a solution containing equal amounts of the four ions, Na^+, K^+, Cl^-, and NO_3^-, is evaporated at the boiling point, which salt will crystallize out first? Explain.

b. If this hot mixture is now filtered, and the filtrate cooled with ice, which salt will crystallize out in largest amount? Explain.

c. Will any of the same salt that crystallized out at the boiling point (question a above) separate out along with this second salt as the solution cools? Explain.

d. What effect would the addition of a little water to the hot filtrate (in question b) have on the purity of the crystals which form when the solution is cooled? Explain.

Approval by instructor of the graph, and of the answers to the questions above _____

1. Preparation and Purification of Potassium Nitrate

Weight of crude salts taken: $NaNO_3$_____ KCl_____

My estimate of the weight of KNO_3 which still remains in the filtrate after the first crystallization of KNO_3 (based on graph, and volume of water used) . . . . . _____ g

Weight of dry crude KNO_3 obtained (both batches) . . . . . _____ g

Theoretical weight of KNO_3, based on the weight of crude salts taken. Show calculations. . . . . _____ g

Percent yield of crude KNO_3[1] . . . . . _____ %

[1] In commercial saltpeter plants, it is possible to obtain nearly a 100% yield of KNO_3, because it is then practical to recirculate the filtrates still containing some KNO_3 with the richer liquors, thus finally obtaining nearly all the KNO_3 in crystalline form.

2. Purification of Potassium Nitrate

After successive recrystallizations, the relative amounts of AgCl formed on testing for Cl^- was as follows:

1st crystallization_____ 2nd recrystallization_____ 3rd recrystallization_____

Tests of the final purified KNO_3 showed the following results:

For Na^+_____ For K^+_____ For NO_3^-_____

Why does successive recrystallization of a salt such as KNO_3 increase its purity?

Weight of pure dry KNO_3 obtained_____ g

Percent of your crude KNO_3 recovered as the pure salt_____ %

3. Purification of Sodium Chloride

If you recrystallized your NaCl, comment on the relative freedom from K^+ and from NO_3^- (1) of the crude salt, (2) of the first crop of crystals on recrystallization, and (3) of a second crop of crystals, if obtained.

Why is the recrystallization less efficient as to yield than in the case of the recrystallization of KNO_3?

Problems

1. Calculate the gross profit one could make in the manufacture of a ton of crude KNO_3 from Chile saltpeter ($NaNO_3$) and muriate of potash (KCl), if a 100% theoretical yield could be obtained. (Use these commercial prices: KNO_3 \$200 per ton, $NaNO_3$ \$50 per ton, and KCl \$30 per ton. Neglect the by-product formed, NaCl.)

\$_____

2. Repeat the calculations of problem 1 on the basis of your actual percent yield of crude KNO_3 (i.e. before recrystallization). Hint: Note that the lower your percent yield, the larger the weights of $NaNO_3$ and KCl are which you must use to obtain a ton of KNO_3.

\$_____

Exercises on the Units of Concentration

In each of these cases, indicate clearly the method of solution, including the proper use of dimensions.

1. Complete the items called for in each of the following:

Solution	*Formula Weight*	*Number of gfw*	*Formality*
(a) 20.0 g NaOH in 250 ml solution	_____	_____	_____
(b) 30.3 g KNO_3 in 500 ml solution	_____	_____	_____
(c) 245 g H_2SO_4 in 3000 ml solution	_____	_____	_____

2. What amount of the solute is present in each of the following solutions?

(a) 500 ml of 4 *F* HCl . . . . . _____ gfw

_____ g

(b) 750 ml of 0.2 *F* HCl . . . . . _____ gfw

_____ g

(c) 750 ml of 0.2 *F* $C_{12}H_{22}O_{11}$ (sugar) . . . . . _____ gfw

_____ g

3. It is desired to measure out 5.0 g of each of the solutes in the following solutions. What volume of each solution should be used?

(a) 3 *F* $NaC_2H_3O_2$ . . . . . _____ ml

(b) 0.1 *F* $CuSO_4$ . . . . . _____ ml

(c) 3 *F* HNO_3 . . . . . _____ ml

4. Given a solution of a substance, as indicated in the first column, with certain other data given in succeeding columns. From this data calculate the corresponding values to fill in the blank spaces. (Thus, for the first case given 9.1 g of HCl in 500 ml of solution, we may calculate thus: we have 9.1 g/36.5 g per gfw = 0.25 gfw; since there are 0.25 gfw in 500 ml, the concentration is 0.25 gfw/0.5 l = 0.5 *F*.)

Substance	*Formula Weight*	*Volume (ml)*	*Formality*	*Number of gfw*	*Weight of Solute (g)*
HCl	36.5	500			9.1
NaCl	58.5		2.0	0.20	
H_3PO_4	98		3.0		4.9
$Q(OH)_2$		3000		0.60	60
H_2XO_3		400	3.0		120

5. Concentrated nitric acid has a density of about 1.42 g/ml, and is about 16.0 *F*. Express this concentration in each of the following ways:

(a) as percent composition . . . . . _____

(b) as g/100 g of solution . . . . . _____

(c) as g/100 g of solvent . . . . . _____

(d) as weight formality . . . . . _____

6. Concentrated hydrochloric acid contains about 37.0% HCl and has a density of 1.184 g/ml. What is the formality of this solution?

_____

7. Concentrated sulfuric acid is about 18.0 *F* and contains 96.0% H_2SO_4. What is the density of this solution?

_____

The Chemistry of Sulfur and Its Compounds — 21

College Chemistry, Chapter 14

Review of Fundamental Concepts

Sulfur compounds:

↑		+6 SO_3, H_2SO_4, SO_4^{--}	Concentrated acid is a strong oxidizing agent.
		+4 SO_2, H_2SO_3, SO_3^{--}	Active either as oxidizing or reducing agent.
o	r	ave +2 $S_2O_3^{--}$	Thiosulfate ion. Decomposes to S and H_2SO_3 in acid solution. Oxidized to $S_4O_6^{--}$ (tetrathionate ion) by free I_2.
		0 S	
	↓	−2 H_2S, S^{--}	Strong reducing agent, usually oxidized to S.

In this experiment we shall study the physical and chemical properties of the element sulfur and its more important compounds. The chart given above summarizes the various oxidation states which are illustrated by sulfur compounds.

As you perform the experiments outlined, keep constantly before you the structural formulas of the compounds involved by reference to the textbook. Recall that sulfur, a sixth group element, may be represented by the electron dot formula $:\dot{\underset{\cdot}{\overset{\cdot\cdot}{S}}}\cdot$. By gaining two electrons from metallic elements, it forms sulfides in which the sulfide ion, S^{--}, has attained the stable configuration of an inert gas. The oxidation state is also −2 in the covalent compound H_2S, where the sulfur atom shares electrons with two hydrogen atoms.

By sharing its electrons with more negative elements such as oxygen, sulfur attains positive oxidation states. In sulfur dioxide, SO_2, four of the sulfur electrons are involved in forming covalent bonds with oxygen. Sulfur dioxide is the anhydride of the weak acid, H_2SO_3, which forms salts with bases in which the ions, HSO_3^- or SO_3^{--} are present.

In sulfur trioxide, all six of the sulfur electrons are involved in forming bonds with oxygen atoms. This oxide is the anhydride of sulfuric acid, H_2SO_4, which is one of the most important industrial inorganic chemicals. Salts of this acid contain the ions, HSO_4^- or SO_4^{--}, which are further illustrations of sulfur in the +6 oxidation state.

In elementary sulfur, the sulfur molecule at ordinary temperatures contains eight atoms arranged in a puckered ring. These rings are oriented to form rhombic crystals at ordinary temperatures, but above 95.5° C., the transition temperature, these molecules rearrange themselves to form monoclinic crystals. Above its melting point, sulfur undergoes some interesting changes in properties with increasing temperature which can be accounted for in terms of changes in the structure of the sulfur molecule.

Experimental Procedure

Special supplies: Thermometer, thistle tube.

Chemicals: Crushed roll sulfur, iron filings, powdered magnesium, mossy zinc, copper turnings, $KMnO_4$, Na_2SO_3, 0.1 *F* solutions of NaCl, $CaCl_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $SbCl_3$, $Pb(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$, $BaCl_2$, $Ba(OH)_2$, 2 *F* Na_2S, Bromine water, 1 *F* Na_2SO_4.

1. Oxidation State Zero, Elementary Sulfur

(a) *Forms of solid sulfur.* Recall the differences in appearance and properties of the two crystalline modifications of sulfur prepared in Experiment 2, Part 5, and record this data in the report sheet.

(b) *Liquid sulfur.* Fill a small test tube about one-third full of crushed sulfur and heat it very *slowly* over a small flame until the sulfur just melts. Raise the temperature gradually and note the color and fluidity of the sulfur from time to time. Continue the heating until the sulfur boils. Pour the molten sulfur into a beaker of cold water and examine the product. Test its solubility in 3 ml of carbon disulfide. (**Caution:** *Handle CS_2 at least five feet from any flame.*)

2. Oxidation State −2. Sulfides and Hydrogen Sulfide (Optional)

(a) *Preparation of a sulfide.* Mix approximately 3.5 g of iron filings with 2 g of crushed sulfur in a crucible supported on a triangle. Place a lid on the

crucible and heat it with a Bunsen burner until the reaction begins. Remove the lid and burner occasionally to note whether the reaction continues with the evolution of heat. Continue the heating to burn off any excess sulfur and allow the crucible

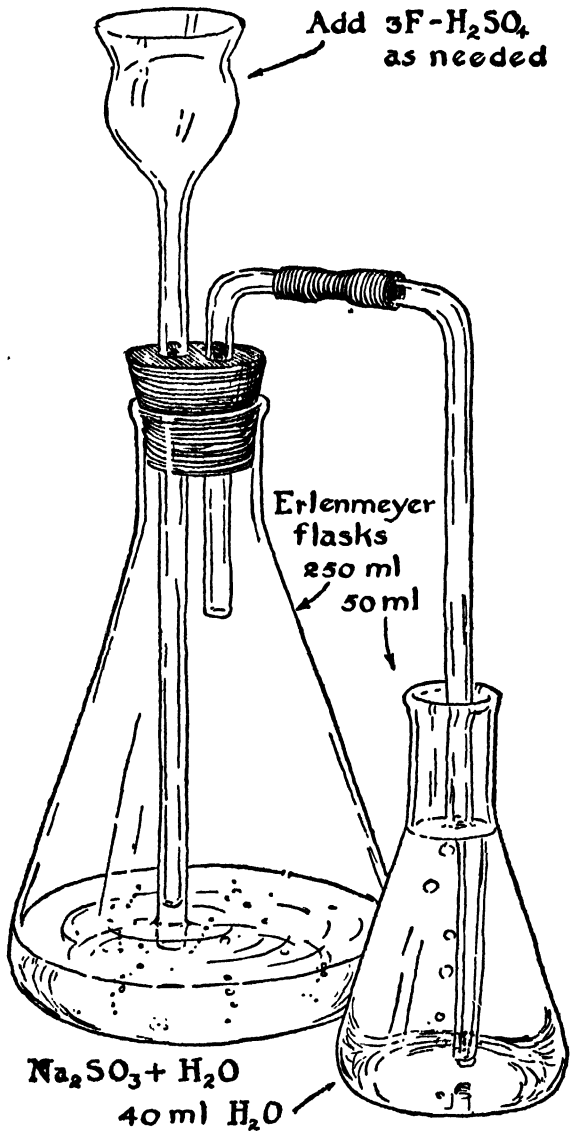


FIG. 21-1. The preparation of sulfur dioxide.

to cool. Write the equation for the reaction. Place a small piece of the compound into 3 ml of 6 *F* HCl in a small test tube and cautiously note the odor of the gas evolved.

(b) *Hydrogen sulfide as a precipitating reagent.* Many metallic sulfides are difficultly soluble in water or in acids, and advantage is taken of this fact in the separation of groups of metals in Qualitative Analysis. (See Study Assign. G.) Using a source of hydrogen sulfide available in your laboratory, (see footnote in Exp. 16, P. 112) saturate 5 ml of each of the following solutions with H_2S gas: 0.1 *F* $CuSO_4$, 0.1 *F* $SbCl_3$, 0.1 *F* $Cd(NO_3)_2$, 0.1 *F* $Zn(NO_3)_2$, 0.1 *F* $CaCl_2$ and 0.1 *F* NaCl. Note in which cases insoluble sulfides are formed. Record the formula and color of each of the precipitates.

(c) *Hydrogen sulfide as a reducing agent.* From its position in the chart of oxidation states, it should be obvious that H_2S can act only as a reducing agent, in which case it may be oxidized to free sulfur or to higher oxidation states depending on the strength of the oxidizing agent used. Saturate each of the following solutions with H_2S: 5 ml each of warm 3 *F* HNO_3, of 0.1 *F* I_2, a freshly prepared solution of H_2SO_3 made by adding a few crystals of Na_2SO_3 and a drop of 6 *F* H_2SO_4 to 5 ml of distilled water. In each case note the products of the reaction and write balanced equations for the oxidation-reduction reactions.

(d) *Polysulfides.* Add a small pinch of powdered sulfur to 5 ml of a 2 *F* Na_2S solution. Warm the mixture gently for a few minutes as you stir the powdered sulfur to wet it. Account for the result obtained by drawing electron-dot formulas for the new ion or ions formed. Acidify the solution with 6 *F* HCl and note the products formed. How is this reaction analogous to the decomposition of hydrogen peroxide?

3. Oxidation State +4. Sulfur Dioxide, Sulfurous Acid, Sulfite Ion

(a) *Preparation of sulfur dioxide.* In the metallurgical industry, large quantities of sulfur dioxide are produced as a by-product during the roasting (oxidation) of metallic sulfides. It may be prepared in the laboratory by burning sulfur (recall Exp. 8), by adding a strong, nonvolatile acid such as sulfuric to a solution containing sulfite ions, or by the reduction of hot concentrated sulfuric acid by certain metals. Set up the generator shown in Figure 21-1. Place about 40 ml of distilled water in the 50-ml flask and dissolve about 15 g of Na_2SO_3 in 25 ml of hot water in the 250-ml flask. Add 5 ml portions of 3 *F* H_2SO_4, as needed to maintain continuous evolution of the gas in order to saturate the water in the small flask. Remove the delivery tube from the flask and collect a 10-cm test tube of the gas by the displacement of air. Determine

for yourself whether this should be done by the upward or downward displacement of air, by estimating its density from its molecular weight and comparing with that of air. Place your thumb over the mouth of the test tube and invert the tube in a 400-ml beaker of water. Note any change in the level of water in the tube as you swirl it gently under the water and estimate the solubility of SO_2 in water.

(b) *Chemical properties of sulfurous acid.* Test the acidity of the saturated solution of SO_2 with a piece of neutral litmus paper. Place 5 ml of the solution in a small test tube, and add a small pinch of powdered magnesium. Note the result.

Prepare a very dilute solution of potassium permanganate by adding a minute crystal of $KMnO_4$ to 5 ml of distilled water, acidified with a drop of 3 *F* H_2SO_4. Add some of the SO_2 solution, drop by drop, until a color change takes place. What happens to the MnO_4^- and HSO_3^- ions during this reaction?

Repeat the above experiment, using 3 ml of saturated bromine water instead of $KMnO_4$. How do you account for the decolorizing of the bromine solution? Test for the presence of sulfate ions in this solution by adding 2 ml of 0.1 *F* $BaCl_2$. Is the precipitate formed soluble in 6 *F* HCl?

To 10 ml of the saturated sulfur dioxide solution in a small beaker add 0.1 *F* $Ba(OH)_2$ solution until a precipitate forms. Is this precipitate soluble in 6 *F* HCl? Compare with result obtained above and write equations for reactions which will account for the results obtained.

4. Oxidation State +6. Sulfuric Acid, Sulfates (Optional)

(a) *Preparation of sulfuric acid by a method analagous to the lead chamber process.* Refer to the textbook for the reactions involved in the lead chamber process and keep them before you as you perform this experiment. Identify the various reactions with the steps in the commercial process and in the simplified version described below.

Set up the apparatus shown in Figure 21-2. Place about 10 g of copper turnings and 25 ml of 18 *F* H_2SO_4 in the flask fitted with the thistle tube. Place about 10 drops (0.5 ml) of 16 *F* HNO_3 in the other reaction flask. Fill the test tube about half-full of 3 *F* NaOH which will serve to neutralize the excess gases (acidic anhydrides) which might otherwise

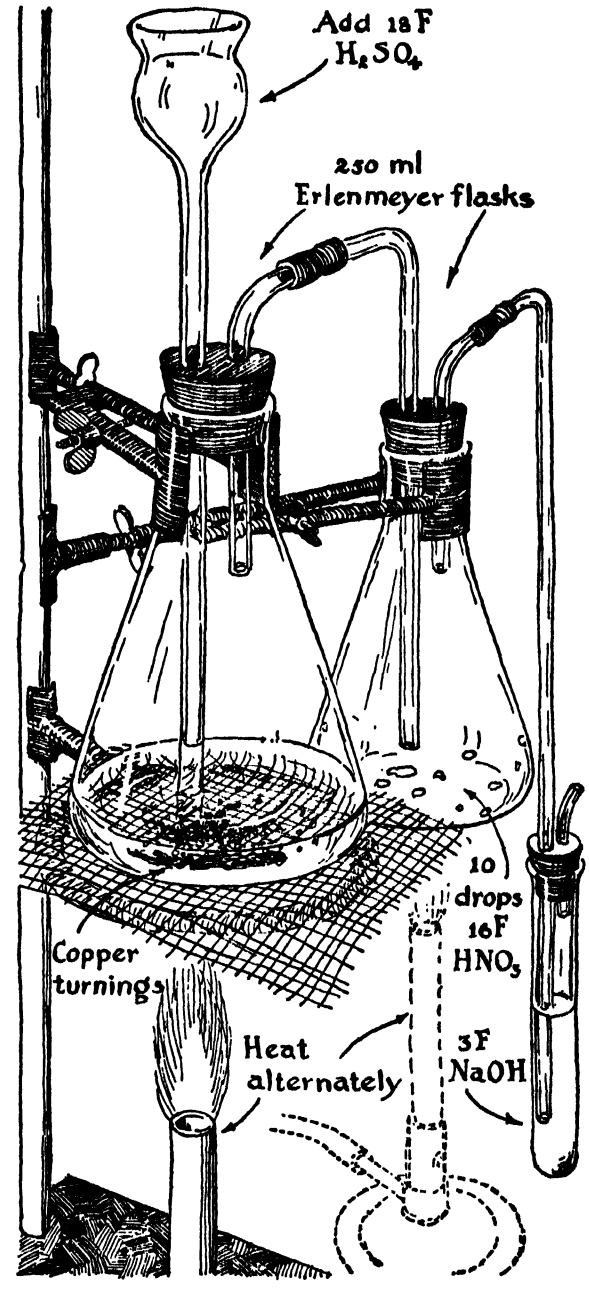


FIG. 21-2. Apparatus to demonstrate the reactions of the lead chamber process for the manufacture of sulfuric acid.

escape into the room. Heat the reaction flask gently until some of the nitric acid decomposes to form some of the oxides of nitrogen necessary for the process. Now heat the flask containing the copper and sulfuric acid gently until the SO_2 produced reacts with the gases in the reaction flask to a point where the brown color disappears. What reaction has taken place? Can you see any crystals of nitrosylsulfuric acid on the sides of the flask? Allow the

apparatus to cool a little, and then open the reaction flask and wash down the sides with 5 to 10 drops of water delivered from a medicine dropper. Note the reappearance of the brown gases. What reaction accounts for this? Now reassemble the apparatus, allow more SO_2 to react with the brown gases until the reaction flask is again colorless, and then wash down the sides of the flask with a few drops of water. This process is repeated over and over in the commercial process, some of the reactions taking place in the "lead chambers," others in the Gay-Lussac tower and the Glover tower.

Pour out the reaction product into a test tube and test the solution for the presence of sulfuric acid by adding 2 or 3 ml of 0.1 *F* $BaCl_2$ to precipitate any sulfate ions present.

(b) *Physical properties of sulfuric acid.* Carefully measure 40 ml of distilled water into your large graduated cylinder and 10 ml of 18 *F* H_2SO_4 into your small graduated cylinder. Take the temperature of the water, and then add slowly the concentrated sulfuric acid to the water. Stir the solution obtained in the large cylinder with the thermometer and note the highest temperature reached. From the change of temperature and the combined weight of the water plus sulfuric acid, calculate the number of calories evolved.

Allow the solution to come to room temperature, and then read the volume of the solution and compare this with the sum of the volumes of the two ingredients mixed. What is the percent change in volume due to mixing?

Place a few drops of concentrated sulfuric acid on a few crystals of sugar in a small evaporating dish. Repeat using a small piece of filter paper. To what property of concentrated sulfuric acid do you attribute the results obtained?

(c) *Chemical properties of sulfuric acid.* Compare the action of concentrated and dilute sulfuric acid with that of concentrated and dilute hydrochloric acid on metals above and below hydrogen in the electromotive force series, by carrying out the following experiment. Place about 5 ml of each of the acids, 18 *F* H_2SO_4, 3 *F* H_2SO_4, 12 *F* HCl, 6 *F* HCl, into 10-cm test tubes and drop a small piece of mossy zinc into each. Heat gently, if necessary, to initiate a reaction. Note cautiously the odor of the gases evolved and write the equations for the reactions. Repeat the experiment using small pieces of copper instead of zinc. How do you account for any differences in results obtained?

Investigate the oxidizing strength of concentrated sulfuric acid by adding 1 ml of 18 *F* H_2SO_4 to 1 g of each of the following salts in 10-cm test tubes: NaCl, NaBr and NaI. Heat each test tube gently and note cautiously the odor, color and acidity of the gases evolved. In which cases are oxidation-reduction reactions involved? Note the relative positions of the halide ions in the electromotive force series (Table XIII, Appendix II).

(d) *Solubility of sulfates.* Add 1 ml of 1 *F* Na_2SO_4 to 3 ml of each of the following solutions in separate 10-cm test tubes: 0.1 *F* $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Ba(NO_3)_2$, $AgNO_3$, $Pb(NO_3)_2$, $Hg_2(NO_3)_2$. Note the cases in which insoluble sulfates are formed and write a solubility rule summarizing your results.

REPORT: Exp. 21

The Chemistry of Sulfur and Its Compounds

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Oxidation State Zero. Elementary Sulfur

(a) Comparison of the physical properties of the allotropic forms of solid sulfur as recalled from Experiment 2:

(b) Changes in color and fluidity of molten sulfur with increasing temperature:

Structural formulas of the two forms of liquid sulfur which are proposed to explain the above result:

Description of the plastic sulfur obtained:

Its solubility in CS_2._____ Is plastic sulfur a form of liquid or solid sulfur?_____

2. Oxidation State −2. Sulfides and Hydrogen Sulfide (Optional)

(a) Equation for reaction between iron and sulfur:_____

Was the reaction exothermic or endothermic?_____

Reaction of hydrochloric acid on ferrous sulfide:_____

(b) Formula and color of insoluble sulfides produced by saturating solutions with H_2S: Cu^{++}_____ _____,

Sb^{+++}_____ _____, Cd^{++}_____ _____, Zn^{++}_____ _____,

Ca^{++}_____ _____, Na^{+}_____ _____.

(c) Equations for the oxidation of H_2S by each of the following:

By 3 *F* HNO_3:_____

By 0.1 *F* I_2:_____

By H_2SO_3:_____

(d) The proposed structure of the ion formed when sulfur dissolves in aqueous sodium sulfide solution:

Equation for reaction of HCl on polysulfide solution:

_____

How is this analogous to the decomposition of hydrogen peroxide?

3. Oxidation State +4. Sulfur dioxide, Sulfurous Acid, Sulfite Ion

(a). Write balanced equations for the reactions for the production of sulfur dioxide:

By burning sulfur: _____

By roasting a sulfide ore (ZnS): _____

By acidifying a sulfite: _____

By reducing sulfuric acid with Copper: _____

Density of SO_2 at standard conditions, estimated from its molecular weight and the molal volume: _____

Density of air at standard conditions is 1.29 g/liter. Sample of SO_2 was collected by the _____ displacement of air.

The extent of solubility of SO_2 gas in water was _____

(b). The reaction of SO_2 and water:

_____

The acidity of this solution was demonstrated by its reaction with powder magnesium:

_____

The oxidation of HSO_3^- ions by acid permanganate:

_____

Saturated bromine water oxidized the HSO_3^- ions as follows:

_____

The precipitate produced by the addition of $BaCl_2$ solution to the resulting solution above:

_____

Is it soluble in 6 *F* HCl? _____

The reaction of the aqueous SO_2 solution with 0.1 *F* $Ba(OH)_2$ solution: _____

The precipitate obtained $\begin{matrix}\text{did}\\\text{did not}\end{matrix}$ or dissolve in dilute HCl.

4. Oxidation State +6. Sulfuric Acid, Sulfates (Optional)

(a). Reactions given in the text for the lead chamber process for the commercial production of H_2SO_4:

Describe the stages in the laboratory experiment corresponding to each of the above reactions.

Are the oxides of nitrogen used up in this process?_____ What role do they play?_____

Was the test for sulfate ions in the reaction vessel positive?_____

Write the equation for this test:_____

(b). The change in temperature noted in mixing sulfuric acid with water_____

The weight of the water used_____. (Density of water = 1.0 approx.)

The weight of sulfuric acid_____. (Density of sulfuric acid = 1.8)

Calories evolved = grams of solution × temperature increase × specific heat. Calories = _____
(Specific heat may be taken as 1.)

The change in volume on mixing was_____. The percent change_____

The effect of sulfuric acid on carbohydrates such as sugar and filter paper:_____

What property of sulfuric acid is illustrated here?_____.

(c). Fill in the following table to indicate the products formed in each case. Mark no reactions with an X.

	Zinc	*Copper*
Conc. HCl	_____	_____
Dilute HCl	_____	_____
Conc. H_2SO_4	_____	_____
Dilute H_2SO_4 . . .	_____	_____

How do you account for any differences in results obtained?

Write the equations for the reactions obtained by adding conc H_2SO_4 to each of the salts:

NaCl:_____

NaBr:_____

NaI:_____

Account for any differences observed in terms of the relative oxidation strength of conc sulfuric and the position of the halides in the electromotive force series.

(d). A solubility rule summarizing the solubility of sulfates of the common metals:

The Chemistry of the Compounds of Nitrogen — 22

College Chemistry, Chapter 15

Review of Fundamental Concepts

Nitrogen compounds:

↑ oxidation ↓ reduction	+5	N_2O_5, HNO_3, NO_3^-	Strong oxidizing agent, usually reduced to NO_2 in concentrated acid, or to NO in dilute acid. With strong reducing agent may go to NH_3.
	+4	NO_2, (N_2O_4)	A heavy brown gas.
	+3	(N_2O_3, HNO_2), NO_2^-	N_2O_3 and HNO_2 are unstable; nitrites are fairly stable. Active as oxidizing or as reducing agent.
	+2	NO	Oxidized by the air to NO_2.
	+1	N_2O	Supports combustion quite vigorously.
	0	N_2	
	−3	NH_3, NH_4OH, NH_4^+	

Nitrogen, the first element in Group V, is an important nonmetal which forms compounds illustrating all the oxidation states from −3 to +5. The chart above summarizes the more important compounds to be considered in this experiment.

In Experiment 9 the properties of elementary nitrogen and ammonia were considered. You should recall the remarkable stability of the *zero* oxidation state where the nitrogen molecule has the structure, :N:::N:, in which the triple bond seems to provide a special degree of stability to the molecule. You should also review the properties of the −3 oxidation state in which the covalent molecule, ammonia, has the structure

$$\begin{matrix} & \cdot\cdot & \\ & \cdot\cdot & \\ H: & N & :H \\ & H & \end{matrix}$$

which readily adds a hydrogen ion to form the ammonium ion.

When nitrogen combines with the more electronegative element oxygen, it forms compounds where nitrogen has positive oxidation states. The chemistry of the +2 and +4 states is of importance, since NO and NO_2 are involved as intermediates in the commercial production of nitric acid by the oxidation of ammonia or of nitrogen. In the +4 state the reversible reaction $2NO_2 \rightleftarrows N_2O_4$, between the colorless gas N_2O_4 and the brown gas NO_2, furnishes an opportunity to apply the Principle of Le Chatelier to this system in chemical equilibrium. Special attention should be given to the +5 oxidation state as illustrated by the very important compound, nitric acid. This acid is not only a strong acid in the sense that its aqueous solutions contain high concentrations of hydrogen ions, but it also is a strong oxidizing agent due to the presence of the nitrate (NO_3^-) ions. It is capable of oxidizing some metals below hydrogen in the electromotive force series as well as many other inorganic and organic substances. It may be reduced to any one of the lower oxidation states of nitrogen depending on the concentration of the nitric acid and the strength of the reducing agent.

The student should be sure to review the methods for balancing oxidation-reduction equations since the chemistry of nitrogen and its compounds is principally concerned with changes in oxidation states.

Experimental Procedure

Chemicals: Cu (turnings), Zn (mossy), Mg (ribbon), Pb (powdered), Sn (mossy), Al (turnings), NH_4NO_3, $NaNO_2$, $Pb(NO_3)_2$, Na_2O_2, Bromine water, 0.1 *F* KI.

1. Preparation of Nitrous Oxide. Oxidation State +1 (Optional). Assemble the apparatus illustrated in Fig. 22-1, and prepare to collect two 15-cm test tubes of gas by displacement of water. Since nitrous oxide is less soluble in hot water than in cold, the water displaced in the beaker may be warm. Place about 3 g of NH_4NO_3 into the clean, dry 15-cm Pyrex test tube which is to serve as the generator. Heat the tube very gently but steadily with a small flame so that the gas is generated at the rate of one bubble per second. **(Caution:** *Ammonium nitrate may explode if heated too rapidly. Especially avoid overheating near the top of the molten nitrate.* If for any reason you need to add more ammonium nitrate to make more gas, allow

the tube to cool, and clean and dry it before recharging it with fresh ammonium nitrate.) After the air has been displaced from the generator, collect two test tubes of the gas. Remove the delivery tube from the water to avoid sucking back water into the generator. What is the equation for the decomposition of NH_4NO_3? Note the color and odor of the gas remaining in the generator. Test

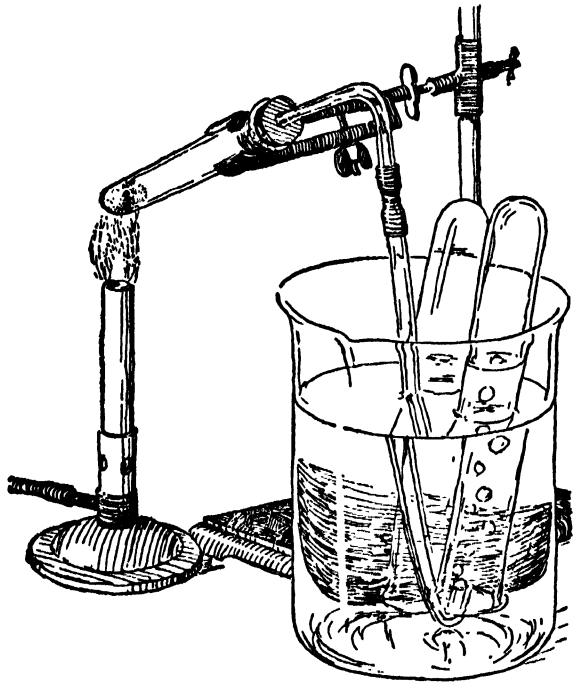


FIG. 22-1. Apparatus for the preparation of the oxides of nitrogen. For N_2O, the generator test tube contains NH_4NO_3; for NO, it contains copper turnings and 6 *F* HNO_3.

one tube of the gas for its ability to support combustion by inserting a glowing splint. Save the other test tube of N_2O for a test with nitric oxide in the next section. Look up the electronic structure of nitrous oxide and suggest how this might account for its activity as an oxidizing agent.

2. The Preparation of Nitric Oxide. Oxidation State +2: Clean out the generator used in the preceding section and place about 3 g of copper turnings into the tube. Prepare to collect four 15-cm test tubes of nitric oxide by displacement of water. Add 15 ml of 6 *F* HNO_3 to the generator, replace the delivery tube connection, and warm the tube gently to initiate the reaction. After the air has been displaced from the apparatus and the gas bubbling through is colorless, collect three test tubes full of the gas and the fourth tube about half-full. What is the reaction for the reduction of dilute nitric acid by copper?

Test one tube of nitric oxide with a glowing splint to see if it will support combustion. Note the colored gas produced when the tube was exposed to the air. Write the equation for the reaction which accounts for this change.

Take the test tube of nitrous oxide saved in Part 1 and place it quickly mouth to mouth with a tube of nitric oxide, so as to avoid undue exposure to the air. Is there any evidence of a reaction similar to that between nitric oxide and oxygen of the air? If you were asked to determine whether a test tube contained oxygen or nitrous oxide, could you use the glowing splint test? What test could be used?

Test the third tube of nitric oxide for its solubility in water by swirling the test tube with its mouth under the water to allow contact of fresh water with the gas in the tube. Note if the water level in the tube rises. Now take the tube out of the water for a few seconds and allow the oxygen of the air to react with the gas as shown by the formation of a brown gas. Invert the test tube under the water and swirl it to note the solubility of the brown gas. Write the equation for the reaction taking place when this gas dissolves in water.

Mark the level of water in the fourth test tube, which is about half-full of nitric oxide, with a wax pencil or a gummed label. Set up the small oxygen generator shown in Figure 22-2. Place about 2 g of sodium peroxide (Na_2O_2) into the dry 15-cm Pyrex test tube and draw up a few ml of water into the medicine dropper. Sodium peroxide reacts vigorously with water to produce oxygen and sodium hydroxide, so allow only a drop of water to fall on the peroxide whenever the flow of oxygen becomes too slow. When the air has been displaced from the generator, place the delivery tube under the marked test tube and allow 8 to 10 bubbles of oxygen to enter. Note whether the level of the water is lowered by the additional oxygen. Recall that in the balanced equation for the reaction that is taking place, two volumes of nitric oxide react with one volume of oxygen to produce two volumes of nitrogen dioxide. Now swirl the test tube with its mouth under the water and note what happens to the water level as the NO_2 reacts with the water. Allow more oxygen to enter the tube until the

gases again turn brown, note the water level, and again allow the gases to dissolve in water. Repeat the process until the water level approaches the top of the tube. Remember that excess oxygen is not soluble in water. What substances are present in the water solution in the test tube? Apply a simple test to verify your answer. What part of one

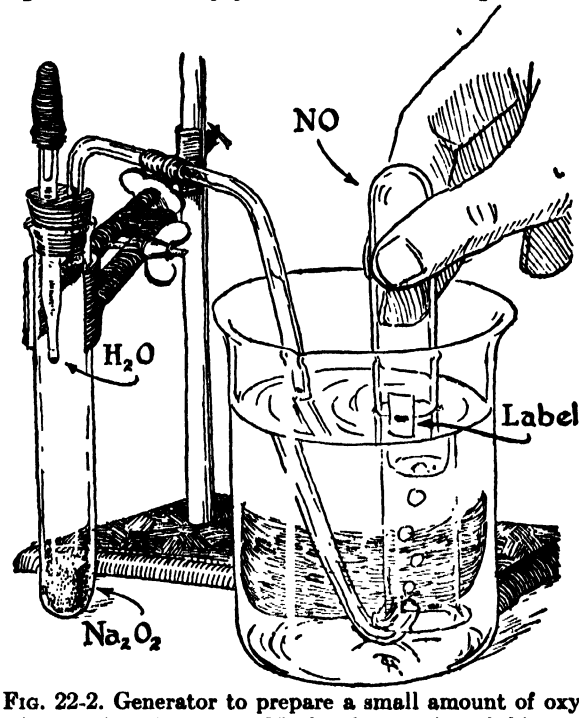


FIG. 22-2. Generator to prepare a small amount of oxygen by the reaction of water on Na_2O_2; the reaction of this oxygen with NO.

of the commercial processes for the production of nitric acid does this experiment illustrate?

3. Nitrites, Nitrous Acid. Oxidation State +3 (Optional). Auto-oxidation-reduction of nitrogen dioxide in an alkaline solution produces the nitrite ion as well as nitrate ion according to the reaction $2\ NO_2 + 2\ OH^- \rightleftarrows NO_2^- + NO_3^- + H_2O$. However, in order to prepare a sample of a nitrite relatively free from nitrate, we shall reduce sodium nitrate by heating it with metallic lead.

Mix about 2 g of $NaNO_3$ with 5 g of powdered lead in a dry test tube and heat the mixture quite strongly for two or three minutes. Do not heat to the point where brown fumes of NO_2 are evolved. Note what happens to the powdered lead, and write the equation for the reaction. Cool the tube and dissolve the sodium nitrite produced by adding 10 ml of water and warming the tube gently. Filter the solution and acidify with a ml of 6 *F* HCl. Note if there is any evidence for the decomposition of the nitrous acid produced, and write the equation for any reaction. Retain the solution for the following test.

Since the nitrite ion is exhibiting an intermediate oxidation state, it may be oxidized to the nitrate ion by some strong oxidizing agents, but in other instances it may be reduced to nitric oxide by sufficiently strong reducing agents. To illustrate this, place 5 ml of 0.1 *F* KI into a 10-cm test tube and 5 ml of bromine water into another test tube. Add the acidified sodium nitrite solution drop by drop to each of the tubes, mix, and note the products of the reactions. Write balanced oxidation-reduction equations for the reactions.

4. Nitrogen Dioxide, Nitrogen Tetroxide. Oxidation State +4. At ordinary temperatures, nitrogen dioxide (NO_2), a red-brown gas, exists in equilibrium with nitrogen tetroxide (N_2O_4), a colorless gas. This mixture of gases can be prepared by the reduction of concentrated nitric acid by copper or by the thermal decomposition of lead nitrate. Write the equation for the latter reaction which we shall use. Set up the apparatus shown in Figure 22-3a. Place about 5 g of $Pb(NO_3)_2$ in the dry 15-cm test tube. Have two pinch clamps ready to place on the pieces of rubber tubing on each end of the 30-cm piece of glass tubing. Heat the lead nitrate gently until decomposition takes place and the brown gas has displaced the air in the apparatus. When the brown gas has been coming out of the end of the glass tube for about a minute, attach the pinch clamps and quickly disconnect the tube from the generator.

We now have a closed system containing the mixture of NO_2 and N_2O_4 gases in chemical equilibrium. In order to study the effect of heat on this reversible reaction, place the closed tube in an upright condition in a 400-ml beaker containing cold water so that the lower third of the tube will be kept cool. (See Figure 22-3b.) Allow several minutes for the gases in the tube to cool, then with a small flame heat the upper third of the tube by fanning the flame back and forth a few times. (Avoid overheating at this point or appreciable amounts of NO_2 may decompose to the colorless gas NO and thus complicate the interpretation of your results.) View the gases in the tube against a piece of white paper and note whether there is

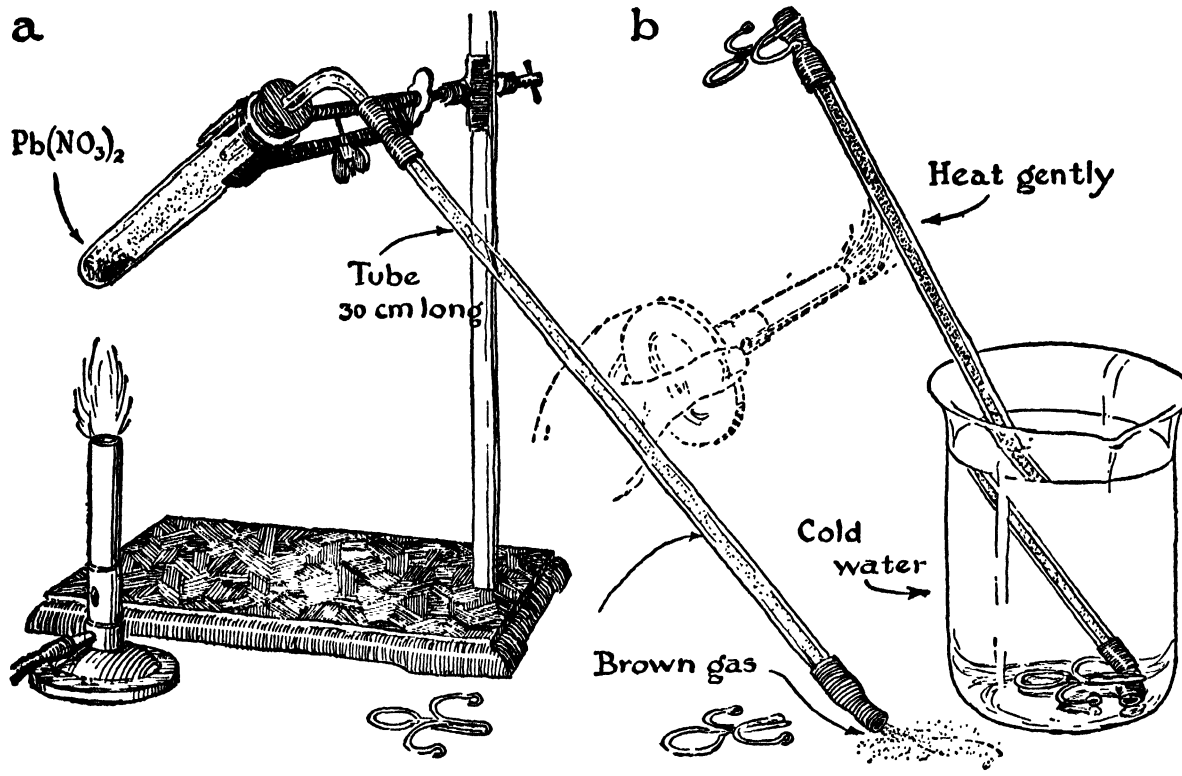


FIG. 22-3. (a) The preparation of nitrogen dioxide and nitrogen tetroxide. (b) The effect of temperature on the dissociation of N_2O_4.

more of the colored gas, NO_2 in the cooler portion or in the heated portion of the tube. Write the equation for the reversible reaction and include the term *heat* on the proper side of the reaction to account for the result obtained. The shift in the equilibrium, in this case caused by the addition of heat, is an illustration of the application of an important principle, Le Chatelier's principle, which will be further applied in the next experiment. Look it up now in the text and note how it applies to the present experiment.

5. Nitric Acid, Nitrates. Oxidation State +5. Many reactions involving the reduction of nitric acid and the decomposition of nitrates have been studied already in the preceding parts of this experiment. We shall illustrate the oxidizing properties of nitric acid further by varying the concentration of the acid and the strength of the reducing agents. Pay particular attention to the oxidation state of the reduction products and what factors influence the extent of reduction.

Add about 3 ml of 16 *F* HNO_3 to a small piece of copper in a 10-cm test tube. Place about 5 ml of 1 *F* HNO_3 into each of two test tubes. Place a small piece of Zn into one and a small strip of Mg ribbon into the other. Note the products of each of the reactions. Pour the solution resulting from the reaction on the zinc into a small beaker, add about 5 ml of 6 *F* NaOH and cover the beaker with a watch glass which has a small piece of moistened red litmus paper on the under side. Warm the beaker gently and note any change in color of the litmus paper.

Recall the product obtained when 6 *F* HNO_3 reacted with copper in Part 2 of this experiment. Summarize your findings concerning nitric acid as an oxidizing agent in the report sheet.

Some metals such as arsenic, antimony and tin are oxidized to insoluble oxides by hot concentrated nitric acid. Put a small piece of tin into about 5 ml of 16 *F* HNO_3 and note the reaction products.

A few metals, such as aluminum or chromium, are rendered passive or inactive in nitric acid. Cover a small piece of Al with 5 ml of 16 *F* HNO_3 and watch for any reaction.

Are nitrate salts of metals generally soluble in water? Make a one sentence solubility rule which holds for most nitrates.

REPORT: Exp. 22

The Chemistry of the Compounds of Nitrogen

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Oxidation State +1. Preparation and Properties of Nitrous Oxide (Optional)

The electron-dot structures proposed for N_2O:

Equation for the decomposition of NH_4NO_3:_____

Properties of N_2O: color_____, odor_____, ability to support combustion_____.

How does the position of the oxygen atom in the N_2O molecule affect its activity as an oxidizing agent?

2. Oxidation State +2. Preparation and Properties of Nitric Oxide

The electron-dot structures proposed for NO:

Why is nitric oxide called an *odd* molecule?

Equation for reaction of dilute nitric acid on copper:

_____

Properties of NO: color_____, odor_____, ability to support combustion_____.

What is the colored gas formed when NO is exposed to air_____.

Equation for this reaction:_____

Does nitrous oxide give up its oxygen to react with NO?_____

To what extent is NO soluble in water?_____. Is NO_2 soluble in water?_____.

How do you account for this?_____

Equation for the reaction of NO_2 with H_2O:

_____

Equation for the production of oxygen from Na_2O_2 and H_2O:

_____

Describe the changes taking place in the test tube half-full of NO gas as oxygen was added: color of gases _____, change in water level_____. Account for these observations:

When test tube was swirled under water, the change in water level noted was_____, color of gases became_____. Account for these observations:

What results were obtained when the above process was repeated?

What substances are present in the aqueous solution in the test tube at the end of the process?

What part of which commercial process for the production of nitric acid does this part of the experiment illustrate?

3. Oxidation State +3. Nitrites and Nitrous Acid (Optional)

Equation for the production of $NaNO_2$ by the reduction of $NaNO_3$ with Pb:

_____

What is the yellow solid formed in the tube?_____.

When the $NaNO_2$ was leached out with water and acidified with dilute HCl the reaction which took place was:

_____

The half-reaction for the reduction of nitrite ion in acid solution:

_____

The half-reaction for the oxidation of nitrite ion in acid solution:

_____

Was bromine water (Br_2) a sufficiently strong oxidizing agent to oxidize nitrite ion?_____. What is your evidence?_____. What happened to the Br_2?:_____

Equation:_____

Was the nitrite ion able to oxidize the iodide ion in the acid solution?_____. What happened to the iodide ion?_____. Equation:_____

If you were given two white crystalline salts, one of which was KI and the other KBr, how would you apply the principle of selective oxidation illustrated by this experiment to determine which salt was KI?

4. Oxidation State +4. The Equilibrium Between NO_2 and N_2O_4

Equation for the preparation of the NO_2, N_2O_4 mixture by the decomposition of $Pb(NO_3)_2$:

_____

The electron-dot structures of NO_2 and of N_2O_4:

Which gas is colored?_____.

Describe the changes which take place in the closed tube when heat is applied to the upper third of the tube:

Write the equation for the reversible reaction involved in the equilibrium system under study here:

_____

Which way was this equilibrium shifted by the application of heat?_____.

In this reaction there are 15,000 calories of heat involved per mole of N_2O_4. On which side of the equation above should the heat term appear with a positive sign?_____.

What is the Principle of Le Chatelier and how does it apply to the interpretation of this experiment?

5. Oxidation State +5. Nitric Acid and Nitrates

From the various experiments carried out in this experiment which involve the use of nitric acid as an oxidizing agent, write balanced equations illustrating its reduction to the +4, +2, and −3 oxidation states.

From +5 to +4:_____

From +5 to +2:_____

From +5 to −3:_____

What was the main product of the reaction when Mg, a very strong reducing agent, reacts with very dilute nitric acid?_____

Summarize the results obtained by making a statement concerning the influence of the strength of the reducing agent and the dilution of the acid on the reduction products.

Equation for reaction of concentrated nitric acid on tin:

_____

How do you explain the action of concentrated nitric acid on aluminum?

A solubility rule concerning the solubility of most metallic nitrates:

The Rate of Decomposition of Sodium Hypochlorite

23

College Chemistry, Chapter 19

Review of Fundamental Concepts

A study of the factors that affect the rate at which a reaction proceeds is both of commercial importance and of great theoretical interest. Even though the energy relations of a reaction are such that one would predict that it should take place readily, it may take place so slowly as to be commercially impractical. The theoretical chemist is interested in what must be done to make the atoms, molecules, or ions collide in an effective manner so that new combinations will result at a desirable rate.

Most reactions with which you have had some experience have been practically instantaneous because they have usually involved the collision of ions in an aqueous solution. Thus, when Ag^+ and Cl^- ions collide, new crystalline grains of the slightly soluble substance AgCl are produced. Many reactions between covalent molecules, however, take place very slowly. For example, the key reaction in the production of fertilizers and explosives, $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 21{,}880$ cal, was made commercially feasible only after years of research revealed the appropriate catalyst and the conditions of temperature, pressure, and concentration which would favor the production of ammonia at a reasonable rate.

Reactions do not take place upon every collision between molecules, and only the more energetic molecules are involved in the effective collisions. Some of the factors which determine both the number of energetic molecules and the chances for their collision are the concentration of molecules, their temperature and pressure, and the presence of a catalyst.

The term "catalyze" means to loosen. Theoretical chemists suggest that in the case of *contact catalysis* the reacting molecules are adsorbed on the surface of the solid catalyst and are subjected to strain which makes them more susceptible to the desired breaking of chemical bonds. In other instances the catalyst may serve as an *intermediate* by reacting with one of the substances to form an intermediate compound, which in turn reacts readily with the other reactant to form the desired substance and regenerate the catalyst.

The reaction which we shall study is the decomposition of sodium hypochlorite in a slightly basic solution (commercial bleaching solution), catalyzed by the presence of an oxide of cobalt.[1]

The net reaction is: $2\ OCl^- \longrightarrow O_2 + 2\ Cl^-$. The rate may be followed by allowing the oxygen formed to displace water and by measuring the volume collected at regular intervals of time. In order to standardize the effect of the catalyst and also minimize any complicating side reactions, it is necessary to add the same amount of cobalt nitrate solution in each of the trials. Only a small portion of the sodium hypochlorite reacts with the cobalt ion to produce the solid cobalt oxide catalyst.

Experimental Procedure

Special supplies: a watch with a second hand, thermometer.
Chemicals: 0.17 *F* $Co(NO_3)_2$ (5%), and 5.25% NaOCl (commercial bleaching solution).

1. Set up the apparatus illustrated in Figure 23-1. Fill the Florence flask with water, and insert its stopper. Fill the delivery tube to the graduated cylinder by blowing into the tube connected to the length of rubber tubing. Close the pinch clamp. Measure carefully 25 ml of sodium hypochlorite solution in a graduated cylinder (or pipette) and pour it into the Erlenmeyer flask. Place exactly 5 ml of the cobalt nitrate solution in a 10-cm test tube, and insert it carefully in the reaction flask. Adjust the glass tubing in the stopper so that the test tube is held loosely in the position shown. Remove the pinch clamp. If your apparatus is

[1] The formula of the oxide of cobalt is not known with certainty, but it is thought to be Co_2O_3, which is probably formed by the reaction $2\ Co^{++} + OCl^- + 2\ H_2O = Co_2O_3 + 4\ H^+ + Cl^-$. CoO_3 has also been suggested in the literature.

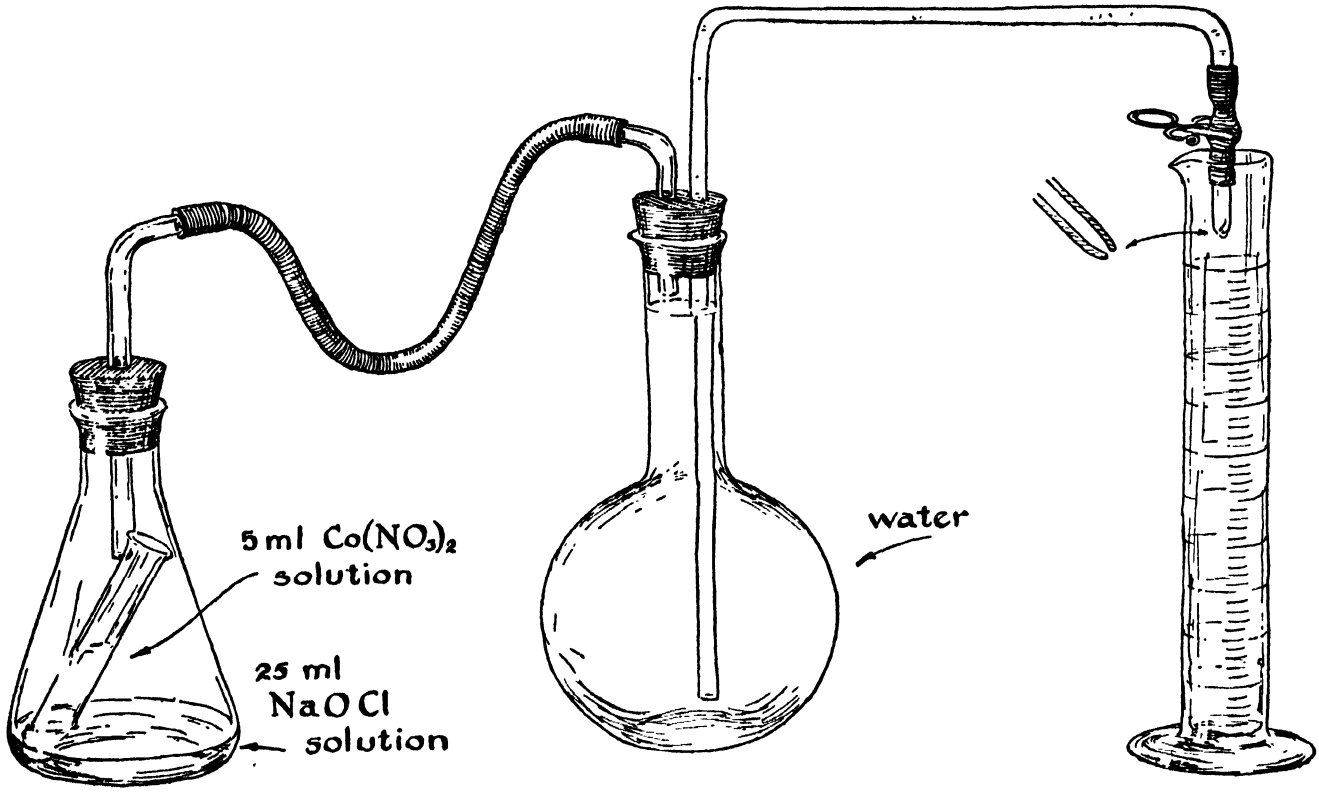


FIG. 23-1. Apparatus to measure the rate of decomposition of sodium hypochlorite.

tight, only a drop or two of water will drop into the graduated cylinder. Have your data sheet ready. Observe the time as you quickly tip over the reaction flask so as to mix the cobalt nitrate solution with the hypochlorite solution. Hold the flask at its neck, and shake it constantly with a gentle swinging motion. Record the volume of water displaced every 30 seconds until a total volume of about 100 ml has been reached. Plot the results on a graph, using time as the abscissa and volume of oxygen as the ordinate.

2. Repeat the procedure at a temperature approximately 10° C above room temperature. The solutions may be conveniently warmed by placing the Erlenmeyer in a larger beaker containing water at about 20° to 30° above room temperature. When the desired temperature has been reached, the Erlenmeyer should be removed from the water bath and connected to the apparatus as before.

3. (Optional.) If time permits, repeat the experiment at a temperature approximately 10° C below room temperature. Use chipped ice and water in the water bath this time.

4. To determine the effect of changing the concentration, repeat the experiment at room temperature, but add 30 ml of water to the hypochlorite solution in the flask so as to effect a twofold dilution in the final volume after mixing.

5. (Optional.) If time permits, the experiment may be repeated at room temperature with a fourfold dilution by adding 90 ml of water to the hypochlorite solution.

Plot all results neatly on the same graph, and label each run. Note the variations in rate which resulted from the changes in temperature and in concentration. Make your comparisons as quantitative as possible in the discussion requested on the report sheet.

REPORT: Exp. 23

The Rate of Decomposition of Sodium Hypochlorite

Name _____

Date _____

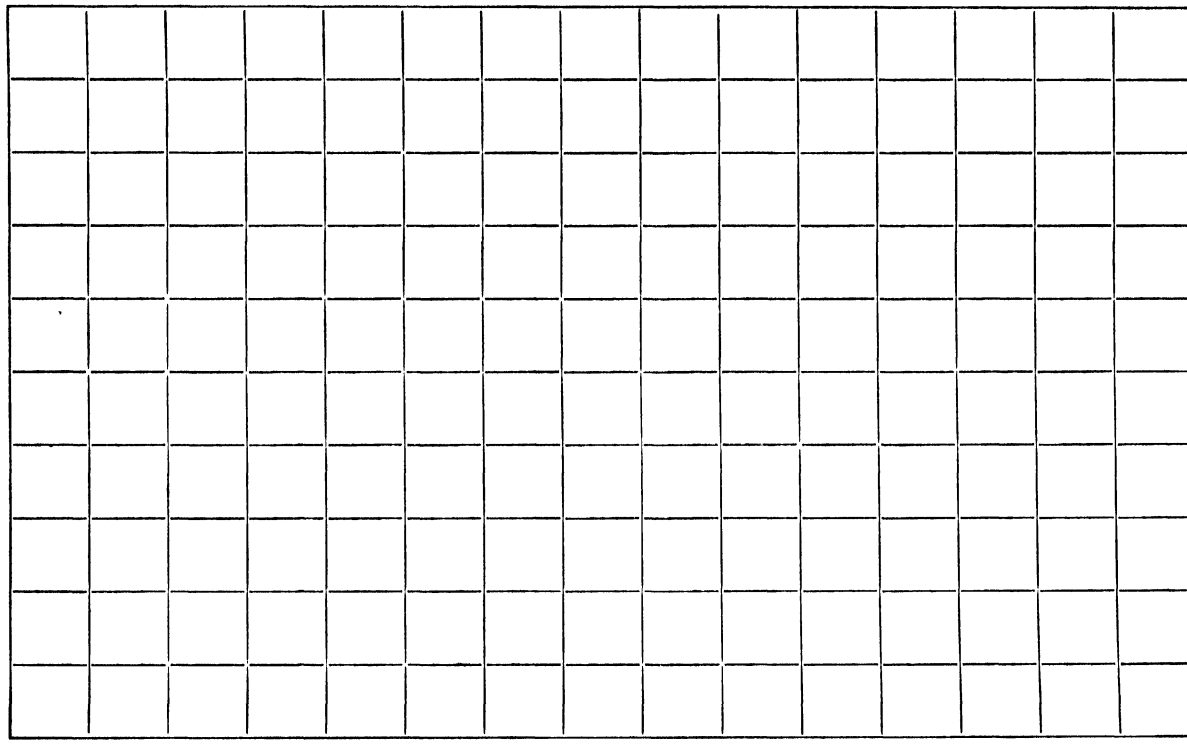
Section _____

Locker Number _____

Summary of Data

Time interval (minutes)	*Volume of oxygen produced (ml)*				
	Room temp. _____° *C*	*Warmer* _____° *C*	*Cooler* _____° *C*	*2-fold dilution*	*4-fold dilution*
0.5					
1.0					
1.5					
2.0					
2.5					
3.0					
3.5					
4.0					
4.5					
5.0					
5.5					
6.0					
6.5					
7.0					
7.5					
8.0					
8.5					
9.0					
9.5					
10.0					
10.5					
11.0					
11.5					
12.0					
12.5					
13.0					
13.5					
14.0					
14.5					
15.0					

Graphical representation of data. Label axes and each curve.



1. Discuss in as quantitative a manner as possible the effect of changes in temperature upon the rate of this reaction.

2. How do you account for this in theoretical terms?

3. Give a reasonably quantitative discussion of the effect of changes in concentration upon the rate of the reaction.

4. How do you account for this in theoretical terms?

5. What is the probable role played by the cobalt oxide catalyst in the mechanism of the decomposition reaction?

Reversible Reactions and Equilibrium 24

College Chemistry, Chapter 19

Review of Fundamental Concepts

The Reversibility of Chemical Reactions

A chemical reaction in which a slightly ionized or a slightly soluble substance is formed, or in which a large amount of energy is released, will generally continue until one or more of the reacting substances is effectively all used. Many reactions, however, even if allowed to proceed for a very long time, do not go to completion. This will be the case if the products formed remain in contact or are intimately mixed with one another in a reactive condition, so that they may reform the initial substances again. Thus, hydrogen gas and iodine vapor at 400° C will interact quite readily to form hydrogen iodide. But, likewise, under the same conditions, hydrogen iodide molecules interact to re-form hydrogen and iodine. This is therefore a reversible reaction. These opposing tendencies may be indicated by the use of double arrows in the equation, thus,

$$H_2 + I_2 \rightleftarrows 2\,HI$$

Chemical Equilibrium

Let us carry out the above opposing reactions as follows. In one bulb, we place one mole each of hydrogen and iodine. In a second similar bulb, we place two moles (the equivalent amount) of hydrogen iodide. The first bulb shows the violet color of iodine vapor; the second is colorless. We shall now heat both bulbs at 400° C for a long time, after which we observe that each bulb has attained the same intensity of violet color. Samples withdrawn for analysis show the same concentration of free iodine in each bulb, and likewise the same concentrations of hydrogen and of hydrogen iodide. Additional heating produces no further changes.

This does not mean that reaction has ceased, but only that the rate at which hydrogen and iodine are interacting to form hydrogen iodide is exactly counterbalanced by an equal rate of dissociation of hydrogen iodide into hydrogen and iodine. *A reaction in which the resultants are being changed back into the reactants at the same rate as the reactants are forming the resultants is said to be in equilibrium.*

Reaction Rates and Le Chatelier's Principle

The rate of a chemical reaction is affected by (1) the temperature, (2) the concentration of the reactants, and (3) the presence of a catalyst. In this experiment, we shall study only the qualitative effect of changes in the concentration of the reactants and products on the equilibrium.[1]

These concentration effects may be most simply interpreted if we keep in mind the kinetic picture of matter as made up of moving molecules. The rate of formation of hydrogen iodide, according to the preceding equation, must be proportional to the number of effective collisions of hydrogen and iodine molecules. (See Fig. 24-1.) If we add more hydrogen gas to the container, thereby increasing the concentration of the hydrogen molecules, we will have more collisions per second of hydrogen and iodine molecules and will thereby increase the rate of the forward reaction. This will momentarily "unbalance" the equilibrium until the concentration of hydrogen iodide molecules has increased enough so that their rate of decomposition (the reverse reaction) has increased to the point where the opposing processes are taking place at equal rates. The over-all effect of adding more hydrogen gas is thus to create a new equilibrium, in which we have more hydrogen, less iodine, and more hydrogen iodide than in the original case. The equilibrium has been "shifted to the right."

Conversely, if some of the iodine is removed from the container, there will be fewer collisions per second of hydrogen and iodine molecules, resulting in a slower forward reaction. The reverse reaction will predominate until a new equilibrium is established, with less hydrogen iodide, more hydrogen, and somewhat less iodine, than in the original mixture. These relationships are in accord with the **Law of Le Chatelier,** that a system in equilibrium tends to shift in such a direction as to restore in so far as possible, the effect of any stress (change in concentration of one of the substances) which has been applied to the system.

The common ion effect is a special case of the application of the law of chemical equilibrium to ionization reactions. For example, in a solution or

[1] We shall consider the quantitative aspects of the law of chemical equilibrium in Experiments 36 and 37.

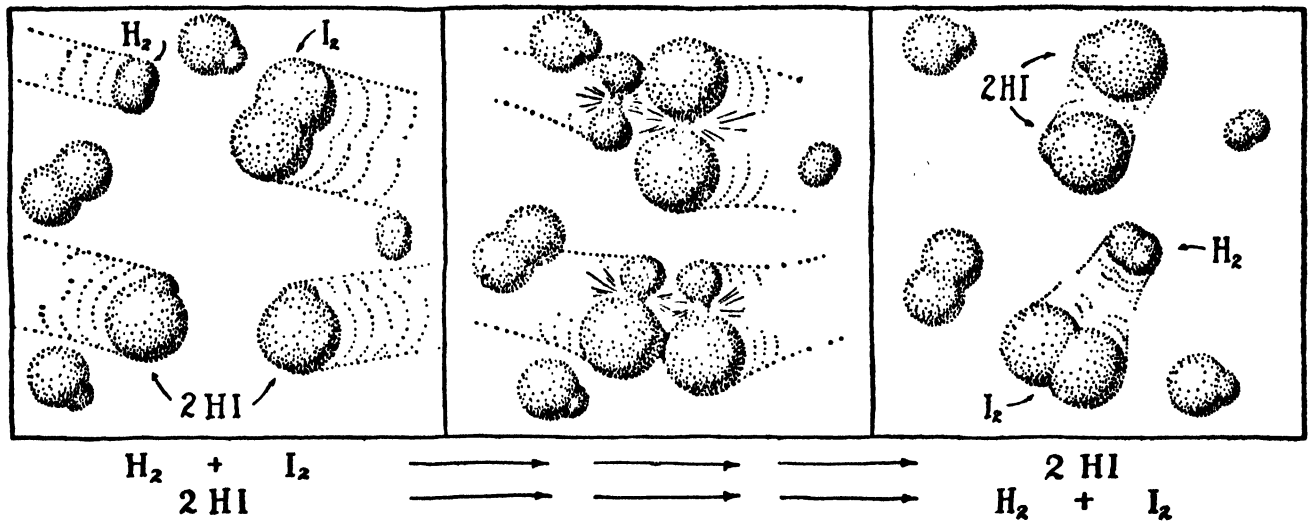


FIG. 24-1 The formation of hydrogen iodide, and the reverse process (its dissociation into hydrogen and iodine), are occurring simultaneously. This results in a chemical equilibrium.

the weak base ammonium hydroxide, we have the equilibrium

$$NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

If we add some ammonium chloride, NH_4Cl, ammonium sulfate, $(NH_4)_2SO_4$, or any other soluble ammonium salt, we will thereby increase the concentration of ammonium ion. There will then be more collisions per second between ammonium ions and hydroxide ions than before, the equilibrium will be shifted to the left, and the hydroxide ion concentration will be decreased. The ammonium ion, since it is common to both the ammonium hydroxide and the ammonium salt added, is called a "common ion".

In the same way, salts that are only very slightly soluble can be made even less soluble by increasing the concentration of a common ion. Thus, in the equilibrium

$$AgCl\ (solid) \rightleftarrows Ag^+ + Cl^-,$$

silver chloride is less soluble in any solution to which additional silver ion, or chloride ion, has been added, than it is in pure water. A higher concentration of either silver ion, Ag^+, or chloride ion, Cl^-, tends to shift the equilibrium to the left.

Experimental Procedure

Chemicals: 6 *F* $HC_2H_3O_2$, 0.25 *F* $(NH_4)_2C_2O_4$, 0.1 *F* $BaCl_2$, 0.1 *F* $CaCl_2$, 0.1 *F* $FeCl_3$, 0.5 *F* $H_2C_2O_4$, 0.1 *F* KCl, 0.1 *F* KCNS, 0.1 *F* $AgNO_3$, 3 *F* $NaC_2H_3O_2$, sat. (5.4 *F*) NaCl, 1 *F* Na_2SO_4.

1. A Test for the Completeness of a Reaction. We shall prepare solid $CaSO_4$ and solid $BaSO_4$ from equivalent amounts of their respective ions. The equilibrium equations are

$$Ca^{++} + SO_4^{--} \rightleftarrows CaSO_4\ (solid),$$

and

$$Ba^{++} + SO_4^{--} \rightleftarrows BaSO_4\ (solid).$$

Consider the following questions while you are doing the experiments. Are these reactions complete or is an equilibrium established between the solid and the ions when there is still a detectable amount of the ions present? Which of the ions, Ca^{++} or Ba^{++}, precipitates SO_4^{--} more completely?

Place 1.0 ml of 1 *F* Na_2SO_4 in each of two test tubes, measuring each sample carefully with your 10-ml graduated cylinder. To one sample add about 15 ml of 0.1 *F* $CaCl_2$, and to the other add about 15 ml of 0.1 *F* $BaCl_2$. (It is necessary to have a slight excess of $CaCl_2$ or $BaCl_2$ in each case.) Heat each tube to boiling, and let it stand, preferably for at least a half hour. (Meanwhile proceed with paragraph 2.) Test each mixture for completeness of precipitation by adding a drop of $CaCl_2$ solution to the $CaSO_4$ mixture, and a drop of $BaCl_2$ solution to the $BaSO_4$ mixture. Add more reagent

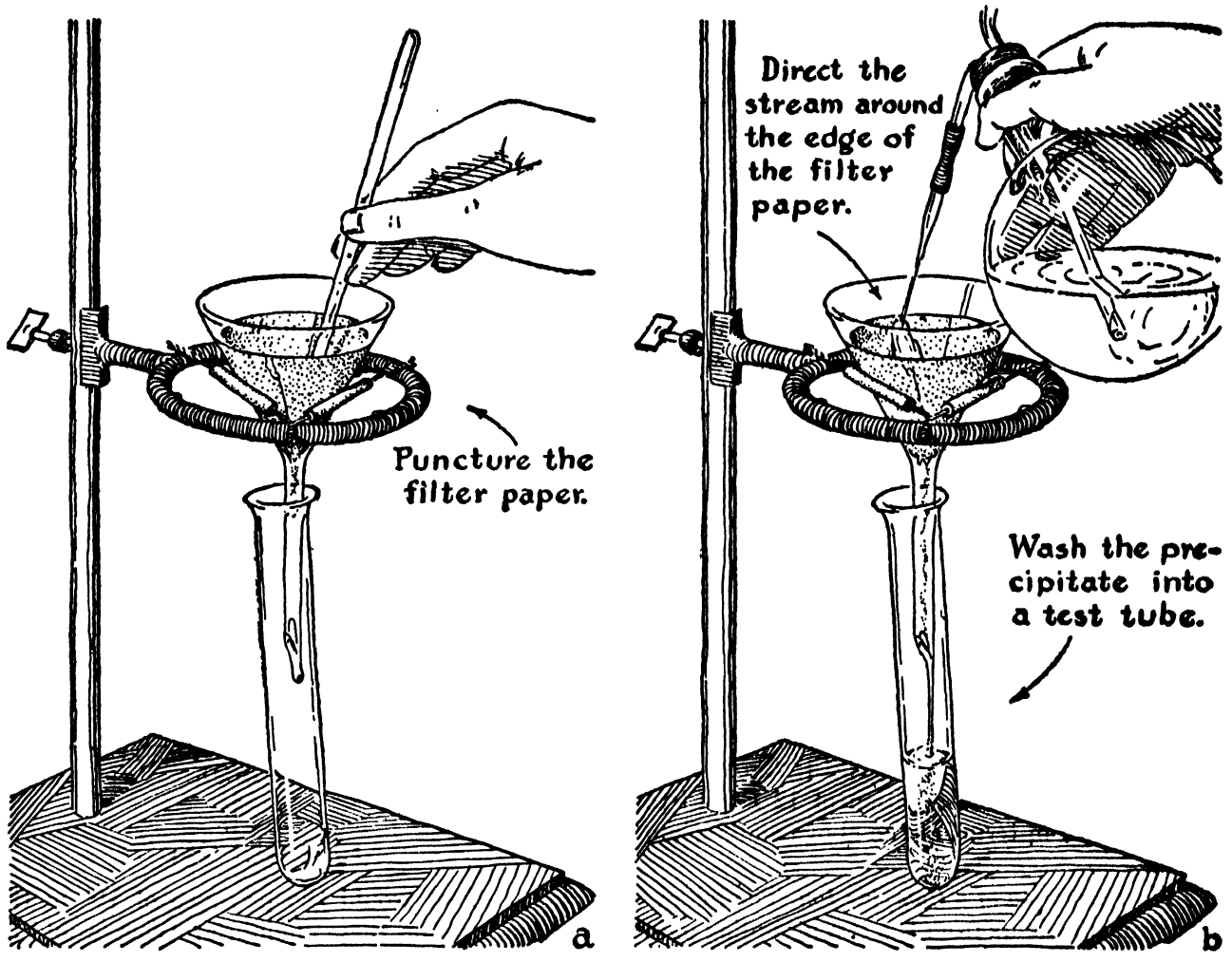


FIG. 24-2. The technique of puncturing the filter paper and washing the precipitate into a test tube.

if needed. If there is no further precipitation, filter or centrifuge[1] each mixture.

Now to the $CaSO_4$ filtrate, add 2 to 3 ml of 0.1 *F* $BaCl_2$. Note the results. To the $BaSO_4$ filtrate, add about 2 to 3 ml of 0.1 *F* $CaCl_2$. Note the results. *Questions.* From these results which of the above equilibrium reactions, for the precipitation of $CaSO_4$ or of $BaSO_4$, took place more completely? What relationship does the residual concentration of SO_4^{--} in the filtrate have to the solubilities of the salts? Which is more soluble, $CaSO_4$ or $BaSO_4$?

[1] If the precipitates have settled completely the filtrates may be decanted from the solids, or they may be placed in 10-cm test tubes and centrifuged. Obtain instructions before using the centrifuge. It is essential that solutions are well balanced before centrifuging. If you filter the $BaSO_4$ mixture, a special fine grained filter paper is necessary, as the precipitate is very fine grained and tends to run through the filter paper.

2. The Shifting of an Equilibrium. The Common Ion Effect

A. *A Saturated Silver Acetate Solution.* Prepare some freshly precipitated silver acetate by mixing 10 ml of 3 *F* $NaC_2H_3O_2$ with 25 ml of 0.1 *F* $AgNO_3$. Let the mixture stand a few minutes to complete the precipitation, then filter it. Drain the precipitate and rinse it with not over 2 ml of distilled water, and again let this drain. Place a clean 15-cm test tube under the funnel, puncture the filter with a stirring rod, and wash the precipitate into the test tube with a small stream of water from the wash bottle; but do not use over 10 ml (⅓ of a test tube) of water. Warm this mixture slightly (it should not be hot, however,) and shake it gently for at least ten minutes to establish the equilibrium of a saturated solution according to the equation

$$AgC_2H_3O_2\ (\text{solid}) \rightleftharpoons Ag^+ + C_2H_3O_2^-.$$

Filter this solution through a dry filter, retaining most of the residue in the original test tube (save this), and divide the filtrate into two 4 to 6-ml portions in small test tubes. Add to these two samples, respectively, about 6 to 10 drops of 3 *F* $NaC_2H_3O_2$, and 6 *F* $HC_2H_3O_2$. Observe the results, which may require several minutes to be noticeable. Explain, in detail, on the basis of the above equilibrium equation.

To the test tube containing the residual solid $AgC_2H_3O_2$, add 1 to 2 ml water, and then several drops of 6 *F* HNO_3. Explain the results.

B. *A Saturated Sodium Chloride Solution.* Measure out 10 ml of a saturated solution of NaCl. Calculate the concentration of the ions, assuming complete ionization. (Solubility of NaCl: 358 g /1000 g H_2O, or 358 g/1358 g solution. Density: 1.200 g/ml. Verify this as 5.4 *F* NaCl.) Add a few ml of concentrated HCl (12 *F*).

$$NaCl\ (solid) \rightleftarrows Na^+ + Cl^-.$$

How do the concentrations of Cl^- in a saturated solution of NaCl and in 12 *F* HCl compare? What is the common ion in HCl and NaCl? Explain the action occurring on the addition of 12 *F* HCl to saturated NaCl in terms of the above equilibrium equation.

C. *The Formation of a Complex Ion.* The following experiment differs from the two preceding ones in the fact that the product formed on the union of the ions is not insoluble, but is a slightly ionized, soluble, complex ion.[1]

$$Fe^{+++} + CNS^- \rightleftarrows Fe(CNS)^{++}$$
(dark red).

Add 10 ml of 0.1 *F* $FeCl_3$ to 10 ml of 0.1 *F* KCNS, and dilute the solution until a medium red color is obtained. About 100 to 125 ml of tap water will be required. Place 10-ml portions of this solution in each of four test tubes. Add 10-ml portions of the following reagents, respectively, to these four tubes:

1. H_2O
2. 0.1 *F* $FeCl_3$
3. 0.1 *F* KCNS
4. 0.1 *F* KCl

Predict the effect of each addition on the color of the solution before making the test. Record the results of the tests as redder or lighter. An increase of redness indicates an increase of the concentration of what substance? What shift in the equilibrium does the formation of this substance indicate? What shift in the equilibrium does a decrease of redness indicate?

3. Application of the Law of Chemical Equilibrium to Analytical Procedure: In qualitative analysis, Ca^{++} is usually precipitated for identification as calcium oxalate,

$$Ca^{++} + C_2O_4^{--} \rightleftarrows CaC_2O_4\ (solid).$$

What are the conditions needed to make the precipitation as complete as possible? The Ca^{++} concentration cannot be varied in the experiment as it is the ion whose presence is being tested for in the unknown. The completeness of the reaction, then, depends on the adjustment of the concentration of the $C_2O_4^{--}$. From which can the highest concentration of $C_2O_4^{--}$ be obtained, from a soluble salt, e.g. $(NH_4)_2C_2O_4$, or from the moderately weak acid, $H_2C_2O_4$? The ionization equations are

$$(NH_4)_2C_2O_4 \longrightarrow 2\,NH_4^+ + C_2O_4^{--}, \text{ and}$$
$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{--}.$$

What effect would the presence of H^+ in the solution have on these equilibria? What would be the effect of the presence of OH^-? Should Ca^{++} be precipitated as CaC_2O_4 in an acidic or in a basic solution? Test out your reasoning by making the following tests.

Mix 10 ml of 0.1 *F* $CaCl_2$ with 10 ml of distilled water, and divide into two 15-cm test tubes. To one add 1 ml of 0.5 *F* $H_2C_2O_4$, and to the other 2 ml of 0.25 *F* $(NH_4)_2C_2O_4$. Compare the results. To the $H_2C_2O_4$ mixture, add 1 to 2 ml of 6 *F* HCl, and mix. Explain the results. Now to this same solution add a slight excess of 6 *F* NH_4OH, and mix. Determine whether the precipitate may be $Ca(OH)_2$ by adding a little 6 *F* NH_4OH to some diluted $CaCl_2$ solution. What is the precipitate? Explain all these results in terms of the equilibrium equations above.

Would the acidity of the solution be of more importance in the precipitation of the salt of a strong acid or in the precipitation of the salt of a weak acid?

[1] See article by Bent and French, J.A.C.S. *63*, 568, on the formula for this complex ion. The ion undoubtedly is hydrated, and may vary in composition from $Fe(H_2O)_4CNS^{++}$ to $Fe(CNS)_6^{---}$.

REPORT: Exp. 24

Reversible Reactions and Equilibrium

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. A Test for the Completeness of a Reaction

(a) Was there in this experiment sufficient SO_4^{--} left in solution after precipitation with an equivalent amount of Ca^{++} to precipitate with Ba^{++}? . . . . . _____

(b) Was there sufficient SO_4^{--} left in solution after precipitation with an equivalent amount of Ba^{++} to precipitate with Ca^{++}? . . . . . _____

(c) Which filtrate, from the $CaSO_4$, or $BaSO_4$, has the higher concentration of SO_4^{--}? _____

(d) Which salt, $CaSO_4$ or $BaSO_4$, is the more soluble, according to your experimental results? . . . . . _____

(e) What are the solubilities (formalities) of $CaSO_4$ and of $BaSO_4$ at room temperature?

Reference source: _____

$CaSO_4$ _____

$BaSO_4$ _____

(f) Which ion, Ca^{++} or Ba^{++}, precipitates SO_4^{--} more completely? . . . . . _____

(g) What additional information would you need to find whether the reaction, $Ba^{++} + SO_4^{--} \rightleftarrows BaSO_4$, is more complete than the reaction of SO_4^{--} with any other metallic ion?

2. The Shifting of an Equilibrium. The Common Ion Effect

A. *Saturated Silver Acetate Solution.* Rewrite the equation for the equilibrium present in a saturated solution of silver acetate:

_____

State whether a precipitate was formed when each of the following was added to the above equilibrium solution:

3 *F* $NaC_2H_3O_2$ _____ 6 *F* $HC_2H_3O_2$ _____

What effect would you predict if 3 *F* $AgNO_3$ (which is too expensive to use) were added to the above equilibrium solution?

_____

Explain concisely, but in some detail, why silver acetate was precipitated in some cases, but not in others.

What happened when 6 *F* HNO_3 was added to the residual solid silver acetate? Explain in terms of the equilibrium equation.

B. *A Saturated Sodium Chloride Solution.*

What is the "common ion" in solutions of NaCl and HCl? . . . . . _____

The Cl^- concentration of the saturated NaCl is approximately . . . . . _____

Is, then, the concentration of Cl^- increased or decreased by adding concentrated HCl?_____

Explain the action occurring on the addition of concentrated HCl to saturated NaCl, in terms of the equilibrium equation, NaCl (solid) $\rightleftharpoons Na^+ + Cl^-$.

C. *The Formation of a Complex Ion.* Compare the colors of the solutions of the tubes 2 to 4 with tube 1, in each case:

(1) H_2O . . . . . _____

(2) $FeCl_3$ . . . . . _____

(3) KCNS . . . . . _____

(4) KCl . . . . . _____

What two ions are most effective in increasing the red color, (as compared with tube 1)?

_____

Interpret the above results in terms of the equilibrium equation, $Fe^{+++} + CNS^- \rightleftharpoons Fe(CNS)^{++}$.

3. Application of the Law of Chemical Equilibrium to Analytical Procedure

Substances Mixed	*Observations (Indicate the Relative Amount of Precipitate)*
(1) $CaCl_2 + H_2C_2O_4$	
(2) $CaCl_2 + (NH_4)_2C_2O_4$	
(3) Results of (1) + HCl	
(4) Results of (3) + excess NH_4OH	
(5) $CaCl_2 + NH_4OH$	

(a) Does the CaC_2O_4 precipitate more completely in an acidic or in a basic solution? _____

(b) Does a solution of $(NH_4)_2C_2O_4$, or a solution of $H_2C_2O_4$ of equivalent concentration, give a higher concentration of $C_2O_4^{--}$? Why?

(c) By use of the equilibrium equation,

$$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^-$$
$$\updownarrow$$
$$H^+ + C_2O_4^{--},$$

show how the concentration of $C_2O_4^{--}$ is affected by the H^+ concentration of the solution.

(d) How does the increasing of the OH^- concentration of the solution affect the $C_2O_4^{--}$ concentration in an oxalic acid solution? What was the precipitate, formed on addition of NH_4OH to the acid solution of $CaCl_2$ and oxalic acid?

(e) How was the equilibrium reaction,

$$Ca^{++} + C_2O_4^{--} \rightleftarrows CaC_2O_4 \text{ (solid)}$$

affected by an increase of H^+ concentration? Explain.

(f) Is it more important to control the H^+ concentration in the precipitation of the salt of a weak acid or of th salt of a strong acid? Why?

Application of Principles

Predict whether the following insoluble salts would be dissolved by the addition of a strong acid such as HNO_3 In each case where solution would take place, write the net ionic equation for any reaction occurring. (See Table XI Appendix II.)

Salts	*Would They Dissolve?*	*Equation, if Any*
$NiCO_3$		
AgCl		
$PbSO_3$		
$PbSO_4$		
ZnS		
MgC_2O_4		
$Mg_3(PO_4)_2$		

Equilibria Involving Volatile and Insoluble Substances. The Transformation of Salts 25

College Chemistry, Chapters 13, 14, 15

Review of Fundamental Concepts

This continues the study of chemical equilibrium with reference to the formation of volatile and insoluble substances (see Tables VII and X, Appendix II) and shows how this may be used in the conversion of one salt to another or in the removal of undesired ions. It is often necessary in analytical procedures to eliminate an ion from a solution before making a test.

The Conversion of a Salt of a Volatile Acid to a Salt of a Non-Volatile Acid

Suppose you have a solution of sodium nitrate which you wish to convert to sodium sulfate. Sulfate ion must be provided from some source, and at the same time a positive ion must be provided which can be removed with the nitrate ion. The latter could be removed, if it formed an insoluble or a volatile compound. Since there are no insoluble nitrates, the precipitation method is not available. Nitric acid has a low boiling point. If, then, sulfuric acid, which provides both hydrogen ion and sulfate ion and has a high boiling point, is used, the equation for the reaction is

$$2\ NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HNO_3.$$

The evaporation of the solution will vaporize the nitric acid and leave the sodium sulfate as a solid residue.[1]

The Conversion of a Salt of a Volatile Acid to a Salt of Another Volatile Acid

If you wish to convert a chloride to a nitrate, or vice versa, another principle is involved. While to some extent during an evaporation, the reaction

$$NaCl + HNO_3 \longrightarrow NaNO_3 + HCl$$

takes place, we also have an oxidation-reduction reaction, in which both chloride ions and nitrate ions are destroyed.

$$4\ H^+ + 3\ Cl^- + NO_3^- \longrightarrow Cl_2 + NOCl + 2\ H_2O.$$

[1] With an excess of sulfuric acid, the principal product will be sodium hydrogen sulfate $NaHSO_4$.

If an excess of nitric acid is added, the chloride ion is eventually all destroyed. To obtain a complete transformation, repeated trials are necessary. Each time nitric acid is added, and the solution evaporated to dryness, the conversion becomes more complete.

The Conversion of a Salt of a Non-Volatile Acid to a Salt of a Volatile Acid

In converting a sulfate to a chloride, the method of treating the sulfate with hydrochloric acid and evaporating the solution is unsuccessful, for on evaporating the solution, the hydrochloric acid, and not the sulfuric acid, evaporates. Two other methods are available. (1) Barium chloride solution in equivalent amount may be added, the barium sulfate filtered out, and the remaining sodium chloride then evaporated to crystals,

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4(solid) + 2\ NaCl.$$

(2) The metal ion may be precipitated out as a hydroxide, or carbonate, filtered, and the precipitate redissolved in hydrochloric acid. The solution is then evaporated to crystals.

$$CuSO_4 + 2\ NaOH \longrightarrow Cu(OH)_2(solid) + Na_2SO_4,$$
$$Cu(OH)_2 + 2\ HCl \longrightarrow CuCl_2 + 2\ H_2O.$$

The Choice of Reagents and Test of Completion

Note that in the examples given for all three cases, no substances were added that would remain in the solution with the product after the reaction was complete. The by-product was always either a precipitate which could be filtered out, or a volatile substance which could be boiled off. The product, if in solution, could be crystallized out as a pure substance.

To see if conversion is complete, a test is made on the product for the negative ion that supposedly has been completely removed.

Experimental Procedure

Chemicals: 0.1 *F* $BaCl_2$, $FeSO_4 \cdot 7H_2O$, 0.1 *F* $AgNO_3$, NaCl, $NaNO_3$, Na_2SO_4, 1 *F* Na_2SO_4.

1. The Conversion of a Salt of a Volatile Acid to the Salt of a Non-Volatile Acid. To about 1 gram of $NaNO_3$, add 5 ml of 3 *F* H_2SO_4. Evaporate the solution to dryness. Dissolve the residue in 5 to 10 ml of water. Test a small portion of this solution for the presence of NO_3^- to see if the conversion is complete.[1] If not complete, add a small excess of H_2SO_4, and repeat the process.

2. The Conversion of a Salt of a Volatile Acid to the Salt of Another Volatile Acid. To about 1 gram of sodium chloride, add 5 ml of 6 *F* HNO_3. Evaporate just to dryness and test a small portion of the residue for Cl^-.[1] If a Cl^- test is obtained, repeat the process with a second 5-ml portion of HNO_3. If a chloride test is still obtained, repeat the process a third time. Is there any difference in the intensities of successive chloride tests?

3. The Conversion of a Salt of a Non-Volatile Acid to the Salt of a Volatile Acid. To about 1 gram of Na_2SO_4 add 5 ml of 6 *F* HCl, and evaporate the solution to dryness. Test a small portion of the residue for sulfate ion. Repeat the process, and again test the residue for sulfate ion. Is this a good method for converting Na_2SO_4 to NaCl?

To 2 ml of 1 *F* Na_2SO_4, add an equivalent amount, 20 ml, of 0.1 *F* $BaCl_2$ solution. The solid $BaSO_4$ may be removed by filtration through a fine filter paper (obtained from the stockroom); or if a centrifuge is available, the mixture may be centrifuged. Obtain instructions, and be sure the centrifuge tube is carefully balanced. Evaporate the filtrate to crystallization and test the crystals formed for SO_4^{--}. Which conversion is more complete, with HCl, or with $BaCl_2$? Explain the difference in behavior.

[1] See Experiment 20 for details of the tests for NO_3^- and for Cl^-.

REPORT: Exp. 25

Equilibria Involving Volatile and Insoluble Substances. The Transformation of Salts

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Conversion of a Salt of a Volatile Acid to the Salt of a Non-Volatile Acid

To what extent can you convert $NaNO_3$ to Na_2SO_4 by evaporating a mixture of $NaNO_3$ and H_2SO_4?

List the principal substances present in separate solutions of $NaNO_3$ and H_2SO_4.

Write the equation for the reaction, if any, which occurs on mixing solutions of $NaNO_3$ and H_2SO_4 at room temperature.

What is the net ionic equation for the reaction, if any, which occurs when this mixture is evaporated to crystallization?

Why should one expect the conversion of $NaNO_3$ to Na_2SO_4 to be successful under the conditions used in the laboratory?

Why is the negative test for NO_3^- in the product a better test of the completion of the reaction than is a positive test for SO_4^{--}?

2. The Conversion of the Salt of a Volatile Acid to the Salt of Another Volatile Acid

To what extent can you convert NaCl to $NaNO_3$ by evaporating a mixture of NaCl and HNO_3? Is repeated treatment with HNO_3 more effective in converting the salts? Explain fully.

Would you expect to be able to convert $NaNO_3$ to NaCl by a similar process? Explain fully.

3. The Conversion of a Salt of a Non-Volatile Acid to the Salt of a Volatile Acid

To what extent can you convert Na_2SO_4 to NaCl by evaporating a mixture of Na_2SO_4 and HCl? Is repeated treatment with HCl more effective in converting the salts? Explain fully.

Was the conversion of Na_2SO_4 to NaCl more successful when using $BaCl_2$ than when using HCl? Explain. What would be the disadvantage of using an excess of $BaCl_2$ in order to make the reaction more nearly complete?

Application of Principles

1. In making each of the following transformations, indicate the reagent(s) and procedures necessary to form the final pure salt, in solid form, from the first named substance. Also write the net ionic equations.

Na_2SO_3 to NaCl	
$MgCl_2$ to $Mg(OH)_2$	
$Mg(OH)_2$ to $MgCl_2$	
$BaCl_2$ to $Ba_3(PO_4)_2$	
K_3PO_4 to KCl	

2. Solutions of the following are mixed. In each case indicate the molecular formulas of any new substances produced. Also, at the right, give the reason for the reaction, if any, thus: no action, precipitate, weak acid, volatile product, etc. If necessary to heat the mixture to form the new substance, indicate this fact.

(a) Sodium carbonate and sulfuric acid . . .	_____	_____
(b) Silver nitrate and aluminum chloride .	_____	_____
(c) Potassium hydroxide and ammonium nitrate .	_____	_____
(d) Magnesium chloride and sulfuric acid . . .	_____	_____
(e) Potassium nitrate and ferric chloride . . .	_____	_____
(f) Sodium sulfate and barium chloride . .	_____	_____
(g) Nitric acid and sodium acetate . .	_____	_____
(h) Phosphoric acid and potassium carbonate .	_____	_____
(i) Nitric acid and calcium hydroxide (solid) . .	_____	_____

Strong and Weak Acids and Bases; Indicators 26

College Chemistry, Chapters 19, 20

Review of Fundamental Concepts

The adjectives, *strong* and *weak*, as applied to acids, bases, or salts, refer to their relative degrees of ionization. A strong acid is "strong"—that is, very reactive as an acid—because of the high concentration of hydrogen ion (H^+) that it contains in solution. A weak acid, although able to neutralize as much base as an equivalent amount of a strong acid, is "weak" because only a small proportion of its molecules are dissociated into hydrogen ion and the anion. It is, therefore, less reactive as an acid. Correspondingly, the strength of a base depends on the extent to which its molecules are dissociated into the cation and hydroxide ion. (See Table XI, The Relative Concentration of Ions in 0.1 *F* Solutions of Electrolytes, Appendix II.)

Measuring H^+ and OH^- Concentrations by Means of Indicators

An *indicator* is a complex organic compound the color of which, when in aqueous solution, depends on the relative concentration of hydrogen and hydroxide ions in the solution. With different indicators, this color change takes place at very different relative hydrogen and hydroxide ion concentrations. Thus, methyl violet exhibits its color change in a moderately acid solution, methyl orange in a slightly acid solution, phenolphthalein in a slightly basic solution, and indigo carmine in a solution which has a considerable hydroxide ion concentration. (See Table XII, The Color Change and *p*H Interval of Some Important Indicators, in Appendix II.)

In this experiment, we shall first prepare a series of solutions of known hydrogen ion and hydroxide ion concentration. This may be done by making tenfold dilutions of 0.1 *F* solutions of the strong acid hydrochloric acid, and of the strong base sodium hydroxide, respectively. Since these substances are thought to be completely ionized in dilute solution, the molarity of the hydrogen ion and of the hydroxide ion, respectively, will be the same as the formality of the corresponding acid or base solution. Solutions of extreme dilution are required, since the ionization of water is so slight that in pure water the concentrations of hydrogen ion and hydroxide ion are each only about 0.0000001 *M*, or 10^{-7} *M*.[1]

We shall use this series of solutions as standards, to learn the colors of several indicators and the concentration range through which a change of color takes place with each indicator. Also, using this method, we shall determine the approximate degree of ionization of acetic acid and of ammonium hydroxide, each at two different concentrations.

It should be noted that the hydrogen ion or hydroxide ion concentration in a solution can be estimated closely by one indicator only if the concentration lies within the color change range of that indicator. As an example, we may consider Congo red, which gives a red color in any solution which contains 0.00001 *M* H^+ *or less*, an intermediate red-blue at 0.0001 *M* H^+, and a blue color at 0.001 *M* H^+ *or greater*. If the color is intermediate between that of the 0.0001 *M* H^+ and the 0.001 *M* H^+ solutions, we might prepare a series of standards in between these limits and make careful color comparisons with our sample. In the absence of such additional standards, we may proceed as follows. If, for example, we judge the color to be about two-thirds of the way from the color of the 0.0001 *M* H^+ standard toward the color of the 0.001 *M* H^+ standard, we would estimate the sample to contain about 0.0007 *M* H^+. The series of expanded numbers given below may help you to express the intermediate values correctly.

10^{-4}	0.0001 *M* H^+ (red-blue to Congo red)
	0.0002
	0.0003
	0.0004
$10^{-3.3}$	0.0005
	0.0006
	0.0007 (2/3 toward the blue)
	0.0008
	0.0009
10^{-3}	0.0010 *M* H^+ (blue to Congo red)

[1] If you are not familiar with exponential notation, review the discussion on "Exponents" in Study Assignment A. The *p*H system of recording hydrogen ion concentration is explained in Experiment 34.

Note especially that half way between 10^{-4} and 10^{-5} is *not* $10^{-4.5}$, since exponential numbers are logarithmic, not linear. (The log of 0.0005 is −3.3. Thus, 0.0005 = $10^{-3.3}$.)

Dilution of Solutions

When diluting a solution of known concentration, the concentration after dilution will be inversely proportional to the volumes before and after dilution. Thus, if we dilute 2 ml of 6 *F* HCl to 200 ml, the concentration will be

$$\frac{2}{200} \times 6\ F = 0.06\ F \text{ HCl.}$$

Experimental Procedure

Chemicals: 1 *F* $HC_2H_3O_2$, 0.1 *F* $HC_2H_3O_2$, 1 *F* $NH_4C_2H_3O_2$, 1 *F* NH_4Cl, 1 *F* NH_4OH, 0.1 *F* NH_4OH, 0.1 *F* HCl, H^+ solutions from 10^{-4} to 10^{-7} *M* H^+, OH^- solutions from 10^{-8} to 10^{-7} *M* OH^-, 1 *F* $NaC_2H_3O_2$, 1 *F* NaCl, 0.1 *F* NaOH. Indicator solutions as follows: Methyl violet, methyl orange, phenolphthalein, alizarin yellow R, and indigo carmine.

1. The Preparation of Solutions of Known H^+ Concentration. Prepare solutions of 0.01 *M* H^+, and 0.001 *M* H^+, by dilution of 0.1 *F* HCl, as follows. First, thoroughly clean two 100 or 200-ml beakers or flasks. Rinse these with tap water, then, with not over 5 ml of distilled water by spraying from your wash bottle. By means of your graduated cylinder, carefully measure 5.0 ml of 0.1 *F* HCl from the stock bottle and add distilled water to make a total volume of 50.0 ml. Pour this back and forth between the graduated cylinder and one of the clean flasks several times to mix it thoroughly. What is now the H^+ concentration of this solution? Leave 5.0 ml (carefully measured) of the solution in the graduated cylinder and make a second tenfold dilution by filling carefully to the 50.0-ml mark with distilled water. Mix as before and transfer to a second flask. The more dilute solutions from 10^{-4} *M* to 10^{-7} *M* H^+ respectively are already prepared for your use.[1]

2. The Colors of Indicators in Acid Solutions. Now prepare a series of clean 10-cm test tubes containing 5 ml each of the acid solutions ranging from 10^{-1} to 10^{-7} *M* H^+. Add to each test tube one drop of methyl violet indicator. Stir each and note the colors[2] which are characteristic of the given H^+ concentrations.

[1] These solutions of very low H^+ concentration are "buffered" solutions. That is, the substances present in the solution act to keep the H^+ concentration in the solution very nearly constant, even when some additional acid or base is added. The carbon dioxide from the air reacts with the water, and forms too much H^+ to maintain a known concentration, without these buffers.

[2] The methyl violet in the stronger acid solutions will fade on long standing.

Save the tubes covering the color change range (three or four tubes) and label each. You will need them in sections 3 and 4. Now prepare another series of tubes containing 5 ml each of the acid solutions from 10^{-1} *M* to 10^{-7} *M* H^+, and test each with one drop of methyl orange indicator. Stir each and note the colors which are characteristic of the given H^+ concentrations. Again save the tubes covering the color change, labelling each, for use in sections 3 and 4. For each indicator, *learn* the range of hydrogen ion concentration through which it changes color, and the respective colors. You will need to fix the appearance and color in your mind as well as possible, for any descriptive names used in your notes will help only partially. Whenever you want to make accurate measurements with indicators, it is necessary to prepare a comparison series with the given indicator and make actual color comparisons. The amount of indicator used, of course, has some effect on the intensity and appearance of the color. The indicators are prepared so that one drop in 5 ml should be ample. An excess should be avoided.

3. The H^+ Concentration of an Unknown Solution. Take a clean test tube, labelled with your name, to your laboratory instructor and obtain a solution of unknown H^+. Test portions of this solution with methyl violet and methyl orange. Report the H^+ concentration of your unknown solution to your instructor at once (see report sheet).

4. The Degree of Ionization of Acetic Acid. Obtain a 5-ml portion of 1 *F* $HC_2H_3O_2$, and test it with one drop of methyl violet indicator. Make as accurate an estimate of the H^+ concentration in the solution as possible, by comparison with your standards. If the color lies between the colors of two of your standards, try to estimate the H^+ concentration in between the values represented by these standards. What would be the color of methyl orange with 1 *F* $HC_2H_3O_2$? Try it if you wish. What

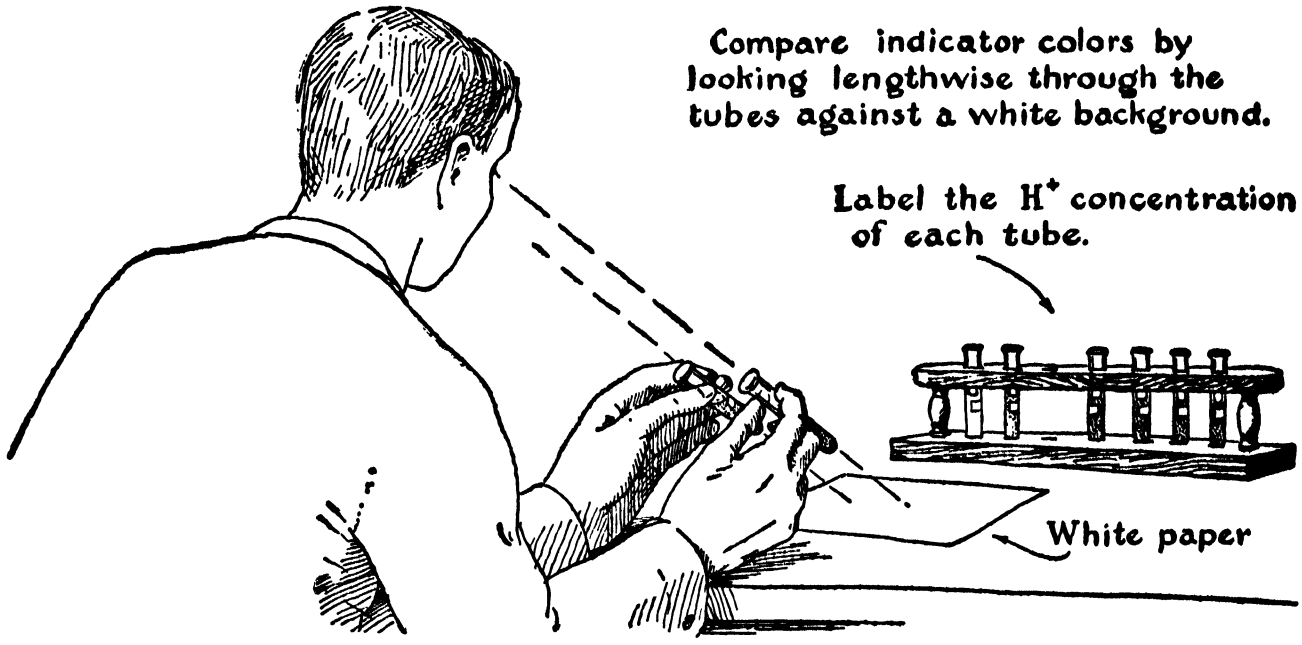


FIG. 26-1. Correct technique for the observation and comparison of indicator colors.

is the concentration of acetate ions in this same solution? Of un-ionized acetic acid molecules? What fraction of all the acetic acid molecules put in solution are broken apart into ions? (Express as percent ionization).

Test also 5-ml samples of 0.1 *F* $HC_2H_3O_2$ with both methyl violet and methyl orange to estimate the H^+ concentration. Calculate the $C_2H_3O_2^-$ concentration and the concentration of un-ionized $HC_2H_3O_2$. Calculate the percent ionized and compare with the percent ionized for a 1 F solution.

5. The Preparation of Solutions of Known OH^- Concentration. Prepare from the stock 0.1 *F* NaOH solution a 50-ml sample of 0.01 *F* NaOH by tenfold dilution as in section 1 for strong acids. Be careful to rinse all vessels used. Keep the solutions stoppered in order to prevent the absorption of carbon dioxide from the air. As with the acid solutions, the more dilute basic solutions, from 10^{-3} to 10^{-7} *M* OH^-, are already prepared for your use. They are likewise buffered solutions. The absorption of carbon dioxide from the air into an unbuffered basic solution would be even more rapid and troublesome than in the case of dilute acid solutions.

6. The Colors of Indicators in Basic Solutions. This time we shall use three different indicators, namely, indigo carmine, alizarin yellow R, and phenolphthalein, to learn to identify the hydroxide ion concentration of solutions. Prepare a series of 10-cm test tubes containing 5 ml each of the alkaline solutions ranging from 10^{-1} to 10^{-7} *M* OH^-. Test each with two drops of indigo carmine indicator.[1] Stir each and note the colors and, in particular, the range of the color change. Keep three or four tubes which cover the range of the color change and label each for use in section 7. Likewise, determine the colors and color range with alizarin yellow R, and with phenolphthalein, respectively. Keep the tubes covering the color change in each case for use in section 7.

7. The Degree of Ionization of Ammonium Hydroxide. Test 5-ml portions of 1 *F* and of 0.1 *F* NH_4OH with indicators to determine the hydroxide ion concentration in each case. What is the concentration of NH_4^+, and of undissociated NH_4OH, in each case? Calculate the percent ionized in each case.

8. Reactions Involving Weak Acids and Weak Bases. To 5 ml of 0.1 *F* HCl add a drop of methyl violet indicator, and then gradually add 1 to 2 ml of 1 *F* $NaC_2H_3O_2$ solution. Try the same experiment again except this time use 1 *F* NaCl in

[1] Indigo carmine indicator does not keep very well. If it is not a deep blue color it must be discarded and a fresh solution prepared.

place of the 1 *F* $NaC_2H_3O_2$. Also try 1 *F* $NH_4C_2H_3O_2$ instead of 1 *F* $NaC_2H_3O_2$. Explain the results and write the net ionic equation for any reaction taking place.

To 5 ml of 0.1 *F* NaOH solution add a drop of alizarin yellow R and then gradually add 1 to 2 ml of 1 *F* NH_4Cl solution. Try the same experiment again, except use 1 *F* NaCl in place of the 1 *F* NH_4Cl. Also try 1 *F* $NH_4C_2H_3O_2$ instead of 1 *F* NH_4Cl. Explain the results and write the net ionic equation for any reaction taking place.

9. The Electrical Conductivity Method for Determining the Degree of Ionization. As an optional alternate or additional procedure, the same apparatus used in Experiment 16 may be used to compare the conductivity of 0.1 *F* $HC_2H_3O_2$ with that of a very dilute solution of hydrochloric acid, prepared as follows. Fill the 10-ml graduated cylinder exactly to the mark with 0.1 *F* HCl, then with the aid of a medicine dropper add this solution drop by drop to 100 ml of distilled water, stirring after each addition, until this solution has the same conductivity as that of the 0.1 *F* $HC_2H_3O_2$. The two solutions can be compared by raising first one, then the other, alternately, to make contact with one of the pairs of electrodes. Be sure the electrodes are the same distance apart, and that you immerse them to the same depth. Make electrical connections only momentarily, as continuous passage of the current will heat the solution and invalidate the results.

Note the precise volume of 0.1 *F* HCl used (first returning any excess from the medicine dropper to the graduated cylinder). From this volume, and the volume of diluted HCl, calculate the concentration of H^+ in the diluted HCl, assuming complete ionization. If we assume that the 0.1 *F* $HC_2H_3O_2$ contains the same H^+ concentration as the diluted HCl,[1] we may calculate the approximate degree of ionization of the 0.1 *F* $HC_2H_3O_2$.

Now replace the 0.1 *F* $HC_2H_3O_2$ by 1 *F* $HC_2H_3O_2$, and continue to add 0.1 *F* HCl from the graduated cylinder to the diluted HCl solution until its conductivity equals that of the 1 *F* $HC_2H_3O_2$. Calculate the degree of ionization as before.

The degree of ionization of 0.1 *F* NH_4OH and of 1 *F* NH_4OH may be determined in an analogous manner. For these, add a measured volume of 0.1 *F* NaOH to 100 ml of distilled water until the conductivity is equal to that of the solution being tested.[2] Calculate the results as in the preceding paragraphs.

10. Review Questions on Ionization and Ionic Substances. It is very much worth while to form the habit of thinking of the various strong and weak acids, bases, and salts, in terms of the actual molecular or ionic species largely present in their aqueous solutions. Study the examples as given in the section of the report sheet headed *Application of Principles*, then calculate the concentration of the principal substances present, in the problems which follow.

[1] Strictly speaking, the ionic concentrations are not quite equal when the conductivities are equal The equivalent conductances at 25° C of the separate ions, in reciprocal ohms, are: H^+ 350, $C_2H_3O_2^-$ 40.8, Cl^- 75.5 (data from Lange, Handbook of Chemistry, 7th ed., P. 1417). The conductivities of equal concentrations of the ions of HCl and of $HC_2H_3O_2$ will be in the ratio of (350+75.5)/(350+40.8), which equals 1.09 to 1. Therefore, you may correct the calculated value of the concentration of H^+ in the acetic acid by multiplying by the factor 1.09.

[2] Here, also, we may correct our calculations for the slight differences in the conductivities of sodium ion and ammonium ion. The equivalent conductances at 25° C are: NH_4^+ 74.5, Na^+ 50.9, and OH^- 192. The conductivities of equal concentrations of the ions of NaOH and of NH_4OH will be in the ratio of (50.9+192)/(74.5+192), which equals 0.91. Therefore you may obtain a corrected value for the OH^- concentration in the NH_4OH solutions, by multiplying by the factor 0.91.

REPORT: Exp. 26

Strong and Weak Acids and Bases, Indicators

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Preparation of Solutions of Known H^+ Concentration. The hydrogen ion concentration in my solution prepared by diluting 5.0 ml of 0.1 *F* HCl to a volume of 50.0 ml is

_____ *M*

2. The Colors of Indicators in Acid Solutions. The indicator colors obtained with various concentrations of hydrogen ion in strong acids are as follows:

Concentration	*Methyl Violet*	*Methyl Orange*
10^{-1} *M* H^+		
10^{-2} *M* H^+		
10^{-3} *M* H^+		
10^{-4} *M* H^+		
10^{-5} *M* H^+		
10^{-6} *M* H^+		
10^{-7} *M* H^+		

3. The H^+ Concentration of an Unknown Solution. My unknown H^+ solution No._____ gave the following indicator colors:

Methyl violet_____ Methyl orange_____

The hydrogen ion concentration is therefore: . . . . . _____ *M*

Instructor's approval of report on unknown . . . . . _____

4. The Degree of Ionization of Acetic Acid. The color of acetic acid solutions with indicators, and the estimated molal concentrations of the substances present are as follows:

Solution	*Methyl Violet*	*Methyl Orange*	*H^+ Concentration*	*$C_2H_3O_2^-$ Concentration*	*$HC_2H_3O_2$ Concentration*	*Percent Ionized*
1 *F* $HC_2H_3O_2$			*M*	*M*	*M*	%
0.1 *F* $HC_2H_3O_2$			*M*	*M*	*M*	%

The calculation of the percent ionization is as follows:

Does the degree of ionization of weak electrolytes—for example, $HC_2H_3O_2$—increase or decrease or remain the same, as the dilution is increased? (This is a general rule.) _____

5. and 6. The Preparation of Solutions of Known OH^- Concentration. The Colors of Indicators in Basic Solutions. The indicator colors obtained with various concentrations of hydroxide ion in strong bases are as follows:

Concentration	*Indigo Carmine*	*Alizarin Yellow R*	*Phenolphthalein*
10^{-1} *M* OH^-			
10^{-2} *M* OH^-			
10^{-3} *M* OH^-			
10^{-4} *M* OH^-			
10^{-5} *M* OH^-			
10^{-6} *M* OH^-			
10^{-7} *M* OH^-			

7. The Degree of Ionization of Ammonium Hydroxide. The color of ammonium hydroxide solutions with indicators, and the estimated molal concentrations of the substances present are as follows:

Solution	*Indigo Carmine*	*Alizarin Yellow R*	*Phenol-phthalein*	OH^- *Conc.*	NH_4^+ *Conc.*	NH_4OH *Conc.*	*Percent Ionized*
1 *F* NH_4OH				*M*	*M*	*M*	%
0.1 *F* NH_4OH				*M*	*M*	*M*	%

The calculation of the percent ionization is as follows:

8. Reactions Involving Weak Acids and Weak Bases. The results obtained are indicated in the following chart.

Solutions Mixed	*Indicator Used and Color Change*
5 ml HCl with $NaC_2H_3O_2$ added	
5 ml HCl with NaCl added	
5 ml HCl with $NH_4C_2H_3O_2$ added	
5 ml NaOH with NH_4Cl added	
5 ml NaOH with NaCl added	
5 ml NaOH with $NH_4C_2H_3O_2$ added	

Explain in words any differences in the effects of the salts on HCl, and write the net ionic equation for any reaction occurring:

Explain in words any differences in the effects of the salts on NaOH, and write the net ionic equation for any reaction occurring:

9. The Electrical Conductivity Method for the Determination of the Degree of Ionization.

	0.1 F $HC_2H_3O_2$	*1 F* $HC_2H_3O_2$	*0.1 F* NH_4OH	*1 F* NH_4OH
Volume of 0.1 *F* HCl (or NaOH for the NH_4OH solutions) added to 100 ml H_2O	ml	ml	ml	ml
Calculated molarity of the H^+ (or OH^-)	*M*	*M*	*M*	*M*
Degree of Ionization	%	%	%	%

The calculation of the percent ionization is as follows:

Again compare the degree of ionization and the concentration of the solutions:

Application of Principles

In interpreting a solution as to the actual form (ions or molecules) in which the dissolved substances are present, the following points should be noted:

(1) Are the substances present largely in ionized form, or as molecules?

(2) Do any of the ions or molecules react with one another? How many moles of reactants used, and of products formed, are there? (Determine from the equation for the reaction.)

(3) In calculating the final concentration of the substances in solution, has there been any dilution effect, either by adding water, or due to the mixing of two or more solutions?

Examples: What is present, and at what concentration in:

(1) 0.1 *F* HCl? . . . . . 0.1 *M* H^+, 0.1 *M* Cl^-

(2) a mixture of 1 gfw of HCl, and 0.5 gfw of NaCl, in 250 ml of solution?

There will be 1 mole H^+, 1.5 mole Cl^-, and 0.5 mole Na^+, in 250 ml (¼ liter) of final solution. The concentration in moles per liter will therefore be four times the number of moles, or . . . 4 *M* H^+, 6 *M* Cl^-, 2 *M* Na^+

(3) a mixture of 300 ml of 1 *F* NH_4OH and 200 ml of 2 *F* HNO_3?

First figure the number of moles of each substance before reaction, then from the equation

NH_4OH	+	H^+	$\rightleftharpoons$	NH_4^+	+	H_2O
1 mole		1 mole		1 mole		
0.3 mole		0.3 mole		0.3 mole		

calculate the number of moles of each substance produced, or remaining in excess. In this case 0.3 mole of NH_4OH will require 0.3 mole of H^+. Since 0.4 mole of H^+ was available, 0.1 mole of H^+ will remain in excess. Finally calculate the concentrations. The following form is useful to summarize the calculations:

	Present before reaction	*Present after reaction*	*Concentration*
300 ml 1 *F* NH_4OH	0.3 mole NH_4OH	0.3 mole NH_4^+	0.6 *M* NH_4^+
200 ml 2 *F* HNO_3	0.4 mole H^+	0.1 mole H^+	0.2 *M* H^+
	0.4 mole NO_3^-	0.4 mole NO_3^-	0.8 *M* NO_3^-
Final volume: 500 ml			

Problems. For each of the following, list at the right the principal substances present. If in solution, give the molarity; and if a solid or a gas, give the number of formula weights or moles formed. Indicate small amounts by "Trace." Any volume changes due to the formation of water may be neglected. In items (5) to (8) inclusive show your **method,** in the space below each item, and also give the **net ionic equation** for any reaction.

(1) 0.01 *F* $Ba(OH)_2$ (assume complete ionization) . . . . . _____

(2) A mixture of 1 gfw Na_2SO_4 and 2 gfw K_2SO_4 in a liter of solution . . . . . _____

(3) 0.1 *F* $HC_2H_3O_2$ . . . . . _____

(4) 0.1 gfw NH_4OH in 100 ml of solution . . . . . _____

(5) A mixture of 0.1 gfw HCl and 0.1 gfw $Ba(OH)_2$ in a liter of solution . . . . _____

(6) A mixture of 250 ml of 0.1 *F* NH_4OH and 250 ml of 0.1 *F* $HC_2H_3O_2$ (neglect hydrolysis) . . . . . _____

(7) One liter of 0.5 *F* $CuSO_4$, saturated with H_2S gas . . . . . _____

(8) 2.4 g (0.1 g at) of magnesium metal dissolved in 250 ml of 2 *F* HCl . . . . _____

The Titration of Acids and Bases — 27

College Chemistry, Chapter 20

Review of Fundamental Concepts

The Equivalent Weights of Acids and Bases

In the neutralization of an acid with a base, one hydrogen atom (either as the free ion, H^+ or as a reactive hydrogen atom in the molecule of a weak acid) reacts with one hydroxide group (as free ion or as radical in the molecule) to form one molecule of water. These amounts are therefore equivalent. Thus we may calculate the equivalent weights of acids and of bases by dividing the respective formula weights by the number of hydrogen atoms or hydroxide groups in the formula, *provided that all these take part in the reaction under consideration.* Consider the reactions

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\,H_2O \quad (1)$$
$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O \quad (2)$$
$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O \quad (3)$$

In equations (1) and (2), the equivalent weight of H_2SO_4 is one-half of its formula weight (½ of 98 g, or 49 g), since both hydrogen atoms are neutralized. The equivalent weight of $Ca(OH)_2$ is half of its formula weight (½ of 74 g, or 37 g), while the equivalent weight of NaOH is its formula weight (40 g). In equation (3), only one of the two hydrogen atoms in H_2SO_4 has been neutralized by the one formula weight of NaOH, which is obviously one equivalent. The equivalent weight of H_2SO_4 in this reaction is, therefore, the same as its formula weight, 98 g.

Sometimes chemists refer to the equivalent weight of an acid or base without reference to a particular reaction, in which case they generally infer the maximum number of equivalents per formula weight.

Normality as a Unit of Concentration

We shall define a new unit of concentration, which is related to molarity and formality in the same way that the equivalent weight is related to the mole and the formula weight. *The normality of a solution expresses the number of equivalents of solute per liter of solution.* The defining equation is

$$\text{Normality} = \frac{\text{equivalents of solute}}{\text{liters of solution}} \text{ or } N = \frac{\text{equiv}}{\text{V (liters)}}$$

One advantage in using this unit is that equal volumes of solutions of the same normality are equivalent chemically and just react with one another. This is not always true when concentrations are expressed in molarity or formality, since reactions do not always take place one formula weight to one formula weight. The following examples will illustrate the meaning of normality. Study also Figure 27-1 to review the distinction between a unit of quantity, such as the equivalent weight, and the corresponding unit of concentration—normality.

Example 1. How many equivalents, and how many grams of NaOH, are there in 200 ml of 0.300 *N* NaOH?

From the defining equation, N = equiv/V(liters),

$$\text{equiv} = N \times \text{V} = 0.300\,\frac{\text{equiv}}{\text{liter}} \times 0.200\ \text{liter} = 0.0600\ \text{equiv.}$$

And to express this as grams,

$$0.0600\ \text{equiv} \times \frac{40.0\ \text{g NaOH}}{\text{equiv}} = 2.40\ \text{g NaOH.}$$

Example 2. What is the normality of a solution which contains 1.11 g $Ca(OH)_2$ dissolved in 2.00 liters of solution? First express 1.11 g $Ca(OH)_2$ as equivalents. The formula weight is 74.0 g. Since there are two replaceable OH groups, the equivalent weight is 74.0/2 or 37.0 g, and the number of equivalents are

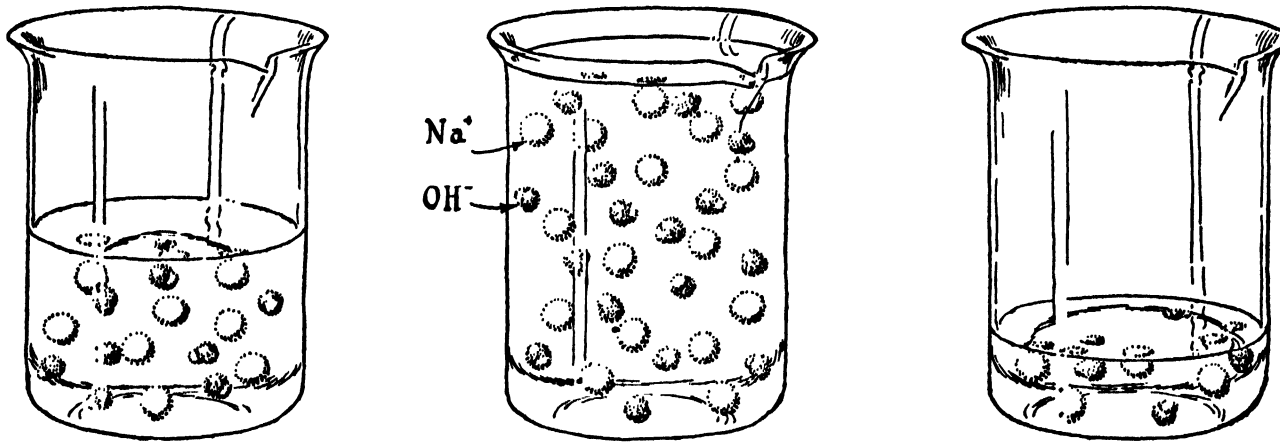
$$\frac{1.11\ \text{g}}{37.0\ \text{g/equiv}} = 0.0300\ \text{equiv.}$$

From the defining equation, we may then calculate the normality:

$$\frac{0.0300\ \text{equiv}}{2.00\ \text{liters}} = 0.0150\ N\ Ca(OH)_2.$$

Example 3. What is the normality of 3 *F* H_2SO_4, when used in the usual manner where both hydrogen atoms in the formula react?

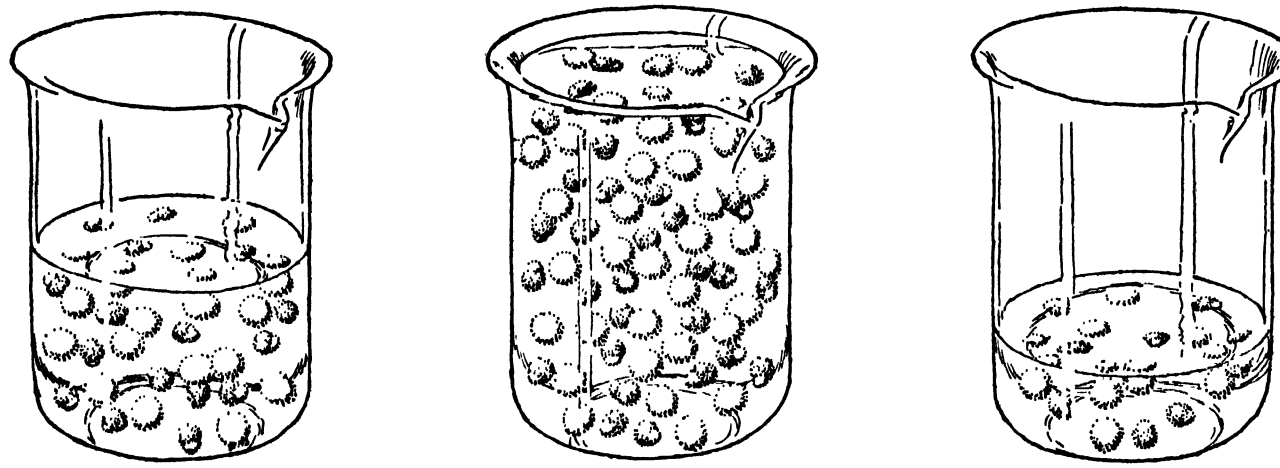
$$\frac{3\ \text{gfw}\ H_2SO_4}{\text{liter}} \times \frac{2\ \text{equiv}}{\text{gfw}} = \frac{6\ \text{equiv}}{\text{liter}} \text{ or } 6\ N\ H_2SO_4$$



1 equiv in 1 liter | 2 equiv in 2 liters | 0.5 equiv in 0.5 liter

The above solutions contain different *amounts* of solute, but are at the same *concentration*, namely 1 *N*, calculated thus:

$$\text{Normality} = \frac{1 \text{ equiv}}{1 \text{ liter}} = \frac{2 \text{ equiv}}{2 \text{ liters}} = \frac{0.5 \text{ equiv}}{0.5 \text{ liter}} = 1\ N$$



2 equiv in 1 liter | 4 equiv in 2 liters | 1 equiv in 0.5 liter

These three lower solutions, likewise, contain different *amounts* of solute, twice as much, respectively, as above, and are each 2 *N* in *concentration:*

$$\text{Normality} = \frac{2 \text{ equiv}}{1 \text{ liter}} = \frac{4 \text{ equiv}}{2 \text{ liters}} = \frac{1 \text{ equiv}}{0.5 \text{ liter}} = 2\ N$$

FIG. 27-1. To illustrate the meaning of normality as a unit of concentration. In this drawing, 1 equivalent is represented by 8 Na^+ ions and 8 OH^- ions, at an enormous scale.

Titration and Standard Solutions

The process of titration consists of the gradual addition of a solution of known concentration to a measured volume of a solution of unknown concentration, or to a weighed amount of sample dissolved in water, until *the same number of equivalents of each substance has been used.* This point is detected by means of a suitable *indicator.* Phenolphthalein, which is red in basic solution and colorless in acid solution, is often used for acid-base titrations. The *end-point,* or point at which a permanent color change occurs after thorough stirring of the solution, is very sharp. Only a drop, or fraction of a drop, of excess solution will bring about the color change. Volumetric analysis can therefore be performed with almost the same precision as the gravimetric process of weighing. The solution of known concentration which is used as the reference standard is called a *standard solution.*

The relative concentrations of the two solutions, and consequently the normality of the unknown solution, can be determined from the relative vol-

umes of the solutions used. Thus, if two solutions, (1) and (2), are titrated to the end-point, we have the fundamental relationship,

equivalents of solution (1) = equivalents of solution (2)

and by the defining equation of normality, namely N = equiv/V, we note that the equivalents of solution (1) = N_1V_1, and of solution (2) = N_2V_2. Therefore,

$$N_1V_1 = N_2V_2, \text{ or transposing, } \frac{N_1}{N_2} = \frac{V_2}{V_1}.$$

The relative volumes required thus will be inversely proportional to the normalities of the solutions.

It should be noted that while the number of grams of reacting substances are seldom equal and the number of moles of reacting substances are only sometimes equal, *the number of equivalents of reacting substances are always equal*—by definition. For this reason, concentrations are expressed in normalities in the equation, $N_1V_1 = N_2V_2$. If any three of the quantities are known, the fourth can be calculated.

Example. What is the normality of a sodium hydroxide solution, if 43.25 ml of it are required to neutralize 50.00 ml of 0.500 N oxalic acid solution? From the equation $N_1V_1 = N_2V_2$, by transposing,

$$N_2 = \frac{N_1V_1}{V_2} = \frac{0.500\ N \times 50.00\ \text{ml}}{43.25\ \text{ml}} = 0.578\ N\ \text{NaOH}.$$

Experimental Procedure

Special supplies: analytical weights, 250-ml volumetric flask, 2 burettes, 1 burette clamp, double.
Chemicals: oxalic acid crystals.

1. The Preparation of a Standard Acid Solution. In this experiment, we shall prepare as a standard solution, 250 ml of 0.5 N oxalic acid. This substance is readily obtained as pure crystals of definite composition, of the formula $H_2C_2O_4 \cdot 2H_2O$. The water of crystallization is a part of the substance as weighed and must, of course, be included in your calculation of the equivalent weight. The hydrogen of the water of crystallization does not contribute to the acidity of the solution, so that from the formula above, there are two replaceable hydrogen atoms per mole.

Calculate the number of grams of oxalic acid crystals needed to prepare 250 ml of 0.5 N solution. (Note: First find the number of equivalents needed, then the weight.) Check your weight calculation with the instructor to be sure you have made no error. Weigh an amount of oxalic acid crystals close to this amount, recording the exact weight. Do not waste time at the balance attempting to adjust the amount to the exact weight calculated. You can calculate the exact normality later, if you know the exact weight used, by dividing the number of equivalents weighed out by the volume of the solution, 0.250 liter.

Place a clean 250-ml volumetric flask on a clean sheet of paper on your desk and, with the aid of a stirring rod, very carefully transfer the weighed crystals, without loss, to the volumetric flask. Rinse the beaker and stirring rod with distilled water, and add these rinsings to the flask. Now add distilled water to the flask until it is about ⅔ full, and mix gently by rotating the flask until solution is complete. Add more water until the bottom of the meniscus of the solution comes to the graduation mark. Be careful not to go past the mark. The last water may be added dropwise with a medicine dropper. Stopper the flask and mix the contents very thoroughly for several minutes by repeatedly inverting and rotating the flask. Hereafter, do nothing that will alter the concentration of this standard solution, such as adding it to a wet vessel, or permitting evaporation of the solution. Calculate the normality of your standard oxalic acid solution. Put the solution just prepared into a clean *dry* flask or bottle. Stopper this container to prevent any evaporation. Label it with the name of the substance, concentration, date, and your initials. Save the solution, for it may be used in the following experiment also.

2. The Preparation of an NaOH Solution for Standardization. Dilute 40 ml of the approximately 6 N desk reagent of NaOH with 440 ml of water. (Desk reagents are not made up with quantitative accuracy to the indicated strength, hence your diluted solution will only be approximately the normality desired, and must be standardized against your oxalic acid.) Place your basic solution in a bottle, close with a rubber stopper,

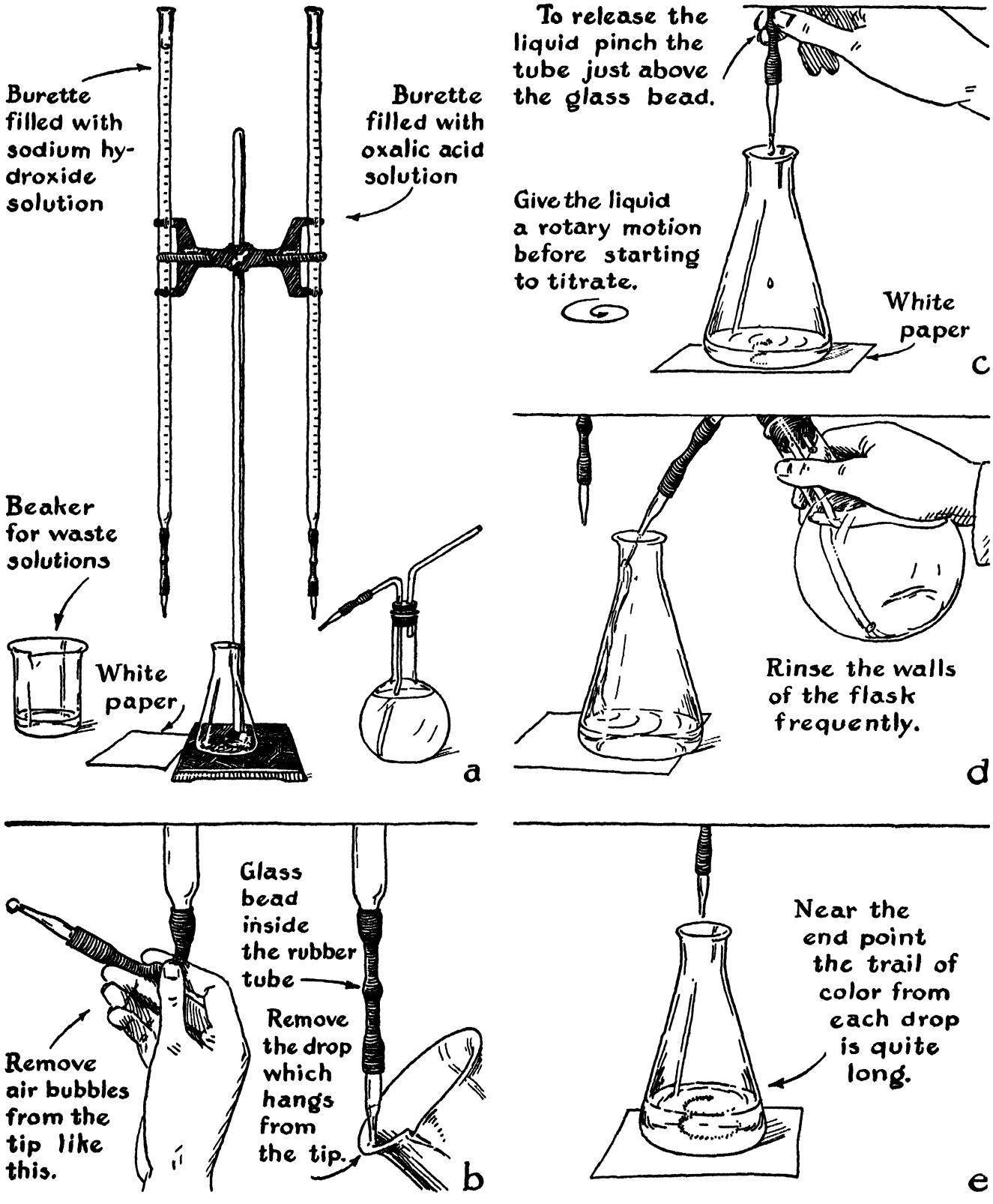


FIG. 27-2. Techniques in the process of titration.

and mix very thoroughly by repeatedly inverting and rotating the solution. Label the bottle and save it for use in the next two experiments. Calculate the approximate normality of your NaOH.

3. The Titration of Your NaOH Solution. Clean two burettes thoroughly. Soap solution and a long burette brush may be used, if needed. Water should flow freely, without forming droplets, over the inside surface of the burette. After rinsing thoroughly with tap water and draining, rinse one burette with a 5-ml portion of your oxalic acid solution. Reject the rinsings. Rinse a second time, again rejecting the rinsings by running them through the burette tip. Fill the burette with the oxalic acid solution, and make sure that there are no air bubbles in the tip of the burette.[1] The burette has a rubber delivery tube containing a glass bead valve. This is operated by placing the fingers on the tube just slightly above the bead and squeezing the tube so as to make a channel in the tubing around the bead, through which the liquid from the burette may flow. (Do not press the rubber tube below the bead, as this would cause it to act as a medicine dropper, expelling liquid, and sucking in an air bubble. This would cause an incorrect reading.) If the burette continues to drip after releasing the pressure, return it to the stockroom and have the rubber tubing replaced.

Fill the second burette with your NaOH solution, taking the same precautions as before in regard to rinsing it. Adjust the level of the liquid in both burettes so that it is at, or slightly below, the zero mark, catching the discharged solution in a beaker. Touch off the drop which adheres to the tip at the side of the beaker. When you read this initial burette volume and also the final volume, estimate the burette reading to the nearest tenth or fifth of the smallest division. With a little practice, you should be able to read a burette to 0.02 ml.

Perform the titration as follows. Run about 20 ml of the oxalic acid solution into a clean, rinsed 200 to 300-ml Erlenmeyer flask. Add 2 drops of phenolphthalein indicator. Now run in NaOH solution, fairly rapidly at first, stirring by a rotary motion of the flask. As the end-point is approached, which is indicated by the fact that the pink color does not disappear so rapidly and trails around the solution as it is rotated, add the NaOH solution slowly, drop by drop, until the final drop, after stirring, leaves a slight pink color which persists in the solution at least 15 seconds. If you have gone past the end-point, add a few drops of oxalic acid, and again approach the end-point. The last drops adhering to both burette tips may be touched off in making the final adjustment. The wash bottle will be found convenient in rinsing down the walls of the flask. Read and record the final volume of solution in each burette. Make two additional titrations of your solutions. Calculate the normality of your NaOH solution, and obtain the instructor's approval. If concordant results are not obtained, additional titrations may be made.

Save both the unused oxalic acid and sodium hydroxide solutions for the next experiment. They should be kept stoppered.

[1] Study Figure 27-2 to learn various convenient techniques in the process of titration.

Supplementary Drill

Note: Use this material as needed, after you have completed the report sheet, to provide additional drill on calculations involving quantity and concentration of solutions. It need not be handed in unless called for. Show your method in each case.

1. How many grams of each of the following are required to just react with 200 ml of 0.35 *N* HNO_3?

   (a) $Mg(OH)_2$ . . . _____ g (c) Na_2CO_3 . . . . _____ g

   (b) CaO . . . . _____ g (d) $NaHCO_3$ . . . . _____ g

2. What is the concentration of each of the following? (Note that dilution does not change the number of equivalents of solute. Use $V_1N_1 = V_2N_2$, or $V_1F_1 = V_2F_2$.)

   (a) 25 ml of 0.4 *N* HCl, diluted to 500 ml volume . . . . . _____ N

   (b) 10 ml of 3 *F* H_2SO_4, diluted to 15 ml volume . . . . . _____ F

   (c) 10 g of NaOH, dissolved in 250 ml H_2O and evaporated to 100 ml final volume _____ N

3. To what volume must each of the following be diluted to give the concentration called for?

   (a) 20 ml of 6 *N* HNO_3, to give a 0.1 *N* solution . . . . . _____ ml

   (b) 36 ml of conc (18 *F*) H_2SO_4 to give a 0.2 *F* solution . . . . . _____ ml

   (c) 36 ml of conc (18 *F*) H_2SO_4 to give a 0.2 *N* solution . . . . . _____ ml

   (d) 100 ml of glacial acetic acid (17 *F*) to make it 6.0 *N* . . . . . _____ ml

4. 60.0 ml of 0.2 *N* NaOH is mixed with 40.0 ml of 0.05 *N* HCl. What is the concentration of the remaining OH^-? (Final volume is 100 ml.) . . . . . _____ N

5. 1.00 g of Ca metal is dissolved in 200 ml of 1.00 *N* HCl. What is the concentration of the remaining H^+ after complete solution of the metal? . . . . . _____ N

The Equivalent Weight of a Solid Acid. Other Volumetric Analyses — 28

College Chemistry, Chapter 20

Review of Fundamental Concepts

This experiment makes further use of principles developed in the preceding experiment. Make sure that you know:

(1) How to find the number of equivalents of the solute in a given volume of solution of known normality,

(2) The relationship between the weight, equivalent weight, and the number of equivalents for a given quantity of a substance,

(3) The relationship between the numbers of equivalents of substances that react. That is, if you have 2 equivalents of NaOH, how many equivalents of H_2SO_4 would be required for neutralization?

These relationships are all summarized by the series of equations:

$$\text{no. of equiv} = \frac{g}{\text{equiv wt}} = N_1V_1 = N_2V_2$$

Experimental Procedure

Special supplies: analytical weights, 2 burettes, vial of unknown solid acid. Bring your own samples of vinegar, citrus fruits or juices, and baking soda.

1. Equivalent Weight of a Solid Acid. Obtain from the assistant a numbered vial containing a sample of a solid unknown acid. Record this number on your report sheet at once. Weigh out three 1 to 2 g samples of the acid, as precisely as you can, into 250-ml Erlenmeyer flasks. Follow the suggestions of Figure 28-1. The second weight for the first sample becomes the first weight for the second sample, and so forth, so that only four weighings are needed for three samples. Record each weight as obtained, and number the flasks to avoid confusion. Dissolve the samples by adding to each flask about 50 ml of distilled water. The exact amount of water is not important; more may be added if needed to dissolve the sample.[1]

[1] A difficultly soluble sample may be allowed to dissolve during the titration, as the base is added. Proceed slowly when near the endpoint, stirring constantly, and be sure the solution is complete before you cease titrating.

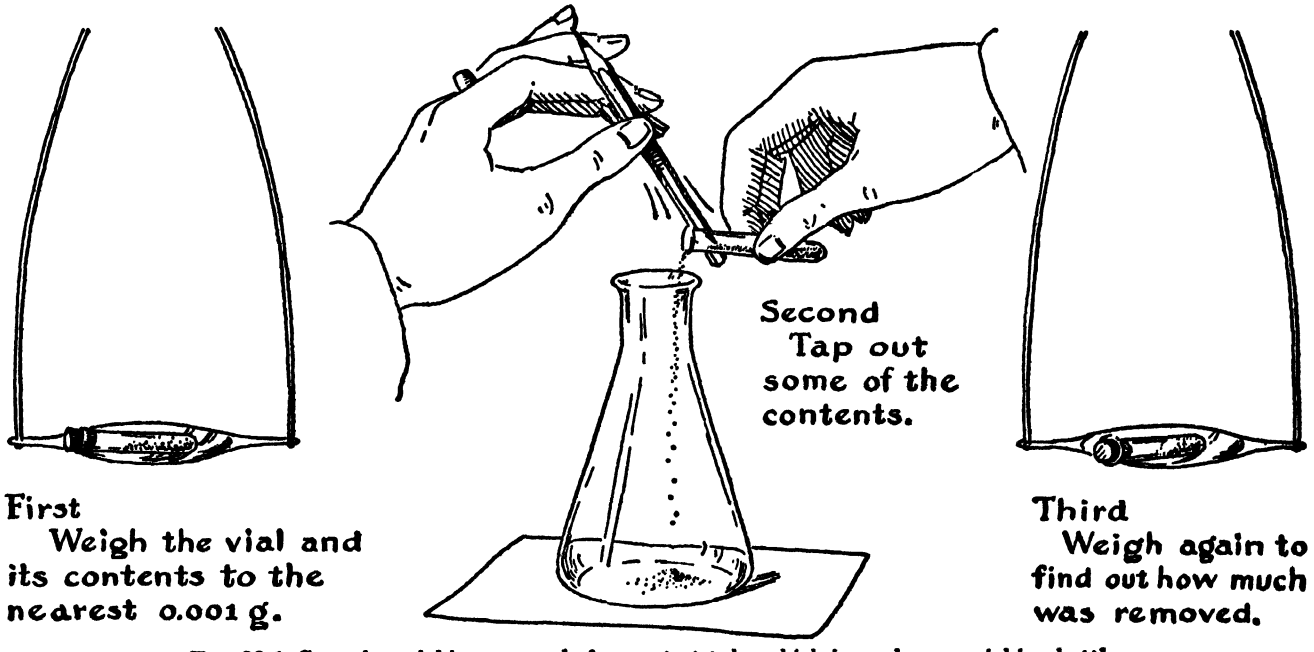


FIG. 28-1. Steps in weighing a sample from a test tube which is used as a weighing bottle.

Clean, rinse, and fill a burette with your standardized NaOH solution.[1] Titrate each sample of acid by running the NaOH solution directly into the flask in which the sample was dissolved, using two drops of phenolphthalein in each flask as an indicator. Titrate to the appearance of the first faint, permanent pink color, after stirring. If you pass the end-point slightly in this first titration, you can calculate quickly the approximate volume needed for successive titrations from the first volume and the relative weights of the samples. Then add the first part of the necessary volume of NaOH rapidly, and approach the end-point slowly by dropwise additions. From the data obtained, calculate the equivalent weight of the unknown acid.

2. Other Volumetric Analyses. Note: No report sheet for this part has been provided. *Your report will be judged by the care with which you prepare a suitable form for the entry of all needed data in good logical order, and for the extension of all calculations.* Do this *after* studying the procedure, but *before* performing the experiment. Carry out one or more of these procedures, as directed by the instructor, and as time permits.

(a) *Determination of Acetic Acid in Vinegar.* Rinse and fill a burette with a light-colored sample of vinegar. (A highly colored vinegar will need to be treated first with adsorbent charcoal to remove the coloring, and filtered through a dry filter.) Fill a second burette with your standard sodium hydroxide solution, as usual, and titrate the two solutions, using phenolphthalein indicator. Check the results by a second titration.

From the average density of vinegar, 1.005 g/ml, calculate the weight of a liter of the vinegar. The weight of the solute in a liter of the solution can be obtained from your experimentally determined normality and the equivalent weight of the solute. Assume that all the acidity of the vinegar is due to acetic acid ($HC_2H_3O_2$). How does your result compare with the legal requirement, which specifies that vinegar must contain not less than 4% acetic acid?

(b) *Determination of Citric Acid in Citrus Fruit.* Squeeze out about 100 ml of lemon, orange, or grapefruit juice. Determine its density by means of a hydrometer or by carefully weighing on the agate bearing triple beam balance, a carefully measured volume, 50 or 100 ml. Place the juice in one burette, and your standard NaOH solution in a second burette. Titrate the solutions, using 5 drops of phenolphthalein indicator. If orange juice is used, keep a sample out for comparison, as the first appearance of the red color of the indicator is rather difficult to detect in such a highly colored solution.

Calculate the acidity of the citrus juice, as percent citric acid in the sample. The formula for citric acid is $H_3C_6H_5O_7$.

(c) *Determination of the Purity of Baking Soda.* Weigh out accurately two 1.5 g samples of baking soda. Place in Erlenmeyer flasks and dissolve each separately in water. Obtain about 100 ml of a standardized H_2SO_4 solution of about 0.5 *N* strength from the instructor and fill a burette with it in the usual manner.[2] Add 2 drops of methyl orange indicator to each solution and titrate to the end-point. A dilute solution of methyl orange in a basic or neutral solution is straw yellow. In an acid, it is pink. The end-point is considered the point at which the solution begins to turn from yellow to orange (not yet pink); that is, when a slight amount of pink color appears with the yellow.

Write the equation for the reaction of sodium bicarbonate, $NaHCO_3$, with H_2SO_4. From the volume of the standard H_2SO_4 used, the equivalents, and hence the grams, of $NaHCO_3$ may be calculated. Express the result as percent of $NaHCO_3$ in the baking soda.

[1] In case of any doubt as to the normality of your NaOH solution prepared in Experiment 27, you may restandardize it against 20-ml portions of a standardized H_2SO_4 solution provided by the instructor for this purpose. Use phenolphthalein as the indicator.

[2] A weak base such as baking soda cannot be titrated with a weak acid such as your oxalic acid solution, hence the use of a sulfuric acid solution. When a weak base is neutralized by a weak acid, the color change of an indicator is so gradual that quantitatively accurate results cannot be obtained.

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

REPORT: Exp. 28

The Equivalent Weight of a Solid Acid, Other Volumetric Analyses

The number of my unknown acid sample is_____

DATA			
Sample Number	*1*	*2*	*3*
Sample vial, 1st weight	g	g	g
2nd weight			
Weight of sample	g	g	g
NaOH burette, 2nd reading	ml	ml	ml
1st reading			
Volume of NaOH	ml	ml	ml
Normality of standard NaOH			*N*

	CALCULATIONS	*1*	*2*	*3*
Equiv of NaOH to titrate the solid acid		equiv	equiv	equiv
Equiv of solid acid in the sample		equiv	equiv	equiv
Weight of one equivalent of solid acid		g	g	g
	Average value			g/equiv

Report your value to the instructor, who will give you the formula of your unknown solid acid . . . . . _____

Calculate your percentage error. (This is a check of your accuracy, in both Exp. 27 and Exp. 28.)

_____%

Problems

Answers

1. 0.613 g of an acid required the addition of 11.70 ml of 0.382 *N* NaOH to neutralize the acid completely. What is the equivalent weight of the acid?

1_____g

2. 1.24 g of a solid basic substance is dissolved in 50.0 ml of water and titrated with 40.2 ml of 0.642 *N* HCl. What is the weight of one equivalent of the basic substance?

2_____g

3. A solid acid has an equivalent weight of 59.0 g. Calculate the weight of a sample of this acid which would be titrated with 45.0 ml of 0.516 *N* NaOH.

3_____g

4. How many ml of 0.643 *N* NaOH are required to titrate 0.784 g of an acid whose equivalent weight is 63.0 g?

4_____ml

5. 0.454 g of an acid of equivalent weight 137 g, requires 39.2 ml of an NaOH solution for titration. What is the normality of the NaOH solution?

5_____*N*

6. 45.0 ml of an NaOH solution required 40.0 ml of a 0.0725 *N* H_2SO_4 solution for titration; 0.462 g of a solid acid required 35.0 ml of the NaOH solution for neutralization. What is the equivalent weight of the solid acid?

6_____g

7. Given a solution of a substance, as indicated in the 1st column, with certain other data given in succeeding columns. From this data calculate the corresponding values to fill in the blank spaces.

Substance	*Formula Weight*	*Equiv Weight*	*Vol (ml)*	*F*	*N*	*No. of gfw*	*No. of Equiv*	*Grams*
HCl	36.5		1500			0.3		
Q $(OH)_2$		29.6			0.2		0.4	
H_3PO_4	98			1				9.8
(X)		50	250	2				100

Exercises on Experimental Errors

(Study Appendix I, Experimental Errors.)

1. Underline the correct answer in the following:

(a) A good analyst

(1) has no need to check his work.

(2) consistently runs checks on important experiments.

(b) A student in titrating ran out of his standardized NaOH solution. To continue the titration, he should

(1) use the 6 *N* NaOH solution from the reagent bottle on the desk as a standard.

(2) borrow a neighboring student's standard NaOH solution.

(3) make up some more NaOH solution and standardize it.

2. Why is the volume in which the solid sample is dissolved not included in your calculations?

3. A number of ways of carrying through the experiment just completed have been suggested by students. Three of the methods suggested are:

(a) One larger quantity of the unknown acid could be weighed. This could be dissolved in water and made up to a known volume, and shaken well. Measured portions of the solution could then be titrated.

(b) The method you have used, to weigh three samples separately and titrate each separately, could be employed.

(c) The weights of the three samples could be added together, and the three volumes of solution added together, thus reducing the calculations to one computation instead of three.

From the above descriptions of the three suggested methods, underline the correct answer in the following:

(1) The method that would best show up any lack in ability to titrate correctly would be:

(a) (b) (c) (None of these)

(2) The method(s) that would best show up any possible error in the student's technique in the entire experiment would be:

(a) (b) (c) (None of these)

(3) The method(s) that would fail to show up any error either in weighing or in titration would be:

(a) (b) (c) (None of these)

4. Underline the correct answer in the following:

(a) A student titrated three 20.00 ml portions of standardized H_2SO_4 solution with his NaOH solution. The volumes of NaOH solution used in the three trials were: 31.85 ml, 31.90 ml, and 31.85 ml. These values indicate a high degree of

(1) accuracy,

(2) precision.

(b) A student determined the value of the equivalent weight of a solid acid as 157.2 grams. The true value was 157.5 grams. This indicates a high degree of

(1) accuracy,

(2) precision.

5. Calculate the percentage error involved in the above case of the solid acid, question 4(b)

_____%

Some Chemical Properties of Chromium and Manganese — 29

College Chemistry, Chapter 29

Review of Fundamental Concepts

Chromium compounds:

		Acidic	Basic	
↑ oxidizing power ↓	+6	$Cr_2O_7^{--}$	CrO_4^{--}	Strong oxidizing agents. Bichromate ion is orange, chromate ion is yellow.
	+3	Cr^{+++}	$Cr(OH)_4^-$	Amphoteric. Chromic ion is green to violet. Chromic hydroxide complex ion is green.
	+2	Cr^{++}		An uncommon ion, because it is such a strong reducing agent that it reduces water to hydrogen gas.
↓ reducing power ↑	0	Cr		The metal.

Manganese compounds:

↑ oxidizing power ↓	+7	MnO_4^-	Permanganate ion, purple. Strong oxidizing agent, reduced to Mn^{++} in acid solution, or to MnO_2 (sometimes to MnO_4^{--}) in neutral or basic solution.
	+6	MnO_4^{--}	Manganate ion, green. Easily reduced to manganese dioxide.
	+4	MnO_2, $MnO(OH)_2$	Brown as precipitated from solution.
	+3	Mn^{+++}, $Mn(OH)_3$	Mn^{+++} is unstable, gives Mn^{++} and MnO_2.
	+2	Mn^{++}	Colorless in solution, pale pink as solid manganous salts. $Mn(OH)_2$ is oxidized by air to $Mn(OH)_3$.
↓ reducing power ↑	0	Mn	The metal.

In the previous experiments on oxidation-reduction, we have seen that during oxidation a substance is changed from a lower oxidation state to a higher oxidation state with the attendant loss of electrons:

$$Cr^{++} \longrightarrow Cr^{+++} + e^- \text{ (an oxidation half-reaction).}$$

During reduction, a substance is changed from a higher oxidation state to a lower oxidation state with the attendant gain of electrons:

$$Mn^{++} + 2e^- \longrightarrow Mn^0 \text{ (a reduction half-reaction).}$$

In order to give you some actual experience with reactions involving changes in oxidation states, we shall consider the chemistry of two of the transition metals, chromium and manganese. These elements are located in the first long period of the periodic table, chromium in Group VI and manganese in Group VII. They are capable of forming bipositive and terpositive ions as typical metals do, and, in addition, tend to coordinate with oxygen to form oxides or negative complex ions in which they have higher oxidation states.

Before beginning the experiment, the student should acquaint himself with the principal oxidation states of chromium and manganese and with the formulas, names, and colors of the ions or compounds which exist. This information may be found in *College Chemistry* and also in the charts above. Since most of the reactions which will be observed are concerned with changes in oxidation states, the student should also review the methods available for balancing oxidation-reduction reactions.

Experimental Procedure

Chemicals: chromium metal, manganese metal (small chips). CrO_3, MnO_2, $(NH_4)_2Cr_2O_7$, KOH, $KClO_3$, Na_2SO_3, $NaBiO_3$, $KMnO_4$, powdered Zn, $FeSO_4 \cdot 7H_2O$, 0.1 *F* $Mn(NO_3)_2$, 0.1 *F* $Cr(NO_3)_3$, 2 *F* Na_2S, 0.1 *F* $BaCl_2$, 0.1 *F* $HgCl_2$, 0.1 *F* $CuSO_4$, 0.1 *F* KBr, 0.1 *F* KI, 1.0 *F* K_2CrO_4, H_2O_2 3% solution, Cl_2 water, CCl_4.

The Chemistry of Chromium

1. ***Oxidation State Cr^0; Properties of Metallic Chromium.***

Select a small piece of metallic chromium about the size of the head of a pin. Note some of its physical properties and also refer to the text for additional characteristics. List these on the record sheet.

Determine the relative activity of the metal by performing the following experiments. Cover the metal with about 1 ml of 6 *F* HNO_3 in a 10-cm test

tube. Warm the test tube gently and watch for any reaction.

Pour off the dilute nitric acid and wash the metal several times with water. Decant the wash water and add about 3 ml of 6 *F* HCl. Warm gently for several minutes, tap the tube, and watch for the rather sudden beginning of a reaction. Test the gas evolved for inflammability. The colored ion first formed is the chromous ion, but this is readily oxidized to chromic ion by exposure to air. The green chromic ion formed is quite probably a coordination complex which includes one or two chlorides substituted for some of the water molecules in the hydrated complex ion.

Pour off the green solution and save it for Part 2. Wash the remaining piece of metal with water several times. Cover it with distilled water and warm it to see if chromium will replace hydrogen from cold or hot water. (See Appendix II, Table VIII.)

2. *Oxidation State +2; The Chromous Ion*

Add a small amount of powdered zinc to the hydrochloric acid solution of chromium obtained above. Warm it gently if necessary to initiate the reaction, then stopper it with a loose plug of cotton. After the reaction has proceeded for several minutes, withdraw some of the solution and add it quickly to a test tube containing 2 or 3 ml of 0.1 *F* $HgCl_2$. Observe carefully the product which is formed. Add another portion of the solution containing the chromous ion to a test tube containing 2 or 3 ml of 1.0 *F* $CuSO_4$ and observe the result.

When metallic chromium is dissolved in dilute sulfuric acid, the chromous ion first formed is not so readily oxidized as it is in the hydrochloric acid solution, and a blue solution containing some chromous ion results. In order to dissolve chromium in sulfuric acid, it is usually necessary first to remove the "oxide film" with dilute HCl. After the metal has started to react with the HCl, it should be washed off with several portions of water and then covered with 5 ml of 3 *F* H_2SO_4. Warm the test tube, if necessary. Test the blue solution obtained for chromous ion by adding portions of it to solutions of $HgCl_2$ and $CuSO_4$ as directed in the preceding paragraph.

Summarize your results by writing equations for the reactions and make a statement concerning the properties of the chromous ion.

3. *Oxidation State +3; The Chromic Ion and Chromic Oxide.*

The chromic ion, Cr^{+++}, forms many types of coordination complexes involving water, chloride ions, or hydroxide ions whose colors vary from violet to green. Note the color of the stock solution of 0.1 *F* $Cr(NO_3)_3$ and compare it with the color of the chromic chloride solution you prepared in Part 1. How do you account for the difference?

To 3 ml of 0.1 *F* chromic nitrate, add 6 *F* NH_4OH drop by drop and observe the precipitate formed. Add more NH_4OH to determine whether this precipitate is soluble in excess ammonia solution. Does the chromic ion form a stable complex in which ammonia molecules are coordinated? (Text, Chap. 22, Table 22-1.)

To 3 ml of 0.1 *F* chromic nitrate, add 6 *F* NaOH drop by drop until a precipitate is formed. How does it compare with the one formed with NH_4OH? Now add several drops more of NaOH until the precipitate disappears. What ion of chromium is now present in the solution? What is the name given to hydroxides or oxides which dissolve either in acids to form cations, or in bases to form anions, as nonmetals do? Write equations for the reactions.

To the solution obtained above with excess NaOH, add 3% hydrogen peroxide solution drop by drop until a color change is noted. What new ion is formed by the oxidation of chromite ion in an alkaline solution? Write a balanced equation for the reaction.

As an illustration of a change in oxidation state which is just the reverse of that in the previous paragraph, place a small, conical pile of powdered ammonium dichromate (about 1 cm high) in a small evaporating dish and ignite it by touching the tip of the cone with a small Bunsen flame. What is the powder which is formed? What are its commercial uses? Write an equation for the reaction.

4. *Oxidation State +6; Chromium Trioxide, Chromates, Dichromates.*

Place about 0.1 g of CrO_3 in a 10-cm test tube and add about 5 ml of water. Test the solution

formed with litmus paper. Is CrO_3 the anhydride of an acid or a base? Is your answer in conformity with the general rules about the acidic and basic properties of metallic oxides and the oxidation state of the metal? Write an equation for the reaction. Is this an oxidation-reduction reaction? Why?

Add 6 *F* NaOH drop by drop to the solution just obtained until there is a color change. What new ion is now present? Write the equation for this reaction. Now add 6 *F* HCl drop by drop until the color changes again. What ion is now present? How is this reaction related to the one just written?

Add 10 drops of 1.0 *F* K_2CrO_4 to 5 ml of water and then add several drops of 0.1 *F* $BaCl_2$. Write the equation for this reaction. Repeat the experiment, but this time add 5 drops of 6 *F* HCl to the diluted chromate solution before adding the barium ion. How do you explain the difference in the result obtained this time? Now add 5 to 10 drops of 6 *F* NaOH to the last test and note the result obtained. How does this series of experiments illustrate the principle of Le Chatelier?

The dichromate ion in acid solution is a relatively good oxidizing agent. (Appendix II, Table XIII.) To illustrate this property, add 1 ml of 1.0 *F* K_2CrO_4 and 1 ml of 3 *F* H_2SO_4 to 5 ml of water and add a few crystals of $FeSO_4 \cdot 7H_2O$. Repeat the experiment, this time using a small amount of solid Na_2SO_3 instead of $FeSO_4$ as the reducing agent. Write the oxidation half-reaction and the reduction half-reactions separately. How many electrons per mole are gained by the dichromate ion when it is reduced?

Add 1 ml of 1.0 *F* K_2CrO_4 and 1 ml of 3 *F* H_2SO_4 to 5 ml of water and then add some 3% H_2O_2 drop by drop. The color formed is thought to be due to a peroxychromic acid whose exact formula is uncertain. This constitutes a rather useful test for the dichromate ion.

The Chemistry of Manganese

1. *Oxidation State Mn^0; Properties of Metallic Manganese.*

Select a small piece of metallic manganese about the side of the head of a pin. Note some of its physical properties and also refer to the text for additional characteristics. List these on the record sheet.

Determine the relative activity of the metal by performing the following experiments. Place the piece of metal in a 10-cm test tube and add about 5 ml of 6 *F* HCl. Note the relative vigor of the reaction and test the gas evolved for inflammability. Write the equation for the reaction.

Pour off the hydrochloric acid, and wash the remaining piece of metal with several portions of water. Cover the metal with distilled water and watch carefully for any reaction of manganese with cold water. Warm the test tube gently and note any difference in the rate of reaction. Write the equation for this reaction.

Pour off the water and add 5 ml of 6 *F* HNO_3. Is manganese passive in this acid?

2. *Oxidation State +2; The Manganous Ion.*

To 3 ml of 0.1 *F* $Mn(NO_3)_2$, add a drop of 2 *F* Na_2S. Note the color of the precipitate and write the equation for the reaction.

Add about 5 drops of 6 *F* NaOH to 3 ml of 0.1 *F* $Mn(NO_3)_2$ and note the color of the precipitate as it is first formed. Note also the darkening of the precipitate at the surface of the suspension. Now add an excess of NaOH to determine whether the precipitate is amphoteric. Write equation for the initial reaction and explain why the precipitate darkens.

To 5 drops of 0.1 *F* $Mn(NO_3)_2$ in 5 ml of water, add 1 ml of 6 *F* HNO_3 and a small amount of solid sodium bismuthate ($NaBiO_3$). The pink color produced is due to the MnO_4^- ion. Refer to Appendix II, Table XIII and note the relative positions of the Mn^{++}—MnO_4^- (H^+) couple and the Bi^{+++}—BiO_3^- (H^+) couple. (The latter couple is listed as BiO^+—Bi_2O_5(H^+).) Write the half-reactions involved in this experiment and combine them into a single, balanced equation.

3. *Oxidation State +3; The Manganic Ion, MnO(OH).*

The brown manganic compound, MnO(OH), which was formed by the oxidation of $Mn(OH)_2$, in Part 2, and the oxide Mn_2O_3 are the only relatively stable compounds containing Mn in the oxidation state, Mn^{+3}. Other salts are unimportant or unstable, and will not be considered.

4. *Oxidation State +4; Manganese Dioxide, MnO_2.*

Manganese dioxide, which constitutes the main source of manganese in nature, is the only important compound of quadri-positive manganese. It may be reduced by carbon to produce the metal. It may serve as an oxidizing agent, in which case it is reduced to manganous ion.

Place a small amount of powdered MnO_2 (about one-fourth the size of a pea) in the bottom of a 10-cm test tube. Add about 5 ml of 12 *F* HCl and cautiously observe the product of the reaction. Write the equation.

To another test tube containing a small amount of MnO_2 add about 5 ml of 0.1 *F* KBr and acidify with 1 ml of 18 *F* H_2SO_4. Warm gently if necessary to initiate the reaction. Then cool, and add 1 ml of CCl_4. Shake, and note the color of the CCl_4 phase. Write the equation for the reaction.

Repeat the experiment using 5 ml of 0.1 *F* KI instead of the KBr solution. Identify the product and write the equation for the reaction.

Cover a very small amount of MnO_2 with about 3 ml of distilled water which is acidified with 1 ml of 6 *F* HNO_3. Now add some 3% H_2O_2 solution, about a ml at a time and warm gently until the MnO_2 has disappeared. In this instance, hydrogen peroxide is acting as a reducing agent in the acid solution, and manganous ion and oxygen are the products of the reaction. (See Fig. 42-1 in this manual for a chart relating the oxidation states of manganese and the action of H_2O_2 in solutions of different acidity or basicity.) Write the balanced equation for the reaction.

5. *Oxidation State +6; The Manganate Ion, MnO_4^{--}.*

Put approximately 3 g of solid KOH and 2 g of $KClO_3$ in a crucible, which is placed in a triangle on an iron ring. Heat the mixture gently until it fuses, then add slowly from a spatula about 2.5 grams of powdered MnO_2. Keep the mixture fused for several minutes; then allow it to cool. Put the cold crucible into a 250-ml beaker and cover it with distilled water. Write the balanced equation for the reaction.

The manganate ion is stable in the alkaline solution, but upon acidification, undergoes auto-oxidation-reduction to the +7 and +4 oxidation states. Decant some of the green solution obtained above and acidify 5 ml of it with several drops of 3 *F* H_2SO_4. Observe the products of this reaction. Now make this same solution basic again by adding several drops of 6 *F* NaOH. Note the change in color. Write the equation for the reversible reaction which is involved here and explain the changes observed on the basis of the principle of Le Chatelier.

To another 5-ml portion of the green manganate solution, add about 2 ml of chlorine water, and note the results. Write the equation for this reaction.

6. *Oxidation State +7; The Permanganate Ion, MnO_4^-.*

Potassium permanganate is probably the most important compound of manganese, since it is one of the stronger oxidizing agents and is very convenient in analytical determinations where volumetric oxidation-reduction reactions can be used. (See Exp. 30, in which you will determine the amount of a reducing agent by titration with a standard $KMnO_4$ solution.)

Prepare an approximately 0.01 *F* solution of $KMnO_4$ by dissolving approximately 0.15 g of $KMnO_4$ in 100 ml of distilled water. Place about 3 ml of this solution into each of four test tubes. Acidify the first with 1 ml of 3 *F* H_2SO_4, add 2 drops of 6 *F* NaOH to the second, add 3 ml of 6 *F* NaOH to the third, and leave the fourth neutral. Now, with a spatula, add a small amount of a reducing agent such as sodium sulfite (Na_2SO_3) to each of the test tubes and observe the color produced in each case. Write the equations for the reactions. How many electrons per mole are gained by the permanganate ion when it is reduced in an acid solution? How many per mole in a slightly basic solution? How many per mole in a strongly basic solution?

REPORT: Exp. 29

Some Chemical Properties of Chromium and Manganese

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

The Chemistry of Chromium

1. Physical properties of Cr^0_____

Behavior with dil. HCl_____

Reaction_____

Behavior with dil. HNO_3_____

Explanation_____

Behavior with water_____

Statement concerning activity of Cr^0_____

2. Reactions by which the Cr^{++} may be produced:

Zn^0 and Cr^{+++}_____

Cr^0 and H^+ (H_2SO_4)_____

Reactions of the chromous ion:

With $HgCl_2$_____

With $CuSO_4$_____

Summary of properties of Cr^{++} ion_____

3. Color and formula of the chromic ion in solutions of:

Chromic chloride_____

Chromic nitrate_____

Reactions of the chromic ion:

With dil. NH_4OH_____

With excess NH_4OH_____ Explanation_____

With dil. NaOH_____

With excess NaOH_____

Explanation_____

Action of H_2O_2 on chromite ion in basic solution

Oxidation half-reaction_____

Reduction half-reaction_____

Balanced net reaction_____

Products of the decomposition of ammonium dichromate: _____

Reaction _____

l. Litmus test water solution of CrO_3 _____ Type anhydride _____

Reaction _____

Is reaction oxid.-red.? _____ Why? _____

Effect of NaOH on color of solution _____ Ion formed _____

Reaction _____

Effect of HCl on above solution color _____ Ion formed _____

Reaction _____

Color and formula of reaction product formed when Ba^{++} is added to aqueous K_2CrO_4 _____

Acid K_2CrO_4 _____. Basic K_2CrO_4 _____

Explanation of the above series of reversible reactions in terms of the principle of Le Chatelier _____

_____

Oxidizing properties of $Cr_2O_7^{--}$ in acid solution:

With ferrous sulfate; half-reactions:

Oxidation: _____

Reduction _____

Balanced net reaction _____

With sodium sulfite; half-reactions:

Oxidation _____

Reduction _____

Balanced net reaction _____

Observed result of effect of H_2O_2 on acid $Cr_2O_7^{--}$ _____

:hemistry of Manganese

Physical properties of Mn^0 _____

Behavior with dil. HCl _____

Reaction _____

Behavior with cold water _____. With hot water _____

Reaction _____

Behavior with dil. HNO_3 _____ Is Mn^0 passive? _____

Reactions of the manganous ion:

With Na_2S _____

Color of precipitate formed _____

With NaOH _____

Color of initial precipitate formed _____

Effect of excess NaOH _____. Conclusion _____

Explanation of darkening of precipitate _____

_____ Formula _____

Oxidation of Mn^{++} by $NaBiO_3$ in acid solution; half-reactions:

Oxidation_____

Reduction_____

Balanced net reaction_____

3. Formulas of stable compounds of manganic ion._____

4. MnO_2 as an oxidizing agent in acid solution:

Reaction with HCl_____

Reaction with Br^-_____

Reaction with I^-_____

Reaction with H_2O_2; balance using half-reactions:

Oxidation_____

Reduction_____

Balanced net reaction:_____

5. Preparation of the manganate ion by oxidation of MnO_2 with $KClO_3$ in KOH.

Reaction_____

Change noted when MnO_4^{--} was acidified_____

Reaction_____

Change when solution is made basic again_____

Reaction_____

Explanation of latter two reversible reactions in terms of the principle of Le Chatelier_____

_____

Reaction of chlorine water with manganate ion:

_____

6. The reduction of permanganate ion in solutions of different acidity or basicity: Write reduction half-reactions.

In acid solution_____

In neutral solution_____

In weakly basic solution_____

In strongly basic solution_____

Titrations Involving Oxidizing and Reducing Agents — 30

College Chemistry, Chapters 29, 12

Review of Fundamental Concepts

The Equivalent Weight in Oxidation-Reduction Processes

The equivalent weight of a substance undergoing oxidation or reduction is the same as the "chemical equivalent" which was discussed in the section on Faraday's Law, Experiment 19. Study this section again. We may calculate the equivalent weight of an oxidizing or reducing agent by dividing its formula weight by the number of electrons gained or lost, as indicated by the half-reaction equation for the process taking place. For example, if potassium bichromate ($K_2Cr_2O_7$) is used to oxidize ferrous sulfate ($FeSO_4 \cdot 7H_2O$) to ferric sulfate, the half-reactions are

$$Cr_2O_7^{--} + 14\,H^+ + 6\,e^- \longrightarrow 7\,H_2O + 2\,Cr^{+++},$$
$$Fe^{++} \longrightarrow Fe^{+++} + 1\,e^-,$$

and the corresponding weights are

Formula weights:

$K_2Cr_2O_7 = 294.22$ $\quad$ $FeSO_4 \cdot 7H_2O = 278.01$

Equivalent weights:

$$\frac{K_2Cr_2O_7}{6} = 49.04 \qquad \frac{FeSO_4 \cdot 7H_2O}{1} = 278.01.$$

Note that we have used the formula weight of the salt, rather than simply of the ion taking part in the reaction, since if one wished to weigh the substances, he would use the solid salts.

Normal Solutions

A normal oxidizing solution, or a normal reducing solution, is one which contains one equivalent (defined as above) per liter of solution.

Indicators

Indicators for oxidation-reduction titrations have not been developed as extensively as they have for acid-base titrations. In principle, they would need to be substances which undergo a color change when they are oxidized or reduced, and of such a nature that their oxidation-reduction potential is in the proper range for the particular titration being performed. In many cases, as in the present experiment, the substance being titrated undergoes a sufficiently sharp color change so that no other indicator is needed.

Volumetric Oxidation-Reduction Processes

In this experiment, we shall prepare a potassium permanganate solution by weighing out approximately the weight desired and dissolving this in the requisite amount of water. This solution will be standardized by titrating it against a sodium oxalate solution of known concentration. Finally, the equivalent weight of an unknown reducing substance will be determined by weighing out small portions and titrating these with the standard potassium permanganate solution.

You may perform an additional optional experiment, if time permits, by determining the amount of calcium in the laboratory tap water. This is done by precipitating the calcium as calcium oxalate (CaC_2O_4), filtering, and dissolving this in dilute sulfuric acid, and titrating against standard potassium permanganate.

Experimental Procedure

Special supplies: 2 burettes, analytical weights.
Chemicals: $KMnO_4$, a standard $Na_2C_2O_4$ solution, 0.5 *F* $H_2C_2O_4$, vials of unknown reducing substances.

1. Standard Potassium Permanganate Solution. Calculate the weight of $KMnO_4$ needed to make up 500 ml of an approximately 0.02 *F* $KMnO_4$ solution. After approval of your calculation, weigh just this amount on the triple beam balance to 0.02 g, dissolve in about 100 ml of boiling distilled water, cool, and dilute to 500 ml with distilled water. The solution cannot be made up to an exact standard due to impurities present. A graduated cylinder is, therefore, sufficiently accurate in measuring these volumes. Mix the solution well by pouring from one container to another several times; place in a clean labeled bottle.

Now standardize this solution by titration against a standard sodium oxalate solution (containing 6.5 to 7.0 g/l), provided by the instructor. He will report to you the exact weight, in grams, of sodium oxalate, $Na_2C_2O_4$, per liter, from which you may calculate the normality of the solution as a reducing agent. Carry out the titration as follows. Fill two clean burettes with the sodium oxalate and potassium permanganate solutions, respectively, having first rinsed each burette with a little of the solution. Into a clean 250-ml Erlenmeyer flask put about 50 to 75 ml of distilled water and 30 ml of 3 *F* H_2SO_4. Now run in about 20 ml of the sodium oxalate solution, heat the contents of the flask almost to boiling, and titrate this, while hot, with the potassium permanganate solution, to the first permanent faint pink color which remains after stirring.[1] At least three titrations should be performed, or until concordant results are obtained.

The oxalate ion, $C_2O_4^{--}$, is oxidized to CO_2 g Write the half-reaction equation for this proc calculate the equivalent weight of $Na_2C_2O_4$ and t normality of the standard sodium oxalate solutio you used. You can then calculate the normality, as an oxidizing agent, of your potassium permanganate solution, based on the inverse relationship between normality and volume, i.e. $V_1N_1 = V_2N_2$. From this normality, and the fact that your solution was made up to be about 0.02 *F*, calculate the number of equivalents per formula weight of $KMnO_4$ in this reaction. Verify this relationship by writing the half-reaction equation for the reduction of MnO_4^- (Mn^{++} is formed) in acid solution. Now write the net ionic equation for the whole oxidation-reduction process.

2. The Equivalent Weight of an Unknown Solid Reducing Agent. Obtain from the stockroom a vial of unknown reducing agent. Record the number on your report sheet. Using this vial as a weighing bottle, weigh out approximately 0.2 g samples to 0.001 g into 400 or 500-ml beakers or flasks, as you did with the $Na_2C_2O_4$. Add 75 ml of distilled water, 30 ml of 3 *F* H_2SO_4, heat to boiling, and titrate as before with your $KMnO_4$. Calculate the equivalent weight of your sample, and report the value at once to your instructor.

3. Calcium in Tap Water. (Optional.) The hardness of water is due largely to the presence of calcium and magnesium salts. Using a graduate, measure a 250-ml portion of water to be examined, and place in a 400-ml beaker. Add 1 ml of 6 *F* HCl and evaporate to a volume of about 50 ml. Add 2 drops of methyl orange indicator, and then ammonium hydroxide drop by drop until the acid is neutralized. If a precipitate appears, just dissolve it by adding a drop or so of dilute HCl. The solutio will now be faintly acid. Heat to boiling and owly about 25 to 30 ml of 0.5 *F* oxalic acid ion. Make alkaline with NH_4OH, boil for a w minutes, and allow the precipitate to settle.

Filter the precipitated CaC_2O_4. If the filtrate is not clear, heat it again and let it stand longer to coagulate into coarser particles. Wash the filte paper repeatedly with a stream of water from your wash bottle, until 20 ml of the wash water will not decolorize a drop of 0.1 *N* $KMnO_4$. Puncture the tip of the filter paper, place a 400-ml beaker under the funnel, and pour about 50 ml of 1 *F* H_2SO_4 in a very gentle stream all over the surface of the paper, to dissolve the precipitate. Rinse the filter with 50 ml of hot water, adding it in small portions. Heat the solution in the beaker to boiling and titrate with your standardized $KMnO_4$ solution. Write equations for the reactions taking place, and calculate the relationship between moles of Ca^{++} present and equivalents of $KMnO_4$ used. Report your results in parts per million, which is the customary manner of reporting water analyses. (Parts per million is the same as milligrams per liter.) Prepare your own report form for this part of the experiment, showing equations, data, and calculated values in a neat, orderly arrangement.

[1] A delay in the decolorization of the potassium permanganate color at the start of the titration is due to an interesting autocatalytic effect. Until a sufficient amount of manganous ion (Mn^{++}) has been formed to catalyze the reaction, the rate is very slow.

REPORT: Exp. 30

Titrations Involving Oxidizing and Reducing Agents

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

I. Standard Potassium Permanganate Solution

Calculated weight of $KMnO_4$ required for 500 ml of 0.02 *F* solution: _____ g

Weight of $Na_2C_2O_4$ per liter, in standard solution used, as reported by the instructor . . . . . _____ g

DATA	*1*	*2*	*3*
$Na_2C_2O_4$ burette, 2nd reading	ml	ml	ml
1st reading			
Volume of $Na_2C_2O_4$ solution used	ml	ml	ml
$KMnO_4$ burette, 2nd reading	ml	ml	ml
1st reading			
Volume of $KMnO_4$ solution used	ml	ml	ml

Write the half-reaction equation for the oxidation of oxalate ion, $C_2O_4^{--}$, to carbon dioxide gas:

_____

Calculate the equivalent weight of $Na_2C_2O_4$ and the normality of the $Na_2C_2O_4$ solution, based on this equation and on the grams per liter:

_____ g/equiv

_____ N

	CALCULATIONS	*1*	*2*	*3*
Normality of $KMnO_4$		*N*	*N*	*N*
		Average value		*N*

From this normality of the $KMnO_4$ and the approximate formality (0.02 *F*) as the solution was prepared, calculate the number of equivalents per formula weight of $KMnO_4$, in this reaction:

_____ equiv per gfw

Verify this by writing the half-reaction equation for the reduction of MnO_4^- to Mn^{++}:

_____

Combine the two half-reactions to give the net ionic equation for the reaction of permanganate ion with oxalate ion in acid solution:

_____

2. The Equivalent Weight of an Unknown Solid Reducing Agent

Number of unknown sample_____

DATA	*1*	*2*	*3*
Initial weight, vial + unknown			
Final weight, vial + unknown			
Weight of unknown			
Final burette reading ($KMnO_4$)			
Initial burette reading			
Volume of .....*N* $KMnO_4$ used			

CALCULATIONS		*1*	*2*	*3*
Equivalents of $KMnO_4$ (and of unknown) in the sample titrated				
Weight of one equivalent of unknown				
	Average value.....g/equiv			

Instructor's report: Your unknown is_____

Percent error _____

3. Calcium in Tap Water (Optional)

Prepare your own report form for this part of the experiment, showing equations, data, and calculated values in a neat, orderly arrangement.

 *Name*_____

Application of Principles

Answers

1. What is the equivalent weight of the following:

   a) $K_2Cr_2O_7$ (reduced to Cr^{+++}) . . . . . _____

   b) Na_2SO_3 (oxidized to a sulfate) . . . . . _____

   c) $KClO_3$ (reduced to a chloride) . . . . . _____

2. Two formula weights of an acid solution of ferric chloride are mixed with a solution containing four formula weights of sodium iodide. How many moles, and grams, of iodine, I_2, will be produced?

   _____ mol

   _____

3. What substances are present, and if in solution at what concentration, in the following:

   a) one formula weight each of stannous chloride and of ferric chloride are mixed in water to make ten liters of solution. (First write the equation.)

   _____

   _____

   _____

   _____

   b) 0.5 mole of chlorine gas, Cl_2, is passed into one liter of a solution containing one formula weight each of potassium iodide and of potassium bromide.

   _____

   _____

   _____

   _____

Some Elementary Experiments in Organic Chemistry

31

College Chemistry, Chapters 30, 7

Review of Fundamental Concepts

Organic chemistry is concerned with the chemistry of the compounds of carbon. In the early history of chemistry it was thought that these naturally-occurring compounds could not be made in the laboratory but required the vital influence of the living organism, hence the name "Organic" was applied to this class of compounds.

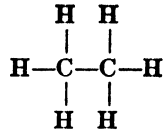
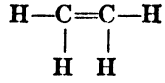
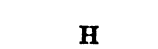
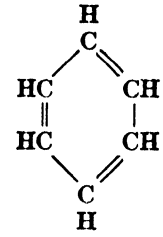
The element carbon has four valence electrons and when it combines with other elements it shares its electrons and forms four covalent bonds. The elements usually combined with carbon are: hydrogen, oxygen, and nitrogen, and less frequently, sulfur, phosphorus, and the halogens. Since carbon atoms have a great tendency to combine with other carbon atoms to form ring structures or chains of carbon atoms, very complex molecules of high molecular weight are possible. The great variety of structural arrangements which result makes possible the existence of virtually an infinite number of different compounds. To date nearly a half-million organic compounds have been isolated from natural sources or have been synthesized in the laboratory.

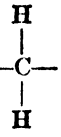
One of the simplifying principles which helps to systematize the study of organic chemistry is the fact that organic compounds may be classified into different types, according to the nature of the functional group present. For instance, the groups $-OH$, $-CHO$, or $-COOH$ each impart a characteristic reactivity to the molecules containing such a group. All alcohols contain the $-OH$ group in addition to the carbon-hydrogen portion of the molecule as is seen by the following illustrations: methyl alcohol is CH_3OH, ethyl alcohol is C_2H_5OH and amyl alcohol is $C_5H_{11}OH$. The general formula, ROH, is assigned to all alcohols containing one hydroxyl group. The letter R stands for the carbon-hydrogen radical to which the functional group is attached.

A summary of some of the types of organic compounds, together with their general formulas and a common illustration is given below.

Alcohol	R—OH	Methyl alcohol	CH_3OH
Ether	R—O—R	Diethyl ether	$(C_2H_5)_2O$
Aldehyde	$R-\overset{H}{\overset{\vert}{C}}=O$	Formaldehyde	HCHO
Ketone	$R-\overset{O}{\overset{\Vert}{C}}-R$	Acetone	$(CH_3)_2CO$
Acid	$R-\overset{O}{\overset{\Vert}{C}}-OH$	Acetic acid	CH_3COOH
Ester	$R-\overset{O}{\overset{\Vert}{C}}-OR$	Ethyl acetate	$CH_3COOC_2H_5$
Amine	$R-NH_2$	Butyl amine	$C_4H_9NH_2$
Amino acid	$R-\overset{H}{\overset{\vert}{C}}(\overset{NH_2}{\vert})-\overset{O}{\overset{\Vert}{C}}-OH$	Glycine	$CH_2(NH_2)COOH$

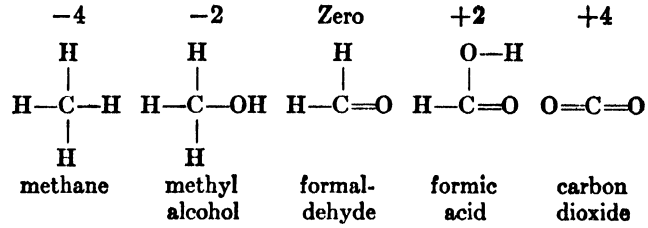
Compounds containing only carbon and hydrogen are called hydrocarbons and are generally classified into two series. The aliphatic series contains the carbon atoms linked together in open chains, while in the aromatic series the carbon atoms are linked together to form closed rings. In the aliphatic series, the hydrocarbon is said to be saturated when all four carbon valences are being satisfied by other carbon or hydrogen atoms. Compounds formed when there are two or more hydrogen atoms less than that required for saturation of the carbon valences are called **unsaturated compounds.** Some illustrations of the various types of hydrocarbons are given below.

Paraffin series (saturated)	C_nH_{2n+2}	Ethane	
Ethylene series (unsaturated)	C_nH_{2n}	Ethylene	
Acetylene series (unsaturated)	C_nH_{2n-2}	Acetylene	
Aromatic series (cyclic, unsaturated)	C_nH_{2n-6}	Benzene	

By adding  units to increase the length of the open chain compounds or to substitute in the side chain it is possible to obtain a very great number of hydrocarbons. In the paraffin series, for example, the gases CH_4, C_2H_6, C_3H_8, C_4H_{10} continue up the homologous series by CH_2 increments to the liquids C_5H_{12}, C_6H_{14} ..... $C_{16}H_{34}$ until finally solid paraffins with as high as 60 or more atoms of carbon per molecule have been reported.

The alcohols, aldehydes, acids, and other types of compounds mentioned before, may be considered to be derivatives of the hydrocarbons in which the functional group or groups have replaced one or more of the hydrogen atoms in the hydrocarbon.

As hydrogen atoms are successively replaced by oxygen atoms, the oxidation number of the carbon atom substituted increases as shown below for the simplest hydrocarbon.



Thus, when methane undergoes complete combustion the carbon atom changes from the −4 to the +4 oxidation state. When methanol undergoes mild oxidation, formaldehyde may be the resulting product, whereas more strenuous oxidation conditions may produce formic acid or carbon dioxide.

Reactions between covalent organic molecules generally take place rather slowly in contrast with the rapid reactions which characterize ionic inorganic compounds. For instance, when an alcohol and organic acid react to form an ester, very little reaction takes place until the mixture is heated for some time in the presence of a dehydrating agent to remove the water formed and shift the equilibrium to the right as in the following equation:

$$R'\text{—}OH + R\text{—}COOH \overset{(H_2SO_4)}{\rightleftarrows} H_2O + R\text{—}COOR'.$$

In the experiments which follow, we shall attempt to survey some of the properties of the various types of hydrocarbons and their derivatives. We shall also illustrate the relative reactivity of some organic compounds.

Experimental Procedure

Chemicals: CaC_2, kerosene, paraffin, benzene, naphthalene, methyl alcohol, ethyl alcohol, amyl alcohol, formaldehyde solution, Br_2 in CCl_4, Cu wire, soda lime, $NaC_2H_3O_2$, salicylic acid, potassium dichromate, CCl_4, 0.1 *F* $AgNO_3$, glacial acetic acid.

1. Properties of Some Hydrocarbons

(a) *Saturated Hydrocarbons, Methane or Paraffin Series.* Using the natural gas supply in the laboratory as a source of methane and ethane, bubble some of the gas slowly through 3 ml of Br_2 solution in CCl_4 for several minutes. Is the bromine decolorized? Collect a test tube of the gas by displacement of water. Is the gas soluble in water? Ignite the gas in the test tube and note the flame produced. Put 1 ml of limewater into the test tube and shake it with the products of combustion. What gaseous product does this test indicate is present? Write the equation for the combustion of ethane in an excess of oxygen.

What are the molecular formulas of the hydrocarbons present in gasoline and in kerosene? Test 3 ml of kerosene with 1 ml of the Br_2 in CCl_4 solution to determine whether there are present any unsaturated compounds which would "add on" the Br_2 and decolorize the reagent. Note also whether the kerosene is miscible with the CCl_4. Place about 5 drops of kerosene in a watch glass and ignite it

with a small flame. Note the type of flame produced.

Place a small fragment of paraffin the size of a small pea in a test tube and add 3 ml of the Br_2 in CCl_4 solution. Does the paraffin dissolve in the CCl_4? Is the bromine decolorized? Ignite a small piece of paraffin on a watch glass. Does it have a high ignition temperature? If you have any difficulty igniting it place a small piece of string in the melted paraffin and use it as a wick. Note the flame produced.

(b) *Unsaturated Hydrocarbons, Open Chain Type.* Of the many types possible here we shall use acetylene, C_2H_2, with the structure, H—C≡C—H, as an illustration of this type compound. Set up the small generator shown in Fig. 22-2 and place a small lump of calcium carbide, CaC_2, in the dry test tube. Draw in a few milliliters of water into the dropper tube. Collect a 15-cm test tube of acetylene by the displacement of water. Allow the rest of the gas generated to bubble through about 3 ml of the Br_2 solution in CCl_4. *Caution:* acetylene is explosive when mixed with air in the proper proportions, so keep the generator away from open flames. When the generator has become inactive, test the combustibility of the tube of acetylene you have collected, taking the precaution to wrap the test tube with a towel before holding its mouth to the flame. How did the flame compare with that produced when methane burned?

(c) *Aromatic Hydrocarbons, Benzene, Naphthalene.* Test 3 ml of benezene with 1 ml of the solution of Br_2 in CCl_4. Is the benzene miscible with the CCl_4? Is the Br_2 solution decolorized? Ignite about 5 drops of benzene on a watch glass, and note the type of flame produced.

Repeat the above tests using a small amount of naphthalene about the size of a pea. What is the structure of the napthalene molecule?

2. Alcohols, R—OH. Write the structural formula for the following alcohols: methyl alcohol, ethyl alcohol, and amyl alcohol. Place 1 ml of each of these alcohols into separate test tubes and note their odor. Add 1 ml of water to each to determine the solubility in a polar solvent. Repeat the solubility test using the nonpolar solvent, CCl_4. Did the length of the hydrocarbon chain have any effect on the solubility tests you observed? What could you predict about the solubility of glycerol, a trihydroxy alcohol with the formula $C_3H_5(OH)_3$, in water and in a hydrocarbon? Answer the same question for the alcohol $C_{16}H_{33}OH$.

3. Aldehydes, R—CHO. Write the structural formula for formaldehyde. What is the oxidation number of the carbon atom in an aldehyde? What compound would be produced when formaldehyde is oxidized to the next higher oxidation state? The Fehling test for aldehydes consists in the oxidation of an aldehyde by the use of an alkaline solution containing the cupric-tartrate complex ion. The latter oxidizing agent is thereby reduced to the insoluble cuprous oxide, Cu_2O. Perform this test as follows: Mix 5 drops of each of the Fehling solutions, A and B, with one ml of water. Warm to 60° C in a water bath and add a few drops of the formaldehyde solution. Note the character of the precipitate formed. This test is also used to detect the presence of a reducing aldehyde group which is one of the characteristic groups of certain sugars.

Make a spiral of copper wire by inserting a 10-inch piece of medium gauge copper wire into a cork to serve as a handle and wind the other end around a glass rod to make a spiral. Place 1 ml of methyl alcohol in a small test tube. Heat the spiral to red heat in a flame and plunge it into the methyl alcohol. Repeat this procedure several times. Can you recognize the odor in the test tube? Note that the wire becomes dark when oxidized in the flame but turns bright again when dipped in the alcohol. Write the equation for the reaction for the oxidation of CH_3OH by CuO.

4. Organic Acids, R—COOH. Organic acids may be prepared from their salts by adding a nonvolatile acid and distilling over the volatile acids. Place about 1 g of $NaC_2H_3O_2$ in a test tube and add 1 ml of 18 *F* H_2SO_4 and warm gently. Note cautiously the odor of the vapors and their effect on moistened neutral litmus paper. Is oxidation-reduction involved here? What is the oxidation state of the carbon atom in the carboxyl group, —COOH?

Write the structural formulas of ethyl alcohol, the aldehyde, and the acid which would be produced by the oxidation of the alcohol. Dissolve 1 g of $K_2Cr_2O_7$ in 5 ml of 3 *F* H_2SO_4. Add 5 drops of ethyl alcohol cautiously. Note the change in color of the oxidizing agent. Note the odor of the vapors, cautiously. A pearlike odor indicates the presence

of acetaldehyde. Now warm the tube gently and test the vapors with moistened neutral litmus paper for any acid vapors. To what is the green color of the solution due? Write the balanced oxidation-reduction equations for this reaction either to the formation of the aldehyde or to the acid.

5. Esters, R—COOR′. Esters are produced by the reaction of organic acids and alcohols in the presence of concentrated sulfuric acid.

Prepare some ethyl acetate by warming gently a mixture of 1 ml ethyl alcohol, 1 ml glacial acetic acid and 10 drops of 18 *F* H_2SO_4. After about three minutes pour the reaction mixture into a small beaker and note the odor.

Repeat the procedure using amyl alcohol and acetic acid and note the odor. What does it resemble?

Repeat again, this time using 1 g of the solid salicylic acid and methyl alcohol. What is the odor noted here?

Write the equation for the preparation of ethyl acetate. Why is sulfuric acid necessary? Compare this reaction with that taking place between NaOH and HCl in aqueous solution as to type of molecules involved and reaction rate.

6. Tests for Halogens in Organic Molecules. We shall use carbon tetrachloride, CCl_4, as an illustrative compound for the following tests.

The Beilstein test is performed by heating the copper wire spiral used in Part 3 and plunging it into the compound containing a substituted halogen. When the wire is returned to the flame a green flame results from the volatilization of the copper halide.

Another test for the presence of a halogen atom in an organic molecule illustrates the conditions necessary to cause the precipitation of AgCl when the ionic compound $AgNO_3$ reacts with a covalent molecule such as CCl_4. First, add 5 drops of CCl_4 to 1 ml of 0.1 *F* $AgNO_3$ and shake the test tube. Is there any sign of reaction? Now, place about 0.2 g of soda lime in a clean 15-cm test tube. Heat to redness and add 2 or 3 drops of CCl_4. Heat the soda lime again and add the CCl_4 as before. Cool the tube and acidify with 8 to 10 ml of 6 *F* HNO_3. Now add 1 ml of 0.1 *F* $AgNO_3$ and note the result. Compare the procedure required above, with the reaction of NaCl and $AgNO_3$ in an aqueous solution. How do you account for this difference in reactivity?

REPORT: Exp. 31

Some Elementary Experiments in Organic Chemistry

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Properties of Hydrocarbons

Fill in the data called for in this table either from information obtainable in the text or experimental determinations.

Hydrocarbon Name	*Formula*	*Type*	*Solubility in Nonpolar Solvent*	*Reaction with Br_2 in CCl_4*	*Type of Flame*
Methane					
Kerosene					
Paraffin					
Acetylene					
Benzene					
Naphthalene					

Equation for the combustion of ethane:_____

Equation for the preparation of acetylene:_____

Compare the ignition temperatures of the various saturated hydrocarbons tested.

_____

How does the ratio of C to H in the molecule affect the amount of carbon in the flame?

_____

If the Br_2 in CCl_4 is decolorized what does this indicate concerning the nature of the hydrocarbon?

_____

Which of the hydrocarbons tested above showed a reaction with Br_2 under the conditions used here?

_____

Equation for the reaction with Br_2:_____

2. Properties of Some Alcohols

Alcohol Name	*Structural Formula*	*Odor*	*Solubility in Polar Solvent*	*Solubility in Nonpolar Solvent*
Methyl alcohol				
Ethyl alcohol				
Amyl alcohol				

What effect does length of the hydrocarbon chain have on the solubility in different type solvents?

_____

What do you predict concerning the solubility of glycerol in water_____,

in a hydrocarbon solvent_____?

What do you predict concerning the solubility of $C_{16}H_{33}OH$ in water_____

in a hydrocarbon solvent_____?

3. Properties of Aldehydes, R—CHO

	Structural Formula	*Oxidation Number of Carbon*
Methyl alcohol . .	_____	_____
Formaldehyde . .	_____	_____
Formic acid . . .	_____	_____

Describe the appearance of the Fehling test_____

What is the precipitate formed?_____. What is the nature of the oxidizing agent present in Fehling solution?_____

In the hot copper wire-methyl alcohol test, what was the odor observed?_____.

Why did the copper wire become bright on plunging it into the methyl alcohol?_____

Write the equation for the reaction of methyl alcohol and hot cupric oxide:

_____

4. Organic Acids, R—COOH

Write the equation for the preparation of acetic acid by the action of 18 *F* H_2SO_4 on sodium acetate:

_____

Is oxidation-reduction involved here?_____.

The structural formula of, and the oxidation number of the substituted carbon in:

Ethyl alcohol	_____	_____
The aldehyde produced by oxidation .	_____	_____
The acid produced by oxidation . .	_____	_____

Write the balanced oxidation-reduction reaction for the effect of acid dichromate solution on ethyl alcohol:

_____

5. Organic Esters, R—COOR′

Write the equation for the preparation of ethyl acetate:

_____

Describe the odor of each of the esters produced. _____, _____,

_____, _____, _____

What is the role of sulfuric acid in the reactions involved here?

_____

Compare the conditions and rate of this reaction with an acid-base reaction.

_____

6. Tests for Halogens in Organic Compounds

Describe the Beilstein test for halogen compounds.

Does aqueous $AgNO_3$ react with carbon tetrachloride?_____

Describe the reaction necessary to obtain a halogen test with CCl_4.

How do you account for the difference in reactivity of organic halides and inorganic halides?

Some Elementary Experiments in Biochemistry 32

College Chemistry, Chapter 31

Review of Fundamental Concepts

Three classes of organic compounds, carbohydrates, proteins and fats, are important constituents of foods. A major portion of the field of biochemstry is concerned with the important role these compounds play in building body tissues and in supplying energy to the body. Since these compounds are very complex in nature, careful attention should be given to the discussion of their structure and properties in the text and in the section which follows.

Carbohydrates, $C_x(H_2O)_y$. The carbohydrates are produced by plants by the process of photosynthesis, in which carbon dioxide from the air and water from the soil combine in the presence of chlorophyll and sunlight to produce compounds containing carbon, hydrogen and oxygen. The fibrous part of the plant is composed of cellulose which is a polysaccharide which consists of possibly 200 units of $C_6H_{10}O_5$. The starch produced by many plants is believed to contain about 30 units of the simple saccharide molecule $(C_6H_{10}O_5)_{30} \cdot H_2O$. The disaccharides are composed of two molecules of monosaccharides linked together. Examples of these are sucrose, maltose and lactose, which vary slightly in structure but have the common formula $C_{12}H_{22}O_{11}$. The monosaccharides with the formula $C_6H_{12}O_6$ contain either an aldehyde or ketone group in their structure which is capable of reducing certain solutions of metal ions. One such reagent is Fehling solution, which, when reduced to red cuprous oxide, constitutes a characteristic test for glucose, fructose, and other reducing sugars such as maltose and lactose. Other carbohydrates which do not reduce Fehling solution, such as sucrose, starch, and even cellulose, will form the simple reducing sugars when hydrolyzed by boiling with dilute acids or bases. During digestion of foods rich in starches such as rice, potatoes or bread, the starch is hydrolyzed to maltose, a disaccharide, and finally to glucose. Enzymes present in the saliva, ptyalin and maltase, catalyze this reaction so that it takes place with ease at body temperature. The glucose is carried by the blood to all parts of the body where it may be oxidized to carbon dioxide and water, accompanied by the liberation of energy for muscular movement and heat. Some of the glucose may be stored in the liver and muscles as glycogen, a polysaccharide composed of glucose units.

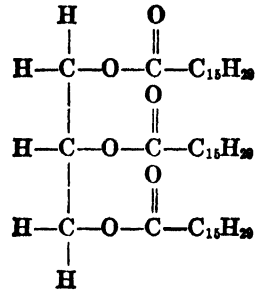
Proteins, Complex Nitrogenous Substances. The elementary composition of proteins averages approximately 52% carbon, 7% hydrogen, 23% oxygen, 16% nitrogen, 0 to 3% sulfur, 0 to 0.8% iodine, and often other elements such as phosphorus, iron and copper are present. The molecular weights of proteins will range from 30,000 to possibly several million. The fundamental building units are amino acids, $CHR(NH_2)COOH$, which are combined by the union of the NH_2 group of one acid with the COOH group of another acid to form a peptide linkage or bond, $\cdots \overset{\overset{H}{|}}{N}\!-\!\overset{\overset{O}{\|}}{C}\cdots$. This linkage is responsible for the color produced in the Biuret test. Due to the presence of both an acid group (COOH) and a basic group (NH_2), the protein molecule is amphoteric in nature and will form a protein salt with an acid or a base. When heated, the polypeptide chains are uncoiled from their characteristic structure as native protein and thereby lose many of their characteristic properties. They are said to be denatured.

During digestion, enzymes, such as pepsin and rennin in the stomach and trypsin and erepsin in the small intestine, catalyze the hydrolysis of proteins into more simple molecules, and finally into amino acids. The amino acids pass through the walls of the intestines into the blood stream and are distributed to all the tissues of the body where they are used to renew tissue which is constantly being broken down in the life process. Excess proteins may be converted to carbohydrates or may be oxidized to carbon dioxide, water, urea, and

ammonium compounds, accompanied by the liberation of energy.

Proteins are produced by both plants and animals but the primary source may be considered to be from plants, since the proteins in such substances as meat, eggs and milk are produced by animals fed on vegetable protein. Such foods as wheat flour, corn flour, oat meal, beans, peas and nuts are important foods containing plant proteins.

Fats, Fatty Acid Esters of Glycerol. Fats are produced in plants and animals by synthesis from carbohydrates. Foods rich in fats include butter, lard, fat meats, cheese, nuts, and vegetable oils. The elements present are carbon, hydrogen, and oxygen which are combined as esters of various fatty acids with the tri-hydroxy alcohol, glycerol. One of the fats present in olive oil is the oleic acid ($C_{15}H_{29}COOH$) ester of glycerol ($C_3H_5(OH)_3$), whose structure is



When this molecule is hydrolyzed, it is split into glycerol and the fatty acid. When this is done in the presence of an alkali such as NaOH the process is called saponification, and the sodium salt of the fatty acid produced is a soap.

When a fat is heated strongly in the presence of a dehydrating agent such as $KHSO_4$, the glycerol portion of the molecule is dehydrated to form the unsaturated aldehyde, acrolein $CH_2=CH-CHO$, which has the peculiar odor of burnt grease. This is a standard test for fats.

During digestion, fats are emulsified and are hydrolyzed in the stomach with the aid of the enzyme lipase, and in the alkaline medium of the small intestines by the enzyme steapsin. The fatty acids and glycerol pass through the intestinal membranes, recombine to form fats, and pass into the blood where they are carried to all parts of the body. They may be oxidized to carbon dioxide and water to furnish heat and energy or they may be stored as fatty tissue to give form to the body and to support the internal organs.

In this experiment we shall observe some of the characteristic tests used to identify carbohydrates, proteins, and fats, and then apply these tests to the various components separated from the common food: milk.

Experimental Procedure

Chemicals: Absorbent cotton, acetone, d-glucose, dried egg albumin, ethyl alcohol, Fehling solutions A and B, lead acetate paper, Methyl orange indicator, Molisch reagent (alpha naphthol in alcohol), olive oil, phenolphthalein indicator, $KHSO_4$, soap chips, soda lime, starch, sucrose, whole milk, 0.1 *F* $CuSO_4$, 0.1 *F* I_2, 0.1 *F* $Pb(C_2H_3O_2)_2$, 0.1 *F* $HgCl_2$.

1. Carbohydrates: Glucose, Sucrose, Starch, Cellulose. Prepare solutions of glucose and sucrose by dissolving 2 g of each in 20 ml of water. Prepare a colloidal suspension of starch by adding a paste made by wetting 1 g of starch with 5 ml of cold water to 50 ml of boiling water and stirring for one minute.

(a) *The Molisch Test for Carbohydrates.* This test is given by all types of carbohydrates, regardless of their complexity. Add five drops of the alcoholic solution of alpha-naphthol to 3 ml of each of the prepared solutions of carbohydrates. Allow about 2 ml of 18 *F* H_2SO_4 to run down the side of each test tube and form a layer at the bottom. Do not mix. Watch for the appearance of a characteristic color at the contact zone after a short time.

(b) *The Fehling Test for Sugars with Reducing Groups.* This test is given by all monosaccharides and those disaccharides which have an aldehyde or ketone group which is not involved in the disaccharide linkage. When the Fehling solutions A and B are mixed, we have an oxidizing agent consisting of the complex cupric tartrate ion in an alkaline medium which can be reduced to the insoluble cuprous oxide.

Add 10 drops of each of the Fehling solutions A and B to 3 ml of water. Mix and divide the solution between three test tubes. Place the tubes in a beaker containing water at about 60° C. Add 2 ml of each of the carbohydrate solutions and allow to

stand for several minutes. Which of the carbohydrates contained a reducing group?

Place a test tube containing 5 ml of the sucrose solution and 1 ml of 12 *F* HCl in a boiling water bath, and allow the sucrose to hydrolyze for about ten minutes. Neutralize the acid solution with 2 ml of 6 *F* NaOH and make the Fehling test as outlined before with some freshly prepared Fehling solution. How do you account for the results now obtained?

(c) *The Hydrolysis of Starch.* In order to determine when the complex starch molecule has been broken down into simpler molecules and finally into glucose, we shall employ the iodine test for starch and the Fehling test for glucose. Prepare the iodine test solution by diluting 2 drops of 0.1 *F* I_2 solution with 1 ml of water. Place one ml of the prepared starch solution on a small watch glass which is resting on a piece of white paper. Add a drop of the dilute iodine solution and note the color of the iodo-starch complex. Repeat the test with one ml of glucose solution, and note the result.

Dilute 25 ml of the starch solution with 100 ml of distilled water. Add 15 ml of 12 *F* HCl and boil for one minute. With a medicine dropper transfer about 1 ml of the solution to a small test tube, neutralize with a few drops of 6 *F* NaOH and add one drop of the iodine solution. View the color against a white background. Continue to boil the solution and withdraw samples at one minute intervals until no color is obtained with the iodine solution. Now test 2 ml of the hydrolyzed starch solution, neutralized with NaOH, with 1 ml of freshly mixed Fehling solution. What has happened to the starch molecule during hydrolysis? How is corn syrup, used for candy making, produced commercially?

(d) (*Optional Experiment*). *The Enzymatic Hydrolysis of Starch by Ptyalin from Saliva.* This experiment will enable you to note the relative ease with which biochemical reactions take place in the presence of enzymes, as compared to the rather strenuous conditions of temperature and acid conconcentration required in the preceding experiment.

Make a fresh suspension of starch as directed before. Place about 25 ml of the suspension in a 50-ml beaker which is suspended in a slightly larger beaker containing water at body temperature (37° C.) In order to follow the course of the hydrolysis, have 5 test tubes ready, numbered 1 to 5 containing 1 ml each of Fehling solution and a similar number containing 1 drop each of dilute iodine solution. Note the time and add about 25 drops of saliva with a medicine dropper to the starch solution. At two-minute intervals, remove a few drops of the solution and add to the iodine solution. Also add 1 ml of the starch to the Fehling solution. When the starch-iodine test has turned from blue to red to colorless, the starch is hydrolyzed. Now heat the test tubes containing the Fehling solution to 60° C in a water bath. Note the test tube in which the reducing sugar first appeared. If the hydrolysis is not complete in the time allotted, repeat the experiment using double the amount of saliva.

(e) *Hydrolysis of Cellulose.* In order to hydrolyze the complex cellulose molecule even more strenuous conditions must be applied. Add 1 ml of 18 *F* H_2SO_4 to a small wad of absorbent cotton on a small watch glass and stir with a glass rod for about three minutes. Pour this solution into 20 ml of water in a small beaker and boil for 10 minutes. Add water from time to time if necessary to replace evaporated water. Remove about 2 ml of the solution, neutralize with a few drops of 6 *F* NaOH and add 1 ml of Fehling solution. Proceed with the boiling until a positive Fehling test is obtained. How does the complexity of the cellulose molecule compare with that of starch?

2. Proteins, Their Characteristic Tests and Properties. We shall use egg albumin, molecular weight 33,400, as our illustration of a protein substance.

(a) *Analysis of Elements Present in Proteins.* Heat about 0.2 g of dried egg albumin with 1 g of soda lime in a small test tube. Hold a moistened red litmus paper at the mouth of the tube and note any change in color. Heat the tube strongly until a charred residue remains. Allow the tube to cool, and then add about 5 ml of 6 *F* HCl to the residue. Hold a small piece of filter paper, moistened with 0.1 *F* lead acetate solution, over the mouth of the tube. If a dark stain of PbS is produced, it is due to H_2S gas evolved as a result of a series of reactions from the sulfur in the protein. What evidence for the presence of carbon, hydrogen and oxygen did you observe during the above tests?

(b) *Color Tests for Proteins.* Dissolve about 0.5 g of dried egg albumin in 50 ml distilled water for use in the following tests.

The Biuret test indicates the presence of the peptide linkage —C(=O)—N(H)—, which is present in all proteins. Prepare a very dilute solution of copper sulfate by diluting 2 drops of the 0.1 *F* $CuSO_4$ reagent with 1 ml of water. Now add 1 ml of 6 *F* NaOH to 1 ml of the egg albumin solution. Mix and add 2 drops of the diluted $CuSO_4$ solution. Watch for a characteristic color to develop.

The Xanthoproteic test is given by most proteins. To 1 ml of egg albumin solution add 5 drops of 16 *F* HNO_3. Heat the mixture for a few minutes. Note the color produced. Allow the tube to cool and cautiously add an excess of 15 *F* NH_4OH. Note the intensification of color which results. Place a drop of 16 *F* HNO_3 on your fingernail, wash it off with water and apply a drop of NH_4OH. Repeat the test using a piece of wool yarn or cloth. The student often inadvertently makes the Xanthproteic test when he spills nitric acid on his skin or on wool and silk clothing.

(c) *Coagulation of Proteins.* Add one drop of 6 *F* acetic acid to 3 ml of egg albumin solution and heat the test tube to boiling for several minutes. What change in the structure of the protein molecule is proposed to account for the change observed? Is the coagulated protein soluble in water? To 3-ml samples of egg albumin in each of three test tubes, add a few drops of 0.1 *F* lead acetate to one, of 0.1 *F* $HgCl_2$ to the second and of 0.1 *F* $CuSO_4$ to the third. Note the precipitates formed in each case, and comment on the effect these salts might have if taken internally. Can you suggest why raw egg whites are recommended as an antidote for mercury poisoning?

(d) *Amphoteric Nature of Proteins.* Dilute 1 drop of 6 *F* HCl with 30 drops of water. Add one drop of this diluted acid and 1 drop of methyl orange indicator to 3 ml of water in a 15-cm test tube. The solution should have a red color, a *p*H of about 3. Mix in about 5 ml of egg albumin solution and note the color now. Methyl orange turns yellow when the *p*H is increased.

Prepare some dilute sodium hydroxide by adding one drop of 6 *F* NaOH to 30 drops of water. Add one drop of the dilute base and a drop of phenolphthalein indicator to 3 ml of water in a 15-cm test tube. Stir in 5 ml of egg albumin solution and note any change in the color of the indicator. Explain with suitable equations the reactions which occurred when the protein solution was added to the acid and to the base. Could it be said that proteins act as buffers?

3. Fats, Their Properties and Characteristic Tests.

(a) *The Solubility of Fats.* Place 5 drops of olive oil, the glyceryl ester of oleic acid, into each of three 10-cm test tubes. To the first tube add 5 ml of water, to the second 5 ml of acetone and to the third add 5 ml of water to which has been added a pinch of soap chips. Shake each tube well and allow to stand for a few minutes. Observe whether solution or emulsification has taken place.

(b) *The Saponification of Fats.* Add 2 ml of olive oil and 1 g of NaOH to 20 ml of ethyl alcohol in a 50-ml Erlenmeyer flask and heat on a water bath maintained at about 75° C for 15 minutes. Cool the solution in a beaker of cold water. Remove a small bit of the solid product (about the size of a pea) with a stirring rod and place it in a 15-cm test tube two-thirds full of distilled water. Place a pipette into the test tube and blow gently through it. What is the nature of the substance dissolved in the tube?

Dissolve most of the remainder of the solid in the flask in some distilled water and place the solution in a 15-cm test tube. Acidify with a few drops of 18 *F* H_2SO_4. Mix with a stirring rod and note the oily material which collects on top of the test tube. Dip a piece of neutral litmus paper into the oily layer and note whether it is neutral like the original oil or acid. What is the oily material? Write equations for the saponification of the olive oil and also for the reaction that takes place upon acidification of the saponified product.

(c) *The Acrolein Test for Fats.* In a dry Pyrex test tube place about 1 g of $KHSO_4$ and 5 drops of olive oil. Heat the test tube rather strongly for a few minutes, and then allow it to cool before noting the characteristic odor of acrolein. *Do not put your nose over the tube while it is hot.* Write the equation for the reaction by which the unsaturated aldehyde, acrolein, is produced by the loss of two moles

of water by the glycerol portion of the fat molecule. Will this test work for all fats?

4. Analysis of the Various Food Constituents Present in Milk.

(a) *Precipitation of Protein Material.* Dilute 20 ml of fresh, whole milk with an equal amount of water in a 50-ml Erlenmeyer flask. Warm to about 50° C. Dilute 1 ml of glacial acetic acid with 10 ml of water and add this dilute acid drop by drop to the warm milk. Shake the flask after each addition and look for the appearance of curds of casein. About 10 to 20 drops usually are sufficient; avoid an excess of acetic acid. Allow the casein to settle and decant the clear liquid through a filter paper in a funnel. Save the filtrate for Part (c). Transfer the casein to the funnel, wash it with water, and let it drain. Remove the casein to a pad of several pieces of filter paper and press it reasonably dry.

Apply the Biuret and the Xanthoproteic tests to small portions of the casein by following the directions given earlier in this experiment.

(b) *Extraction of Fat.* Place the remainder of the casein in a small beaker and work 5 ml of acetone into the coagulated material for several minutes. Decant off the acetone into a small evaporating dish. Extract the casein with another 5-ml portion of acetone and add this solution to the previous extract. Evaporate away the acetone over a beaker of boiling water. Note the appearance of the residue and the nature of the spot produced when some filter paper is touched to it. There will not be enough fat extracted to run the Acrolein test, but if some cream off the whole milk is available it may be tested in this way.

(c) *Test for Carbohydrates.* Heat the filtrate obtained in (a) to boiling for a few minutes. Filter out the additional proteins coagulated by heating. Cool the filtrate and add about 2 ml of 0.1 *F* lead acetate to precipitate out other proteins. Filter again and test the filtrate for the presence of milk sugar, lactose, which is a reducing disaccharide, by applying the Fehling solution test to 1 or 2 ml of the clear solution. If you wish, you may allow the filtrate to evaporate until the next laboratory period and note the crystals of lactose which result.

REPORT: Exp. 32

Some Elementary Experiments in Biochemistry

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Carbohydrates

(a) Describe the appearance of the *Molisch test.*

This test was given by the following carbohydrates tested:

(b) The *Fehling test* consists of the reduction of the complex_____ion in an alkaline medium to the insoluble_____. The group responsible for the reduction is_____. The carbohydrate(s) which gave a positive test_____. What is the molecular formula of glucose_____, of sucrose_____, of starch_____?

How do you account for the positive Fehling test obtained after sucrose was boiled in an acid solution?

(c) *The Hydrolysis of Starch.*

Describe the appearance of the test obtained when dilute iodine solution was added to a starch solution _____, to glucose_____. What changes in color were noted in the iodine-starch test as the hydrolysis of the starch proceeded?_____

What happened to the starch molecule during hydrolysis?

Account for the Fehling test obtained after the hydrolysis was complete.

(d) (Optional Experiment). *The Enzymatic Hydrolysis of Starch.*

How do you account for the relative ease of hydrolysis of starch under the conditions of this experiment compared to those in Part (c)?

What is known about the chemical nature of enzymes?

How are carbohydrates digested in the body?

(e) *The Hydrolysis of Cellulose.*

How does the complexity of the cellulose molecule compare with that of starch?

Was the Fehling test positive after the treatment with concentrated sulfuric acid and boiling?

_____

What happened to the cellulose molecule during the boiling treatment?

Can the digestive system of man hydrolyze and use cellulose?_____.

Can animals use cellulose as food?_____.

2. Proteins

(a) *Elementary Analysis.*

What elements were shown to be present by the reaction of soda lime on egg albumin?_____

How are these elements present in the protein molecule?_____

What are the basic building units which combine to make up the complex protein molecules?

What was the basis of the test for sulfur?

Write the formulas for two amino acids containing sulfur.

What evidence for the presence of carbon, hydrogen and oxygen did you observe during the above tests?

(b) Describe the appearance of the *Biuret test* _____

Is this test given by all proteins?_____. Why?_____

The *Xanthoproteic test* consists in the production of a_____color when the protein is treated with concentrated nitric acid. When treated with concentrated ammonium hydroxide the color was_____.

(c) *Coagulation of Proteins.*

Describe the change which took place when the slightly acidified protein solution was heated to boiling.

What change in the structure of the protein molecule is proposed to account for the change observed?

Is the protein now soluble in water?_____.

Describe the results obtained when the salts of heavy metals were added to the egg albumin solution.

Are these salts toxic when taken internally?_____. What is the antidote usually prescribed?_____. Why?_____

(d) *Amphoteric Nature of Proteins.*

Refer to Table XII, Appendix II, on the colors of indicators, and determine the effect of adding the protein solution to a) the slightly acid solution_____and b) the slightly basic solution_____.

Explain the results obtained by writing suitable equations for the reaction which took place in each case.

Protein acting as a base:_____

Protein acting as an acid:_____

Do proteins act as buffers in the body?_____. Explain:

 *Name*_____

3. Fats

What is the structural formula for the fat olein, which is the major component of the olive oil used in this experiment?

(a) *Solubility.* Record the case(s) in which the olive oil dissolved_____, in which emulsification took place_____.

(b) *The Saponification of Fats.* What is the meaning of the term saponify?_____

The equation for the saponification of olive oil by NaOH:

What were the properties of the aqueous solution of the product obtained by saponification?

When the water solution was acidified what was the oily product formed?_____. Write the equation for the reaction of acid on the saponified product:

(c) *The Acrolein Test.* Describe the odor of acrolein_____

Is this test applicable to all fats?_____

Write the equation for the reaction by which acrolein is produced by dehydration of the glycerol portion of the fat molecule:

4. Analysis of milk.

(a) *Protein Constituents.* Describe the nature of the material which precipitated out from the slightly acidified milk.

What is the material called?_____. What are some of its uses?_____

Describe the appearance of the Biuret test_____, and of the Xanthoproteic test_____.

(b) *Extraction of Fats.* Did the acetone extract any of the fats which were present in the coagulated protein fraction?_____

How did you recognize the residue obtained upon the evaporation of the acetone as a fat?

_____

If a sample of cream or butterfat was available did you obtain a positive acrolein test?

_____

(c) *Carbohydrates Present in Milk.* What was the nature of the material precipitated by boiling the filtrate obtained in Part (a)?_____; by the lead acetate solution?_____

Did the resulting clear solution give a positive Fehling test?_____

What is the sugar present in milk?_____

Thermochemistry. The Heat of Neutralization 33

College Chemistry, Chapter 23

Review of Fundamental Concepts

Chemical thermodynamics is the study of the amounts of energy involved during chemical changes. Such questions as how much electrical energy can be produced by a certain amount of chemical change taking place in an electrical cell or battery are considered. In other instances it is concerned with the amount of energy in the form of work that can be done by chemical means. In the present experiment we shall be concerned with the amount of energy in the form of heat which is involved during a chemical reaction. This part of thermodynamic chemistry is called **thermochemistry.**

Reactions which involve the evolution of heat are called exothermic reactions, while those which absorb heat are said to be endothermic reactions. The general term, heat of reaction, may be classified into several more specific categories. For instance, the heat of combustion is the amount of heat evolved when one mole of a combustible substance, such as carbon or methane, undergoes combustion. The heat of formation of a compound is the amount of heat involved when one mole of the compound is formed directly from the elements composing it. The heats of vaporization, fusion and sublimation are concerned with changes in state. The heat of neutralization, which we shall measure in this experiment, is defined as the amount of heat evolved when one mole of water is produced by the reaction of an acid and a base.

The heats of reaction are usually expressed in the units: calories per mole. They are experimentally determined by allowing the reaction to take place in an insulated device called a calorimeter. The heat involved is determined by noting the change in temperature in the water surrounding the reaction chamber. Since the heat capacity (specific heat) of water is one calorie per gram per degree centigrade, the heat involved can be obtained by simply multiplying the weight of the water present by the change in temperature. A correction for the heat which is absorbed by the calorimeter apparatus must also be taken into account in the calculations.

Experimental Procedure

Special supplies: A thermometer, preferably one graduated to 0.1° or 0.2° C. Less precise results will be obtained with a thermometer with 1° graduations.

Chemicals: 1 *F* NaOH, 1 *F* HCl, 1 *F* HNO_3, 1 *F* $HC_2H_3O_2$, 1 *F* KOH.

To measure the heat of neutralization we shall allow solutions containing equivalent amounts of acid and base to react in a simple calorimeter consisting of a 250-ml beaker inside a slightly larger 400-ml beaker. Some loosely crumpled filter paper should be placed in the bottom of the larger beaker, and a few strips of paper may be inserted between the beakers to insulate the sides. A square of cardboard, with a small hole in the middle for the thermometer, may serve as a lid.

In order to determine the correction to be made for the heat lost to the calorimeter and thermometer, the following determination, run under similar conditions to those to be used later, should be made in duplicate. Obtain about 250 ml of distilled water and adjust its temperature to that of the room or very slightly below room temperature. Carefully measure exactly 100 ml of this water into the calorimeter, using a clean graduated cylinder. Obtain another 250 ml of distilled water and heat it to approximately 10° C higher than room temperature. Measure out exactly 100 ml into the graduated cylinder and determine its temperature as accurately as possible, estimating the nearest 0.1° C. Transfer the thermometer to the calorimeter and read the temperature of this water again. Note the time, then add the measured warm water to the calorimeter, and stir thoroughly with the thermometer. Read the temperature at the end of each minute for five minutes. Plot on some graph paper the temperatures to the nearest 0.1° C as ordinates against the time in minutes as abscissa.

Extrapolate the curve connecting the plotted points back to zero time to obtain the highest temperature attained immediately following the mixing. Calculate the heat lost by the warm water by multiplying its decrease in temperature by its weight, 100 g. (Assume the density of water to be 1.0 and that its specific heat is 1.0.) Calculate the heat gained by the cooler water by multiplying its increase in temperature by its weight, 100 g. The difference between the heat lost and that gained by the water is the heat gained by the calorimeter and thermometer. This number of calories, divided by the change in temperature of the calorimeter is called the water equivalent of the apparatus. Repeat this determination to check your results.

The following example is given to illustrate the use of the water equivalent in a determination: How much heat was liberated by a reaction taking place in a calorimeter, whose water equivalent is 4 calories per degree, if the temperature of 100 ml of solution was raised 6.5° C by the reaction? Calories gained by the water = 100 × 6.5. (Assume density of solution and its specific heat are each 1.0.) To this must be added the heat lost to the calorimeter: the water equivalent 4 cal/degree × 6.5° = 26 cal. Thus the heat involved in this reaction was 650 cal + 26 cal or 676 cal.

1. The Determination of the Heat of Neutralization of a Strong Base by a Strong Acid

Prepare to run duplicate determinations first with 100 ml each of 1 *F* NaOH and 1 *F* HCl and then use a different pair: 1 *F* KOH and 1 *F* HNO_3. Be sure that the temperature of each solution is at, or very nearly at, room temperature so as to avoid errors caused by mixing solutions at different temperatures. Use a clean, dry graduated cylinder to measure out exactly 100 ml of the solution of base into the calorimeter. Measure exactly 100 ml of the acid solution and accurately determine the temperature of each solution to the nearest 0.1° C. Note the time and pour the acid into the base and stir thoroughly. Read the temperature at one-minute intervals for five minutes. Plot the temperatures against time and extrapolate to zero time so as to obtain the highest temperature reached when mixed.

Record the data for both pairs of strong bases and acids, and calculate the heat of neutralization per mole of water produced.

Write the net ionic reaction for the neutralization of a strong acid by a strong base. The accepted value for the heat of neutralization of strong acids and strong bases is 13,700 calories. How do you account for the fact that this value is essentially the same for all strong acid—strong base neutralizations?

2. The Heat of Neutralization of a Weak Acid by a Strong Base

Following the same procedure as outlined above, determine the heat of neutralization of the strong base, NaOH and the weak acid, acetic acid. Record the data obtained in the report sheet.

How do you account for the different value obtained in this experiment? Write the equation for the net reaction involved here. How does it differ from the one for the neutralization of a strong base and strong acid?

What value for the heat of neutralization would you expect from the reaction of ammonium hydroxide and hydrochloric acid? Explain the reason for your answer.

Consider the following data for another weak acid, hydrocyanic acid, and its neutralization by sodium hydroxide. The heat of neutralization is only 2,900 calories per mole. For a strong acid—strong base the value is 13,700 calories per mole. How many calories must be involved in the dissociation process of the weak acid? Write equations for the three processes involved and include the heat term appropriate to each.

REPORT: Exp. 33

Thermochemistry, the Heat of Neutralization

Name _____

Date _____

Section _____

Locker Number _____

Determination of the Water Equivalent of the Calorimeter

	1	*2*
Weight of water at lower temperature	_____ g	_____ g
Weight of water at higher temperature	_____ g	_____ g
Lower temperature	_____ ° C	_____ ° C
Higher temperature	_____ ° C	_____ ° C
Final temperature after mixing	_____ ° C	_____ ° C
(1) Heat lost by the warm water	_____ cal	_____ cal
(2) Heat gained by the cold water	_____ cal	_____ cal
Heat lost to calorimeter (1)—(2)	_____ cal	_____ cal
Water equivalent of the calorimeter	_____ cal/° C	_____ cal/° C

The Heat of Neutralization of Hydrochloric Acid and Sodium Hydroxide

	1	*2*
Weight of 1 *F* acid solution	_____ g	_____ g
Weight of 1 *F* base solution	_____ g	_____ g
Original temperature of solutions	_____ ° C	_____ ° C
Final temperature after reaction	_____ ° C	_____ ° C
Calories absorbed by aqueous solution[1]	_____ cal	_____ cal
Calories absorbed by apparatus	_____ cal	_____ cal
Total calories evolved	_____ cal	_____ cal
Number of moles of water formed	_____ moles	_____ moles
Heat of neutralization	_____ cal/mole	_____ cal/mole
Accepted value	_____ cal/mole	_____ cal/mole

[1] Assume a specific heat of 1 calorie per gram per degree for these aqueous solutions, and also for those in the data on the next page.

The Heat of Neutralization of Nitric Acid by Potassium Hydroxide

	1	*2*
Weight of 1 *F* acid solution	_____ g	_____ g
Weight of 1 *F* base solution	_____ g	_____ g
Original temperature of solutions	_____ ° C	_____ ° C
Final temperature after reaction	_____ ° C	_____ ° C
Calories absorbed by aqueous solution[1]	_____ cal	_____ cal
Calories absorbed by apparatus	_____ cal	_____ cal
Total calories evolved	_____ cal	_____ cal
Number of moles of water formed	_____ moles	_____ moles
Heat of neutralization	_____ cal/mole	_____ cal/mole

The net ionic equation for the neutralization of a strong acid by a strong base:

How do you account for the fact that the heat of neutralization is essentially the same for all strong acids and strong bases?

The Heat of Neutralization of Acetic Acid by Sodium Hydroxide

	1	*2*
Weight of 1 *F* acid solution	_____ g	_____ g
Weight of 1 F base solution	_____ g	_____ g
Original temperature of solutions	_____ ° C	_____ ° C
Final temperature after reaction	_____ ° C	_____ ° C
Calories absorbed by aqueous solution[1]	_____ cal	_____ cal
Calories absorbed by apparatus	_____ cal	_____ cal
Total calories evolved	_____ cal	_____ cal
Number moles of water formed	_____ moles	_____ moles
Heat of neutralization	_____ cal/mole	_____ cal/mole

How do you account for the different value obtained in this experiment?

Write the equation for the net ionic reaction involved here: _____

How does it differ from that written for a strong acid—strong base?

What value for the heat of neutralization of ammonium hydroxide and hydrochloric acid would you expect?

Why?

How do you account for the low value for the heat of neutralization of hydrocyanic acid?

Write equations for the three processes involved and include the heat term appropriate to each:

[1] See footnote on the preceeding page.

PRINCIPLES OF IONIC EQUILIBRIA

Basic to the Qualitative Analysis Procedure

To the Student:

The study of qualitative analysis is not a separate subject; it is an integral part of the general chemistry course. As you undertake the study of the procedures of the scheme of qualitative analysis used in Experiments 39–44, you will bring into active service all of the important principles which you have learned so far.

It is particularly important that you fully understand the *principles relating to the equilibria of ions* in solution. The next group of experiments (Exp. 34–38 and Study Assignment E) are presented as an integral part of the qualitative analysis section of this manual so that you can study these important principles first in separate experiments.

For example, studies of the equilibria involving the ions of water and the ions of weak acids and bases should help you to understand how the concentration of hydrogen ion (*p*H), or of other ions, such as hydroxide, sulfide, or carbonate ions, may be calculated or controlled as is necessary in the group separations. A study of the solubility product principle should make clear the factors which regulate the formation and dissolution of slightly soluble substances. Acquaintance with hydrolysis, buffer action, amphoteric substances, complex ions, and equilibrium constants such as K_{sp} or K_i will make the directions in the qualitative scheme take on real meaning. Without this background the analytical procedure would mean little more to you, so far as chemical training is concerned, than would a set of recipes in a cookbook.

Types of Equilibria—The Ions of Water, *p*H, Hydrolysis — 34

College Chemistry, Chapter 20

Review of Fundamental Concepts

The Ions of Water

A summary of the experimental observations regarding the ionization of water should emphasize these two opposite viewpoints:

(1) Hydrogen ions and hydroxide ions react with each other quite completely, as evidenced by the various titration experiments involving acids and bases, and as interpreted by the following net ionic equation for the reaction taking place when a strong acid reacts with a strong base,

$$H^+ + OH^- \longrightarrow H_2O.$$

(2) The electrical conductivity of very pure water, while too small for any but the most refined measurements, indicates a slight but definite dissociation of the water molecule into hydrogen and hydroxide ions,

$$H_2O \longrightarrow H^+ + OH^-.$$

Since these two opposing tendencies must be going on all the time, we have in any sample of water, pure or impure, the equilibrium represented by the reversible reaction:

$$H_2O \rightleftarrows H^+ + OH^-.$$

In water, when we have no other ions present which will unite with either the hydrogen ions or the hydroxide ions, the concentration of the ions, at 25° C, from conductivity data, is:

concentration of hydrogen ion, $(H^+) = 10^{-7}\ M$
concentration of hydroxide ion, $(OH)^- = 10^{-7}\ M$.

The Equilibrium Constant Expression for the Water Reaction

The equilibrium constant for the water reaction may be written:

$$\frac{(H^+)(OH^-)}{(H_2O)} = K_1, \text{ or } (H^+)(OH^-) = K_1(H_2O), \text{ or,}$$

since the quantity, (H_2O), is practically a constant, $K_1(H_2O)$ will also be a constant, K, and the expression may be written, for *any aqueous solution*, at 25° C,

$$(H^+)(OH^-) = K = 10^{-14}.$$

The evaluation of the constant, K, as 10^{-14} is obtained by substituting the actual concentrations of the ions in pure water in this equation. However, the same constant, of course, applies in any situation where water is present, in pure water, and in

aqueous solutions of acids, bases, or salts. It is, therefore, possible to calculate the hydrogen ion concentration in a basic solution and the hydroxide ion concentration in an acid solution. Thus, in a 0.01 *F* hydrochloric acid solution, the hydroxide ion concentration is 10^{-12} *M*, since 10^{-2} *M* H^+ $\times$ 10^{-12} *M* OH^- equals the constant 10^{-14}.

The pH of a Solution

Chemists frequently designate the relative concentrations of hydrogen ion and hydroxide ion in a solution, especially between the range from 1 *M* H^+ (10^{-14} *M* OH^-) to 1 *M* OH^- (10^{-14} *M* H^+), by a different system of notation, based on the concentration of hydrogen ion alone. This is called the *p*H of the solution and is defined by the equation

$$pH = -\log (H^+).$$

The meaning of *p*H, which, you should note, is a *logarithmic* function, is illustrated by the following selected corresponding values:

1 *M* H^+ or 10^0 *M*	H^+	10^{-14} *M* OH^-	*p*H = 0
10^{-4} *M*	H^+	10^{-10} *M* OH^-	*p*H = 4
10^{-7} *M*	H^+	10^{-7} *M* OH^-	*p*H = 7
10^{-11} *M*	H^+	10^{-3} *M* OH^-	*p*H = 11
10^{-14} *M*	H^+	10^0 *M* OH^- or 1 *M* OH^-	*p*H = 14

Note that in any such cases, when the hydrogen ion concentration is a simple power of 10, the *p*H is the exponent of 10 with the minus sign dropped.

To calculate the *p*H for intermediate values of the hydrogen ion concentration, which cannot be expressed as simple, integral powers of 10, we simply look up the logarithm of the hydrogen ion concentration and change the sign. Be careful to include both mantissa and characteristic in the expression for the logarithm of the hydrogen ion concentration. Note the following:

Example: What is the *p*H of a 1 *F* acetic acid solution, in which the hydrogen ion concentration is 0.004 *M* or 4×10^{-3} *M*?

$$pH = -\log (H^+) = -\log (4 \times 10^{-3})$$
$$= -(\log 4 + \log 10^{-3})$$
$$= -(0.60 - 3) = -(-2.4) = 2.4$$

The *p*H is 2.4; that is, the number $4 \times 10^{-3} = 10^{-2.4}$.

To calculate the hydrogen ion concentration from the *p*H, which is the reverse of the above calculation, note the following cases:

Example 1: What is the hydrogen ion concentration of a solution which has a *p*H of 4.3?

If the *p*H is 4.3, the H^+ concentration is $10^{-4.3}$ *M*. This exponent, or logarithm, may be broken into the positive mantissa and the negative characteristic thus:

$$10^{-4.3} = 10^{0.7-5} = 10^{0.7} \times 10^{-5}$$
$$= 5.0 \times 10^{-5} \text{ (The antilog of 0.7 is 5.0.)}$$

The H^+ concentration is 5.0×10^{-5} *M*, which is the same as $10^{-4.3}$ *M*.

Example 2: What is the hydroxide ion concentration of a solution which has a *p*H of 11.7?

This is a basic solution, but we first calculate the hydrogen ion concentration as in Example 1:

If the *p*H is 11.7, the H^+ concentration is $10^{-11.7}$ *M*.

$$10^{-11.7} = 10^{0.3-12} = 10^{0.3} \times 10^{-12}$$
$$= 2.0 \times 10^{-12} \text{ (Antilog of 0.3 is 2.0.)}$$

The H^+ concentration is 2.0×10^{-12} *M*. We use this to calculate the OH^- concentration, from the ionization equilibrium for water:

$$(H^+)(OH^-) = 10^{-14}, \text{ or}$$
$$(OH^-) = \frac{10^{-14}}{(H^+)} = \frac{1 \times 10^{-14}}{2 \times 10^{-12}}$$
$$= 0.5 \times 10^{-2} \text{ or } 5.0 \times 10^{-3} \text{ } M \text{ } OH^-.$$

The Hydrolysis of a Salt

The word "hydrolysis" means "reaction with water." Certain salts and a number of organic compounds hydrolyze. The hydrolysis of a salt is frequently spoken of as the reversal of the neutralization process. *Hydrolysis always involves a shift to the right of the reaction*

$$HOH \rightleftharpoons H^+ + OH^-.$$

This reaction will be shifted to the right whenever salts of weak acids or bases are present, resulting in a solution which will be acidic if the OH^- concentration has been reduced by the formation of a weak base, basic if the H^+ concentration has been reduced by the formation of a weak acid, or still neutral if both H^+ and OH^- ions have reacted with the ions of the salt to the same extent.

As an *example of hydrolysis*, let us study the behavior of a 0.1 *F* sodium cyanide solution, NaCN. Such a solution is distinctly red to phenolphthalein, showing an excess of hydroxide ions. These hydroxide ions have resulted because the cyanide ions in the solution react with hydrogen ions from the water to form the weak acid HCN. More water then ionizes to maintain the equilibrium, thus creating an excess of hydroxide ions:

$$\begin{array}{l} HOH \rightleftarrows H^+ + OH^- \\ \quad\quad + \\ \quad\quad CN^- \\ \quad\quad \downarrow\uparrow \\ \quad\quad HCN \end{array}$$

Note that there is a competition of OH^- ions for H^+ ions to form HOH, and also of CN^- ions for H^+ ions to form HCN. The ultimate position of the equilibrium will depend on how poorly the HCN is ionized as compared with the water. The above may be more conveniently represented by the *net ionic equation* for the hydrolysis:

$$CN^- + HOH \rightleftarrows HCN + OH^-.$$

Note that *water* itself always enters into the hydrolysis equation, not just the H^+ ion (or OH^- ion in other examples). Since there is no tendency for Na^+ ions to react with OH^- ions, Na^+ ion is not a part of the hydrolysis reaction. Note also that the hydrolysis equation is just the reverse of the equation for the neutralization of the weak acid HCN by the strong base NaOH.

Polyvalent ions of weak bases or weak acids will hydrolyze in steps. For example, in a solution of sodium carbonate, which is distinctly basic, the carbonate ion will hydrolyze in steps as follows:

$$\begin{array}{l} CO_3^{--} + HOH \rightleftarrows HCO_3^- + OH^- \\ HCO_3^- + HOH \rightleftarrows H_2CO_3 + OH^- \end{array}$$

In such cases the OH^- formed by the first step represses the second step so that it occurs to a very slight extent, and no CO_2 results from the very small amount of H_2CO_3 formed.

Similarly, the hydrolysis of Al^{+++}, Fe^{+++}, Cu^{++}, etc., results in an acid solution, but usually no precipitate of $Al(OH)_3$, $Fe(OH)_3$, or $Cu(OH)_2$ is formed unless some ion is present which uses up the H^+ ion formed and thus promotes the hydrolysis to completion. In the preparation of reagent shelf solutions of ferric salts, stannous and stannic salts, and some others, additional H^+ ion is added to reverse the hydrolysis so that the metallic hydroxides will not be precipitated.

The Degree of Hydrolysis

As explained above, the extent of hydrolysis depends on the formation of a weak acid, a weak base, or both, by the reaction of the ions of the salt with water. If only a weak acid or a weak base is formed, we may determine the extent of hydrolysis by measuring the OH^- ion or H^+ ion concentration by means of indicators.

For example, a 0.1 *F* Na_2CO_3 solution is red to phenolphthalein and gives an orange-red color with alizarin yellow R, such that we may estimate the OH^- ion concentration as about 0.004 *M*. As discussed above, the equation is

$$CO_3^{--} + HOH \rightleftarrows HCO_3^- + OH^-.$$

Now if this reaction had proceeded to completion, the 0.1 *M* CO_3^{--} would have produced 0.1 *M* OH^-. Since only 0.004 *M* OH^- resulted, the *fraction of the salt hydrolyzed* is

$$\frac{0.004\,M}{0.1\,M} = 0.04, \text{ or } 4\%.$$

If both a weak base and a weak acid are produced, the solution may remain about neutral, but hydrolysis will always occur to a greater extent than for either the positive ion or the negative ion separately. This is due to the effect of each reaction on the other. As an extreme example, if Fe^{+++} ion and CO_3^{--} ion are mixed, the H^+ ions and OH^- ions produced by each separate hydrolysis will neutralize one another, so that each hydrolysis will take place to a greater extent, in fact through all the possible steps of hydrolysis. As a result, $Fe(OH)_3$, not $Fe_2(CO_3)_3$, is precipitated, and CO_2 gas is evolved. The equations for these reactions are:

$$\begin{array}{l} Fe^{+++} + 3\ HOH \rightleftarrows Fe(OH)_3 + 3\ H^+ \\ CO_3^{--} + 2\ HOH \rightleftarrows H_2CO_3 + 2\ OH^- \end{array}$$

Combining these by neutralization of the H^+ and OH^-,

$$2\,Fe^{+++} + 3\,CO_3^{--} + 6\,HOH \longrightarrow \underline{2\,Fe(OH)_3} + 3\,H_2CO_3$$
$$\downarrow$$
$$3\,H_2O + 3\,CO_2.$$

Preliminary Work

Before starting the experimental procedure, complete the Indicator Chart in the report sheet. Record on the chart the colors of the indicators which you have studied in previous experiments: methyl violet, methyl orange, phenolphthalein, alizarin yellow R, and indigo carmine. Record these by inserting at each *p*H position the color (abbreviate: B = blue, and so forth) given by that indicator at that *p*H. The chart is completed for methyl red as an example.

Experimental Procedure

Chemicals: Al (powdered), $Al_2(SO_4)_3$ or alum, $NH_4C_2H_3O_2$, 1 *F* $NH_4C_2H_3O_2$, $(NH_4)_2CO_3$, NH_4Cl, 1 *F* NH_4Cl, H^+ and OH^- solutions from 10^{-4} *M* H^+ to 10^{-4} *M* OH^-, i.e. *p*H 4 to *p*H 11, 1 *F* $NaC_2H_3O_2$, $NaHCO_3$, 1 *F* Na_2CO_3, 1 *F* NaCl, S (powdered), and the indicator solutions: methyl violet, methyl orange, methyl red, brom-cresol purple, brom-thymol blue, phenolphthalein, alizarin yellow R, and indigo carmine.

1. Indicators that Change Color Near the Neutral Point. To complete the chart, information should be obtained on indicators which change color in the range from *p*H 5 to *p*H 8. Use the prepared H^+ and OH^- solutions covering this range to determine the color change which the indicators brom-cresol purple, brom-thymol blue, and phenol red undergo in solutions of varying *p*H. For each indicator prepare a set of clean 10-cm test tubes, containing respectively 5 ml of the standard solutions varying from *p*H 5 to *p*H 8. To each test tube of one set add two drops of brom-cresol purple; mix this, and note the particular *p*H range in which the color change is most marked. Do the same for the other two indicators. Record the results on the report sheet on the line corresponding to the indicator used.[1] Have the instructor approve your chart before continuing with the experiment, so that any errors may be corrected.

2. The Hydrolysis of Salts. The solutions to be tested for hydrolysis are: 1 *F* $NaC_2H_3O_2$, 1 *F* NaCl, 1 *F* NH_4Cl, 1 *F* $NH_4C_2H_3O_2$, and 1 *F* Na_2CO_3. Test 5-ml portions of these salt solutions[2] with one or more indicators which change in color in the *p*H range, 5 to 9. If a solution is out of the range of these indicators, use other indicators that change in a still more acidic or basic solution, as your evidence dictates. In this manner, determine the approximate *p*H of each solution as accurately as you can. Record your results on the report sheet. In the case of sodium acetate, the hydrolysis is due to the formation of what poorly ionized substance? What ion from the salt must, therefore, be involved in the hydrolysis? Write the equation for the net ionic reaction which takes place in the hydrolysis of a sodium acetate solution. Remember that, although H^+ is used up in the reaction, it is partially replaced by further ionization of water, so that the main substance used up is water rather than H^+. Also write equations for any hydrolysis which takes place in the other solutions tested.

3. The Degree of Hydrolysis.

A. *Salts of a Strong Base and a Weak Acid.* In the hydrolysis of sodium carbonate, the net ionic reaction is

$$CO_3^{--} + HOH \rightleftarrows HCO_3^- + OH^-.$$

What would have been the hydroxide ion concentration, if the hydrolysis of the 1 *F* Na_2CO_3 solution had proceeded to completion? By comparing the actual OH^- concentration just obtained by experiment with this hypothetical value for complete hydrolysis, calculate the percent of the salt which did hydrolyze. In a similar manner, calculate the percent of the sodium acetate which hydrolyzed in the 1 *F* $NaC_2H_3O_2$. Carbonic acid, the acid in a "soda," is a much weaker acid than acetic acid, the acid in vinegar. Make a general statement relating the degree of hydrolysis with the strength of the acid (or base) formed by the hydrolysis reaction.

B. *Salts of a Weak Base With Strong and With Weak Acids.*

(1) *Hydrolysis of Ammonium Salts.* Remove the stopper and smell (use caution) the bottles of solid ammonium chloride, ammonium acetate, and ammonium carbonate on the laboratory shelf. There is enough water adsorbed on each of the apparently dry salts to make hydrolysis possible. Explain the result, remembering that NH_4OH is unstable and decomposes readily into NH_3 and H_2O.

(2) *Hydrolysis of Aluminum Sulfide.* The instructor will prepare a quantity of aluminum sulfide as a class demonstration, using powdered aluminum and powdered sulfur in the proportion of about 4 g of Al to 10 g of S. The reagents are mixed thoroughly and transferred to a clay crucible which is placed in an extremely well ventilated place free from fire hazard, preferably outdoors. The mixture is then ignited by means of a fuse of magnesium ribbon. When cool, the product, Al_2S_3, is broken into small pieces with a hammer or in an iron mortar.

Take a small piece of this aluminum sulfide, and

[1] You may compare your results, both for these indicators and for those used previously, with the data in Table XII, Appendix II.

[2] Traces of impurities in the 1 *F* NaCl may cause incorrect results. Test a solution of a gram of reagent grade NaCl in 20 ml of distilled water.

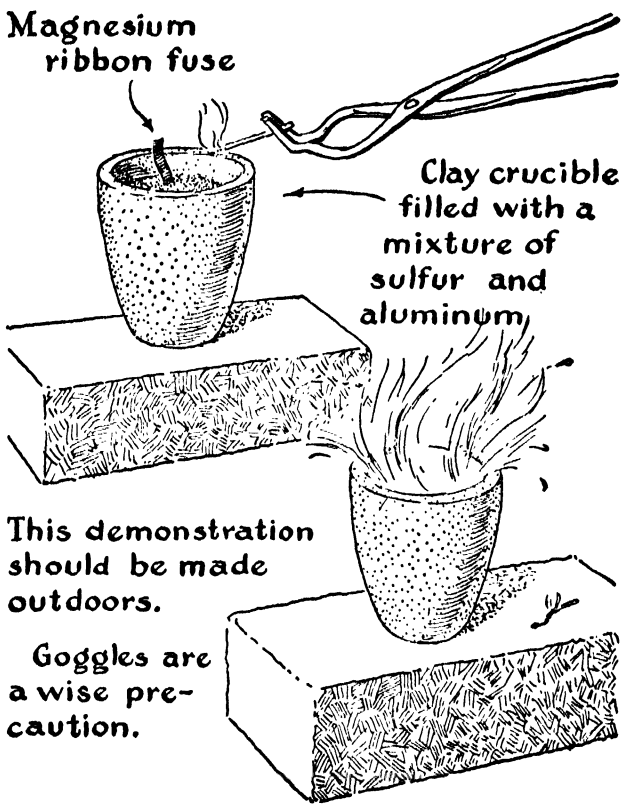


FIG. 34-1. The preparation of aluminum sulfide.

add it to 10 or 15 ml of water in a small beaker or test tube. Note any evidence of the formation of a gas or precipitate. Write the equation for this hydrolysis reaction, remembering that the salt is present this time at the beginning as a solid, not as ions. What would you conclude about the relative degree of hydrolysis in any case where the acid and base formed are both extremely weak, or where the products are both removed from the sphere of action by precipitation or gas evolution?

4. An Application of Hydrolysis. Practically all baking powders consist of a mixture of sodium hydrogen carbonate with some solid substance which furnishes H^+ when water is added. In alum baking powders, this H^+ is furnished by the hydrolysis of alum, $KAl(SO_4)_2 \cdot 12\ H_2O$.

Place about 3 grams of solid alum or of aluminum sulfate in one dry beaker, and 3 grams of solid sodium hydrogen carbonate in a second dry beaker. Mix a little of each of these together in a third dry beaker. Is there a reaction? Now add 10 ml of water to each beaker and note the results. Test samples of the two separate salt solutions with litmus paper and suitable indicators to determine their approximate *p*H.[1] Finally mix the two salt solutions. Explain the results and write net equations for all reactions involved.

---

[1] The slight ionization of HCO_3^- as a very weak acid is counterbalanced by its hydrolysis, so that a hydrogen carbonate solution is slightly basic. On boiling, it changes to CO_3^{--} and CO_2:

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--} \quad \text{(ionization)}$$
$$HCO_3^- + HOH \rightleftarrows OH^- + H_2CO_3 \quad \text{(hydrolysis)}$$
$$2\ HCO_3^- \longrightarrow CO_3^{--} + H_2O + CO_2 \quad \text{(on boiling).}$$

REPORT: Exp. 34

Types of Equilibria—Ions of Water, *p*H, Hydrolysis

*Name*_____

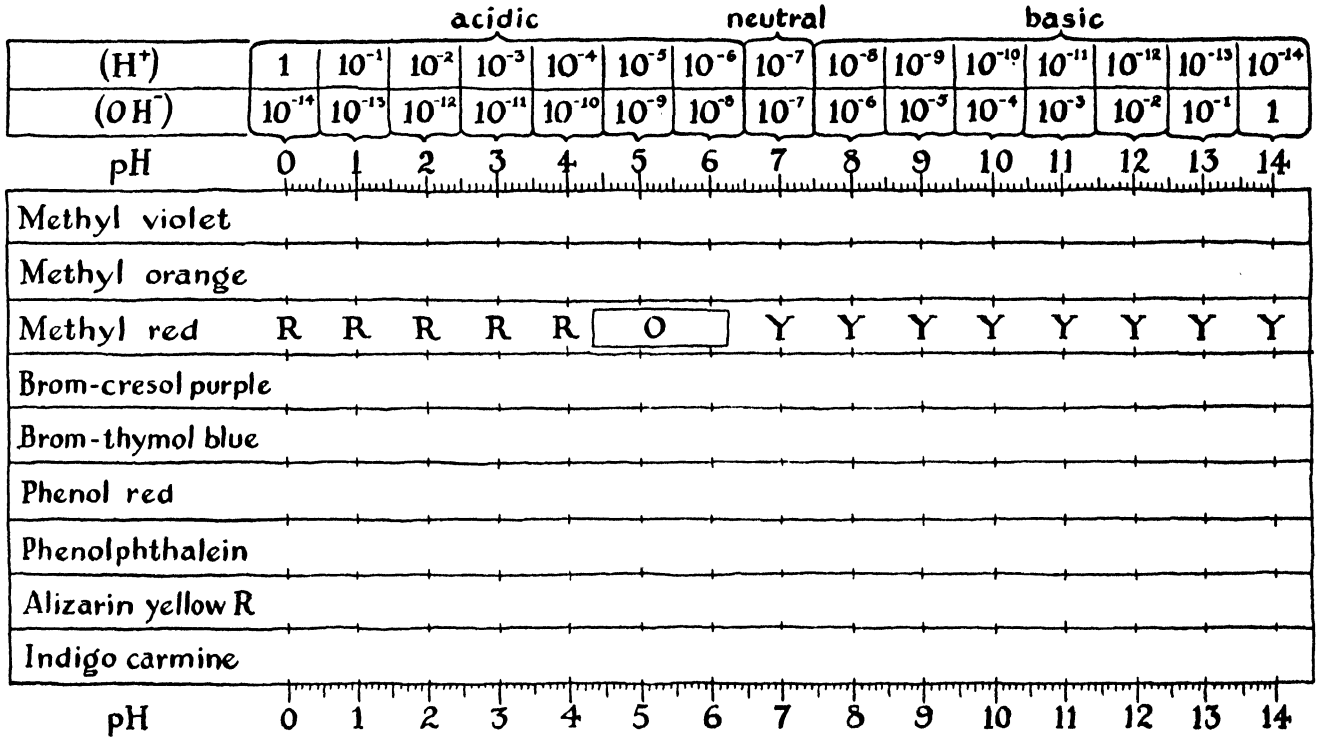
*Date*_____

*Section*_____

*Locker Number*_____

Preliminary Work, and 1. Indicators that Turn Near the Neutral Point.

Complete the chart below, as directed.



Abbreviations: B = blue, V = violet, BV = blue violet, P = purple, R = red, O = orange, Y = yellow, G = green C = colorless. Colored crayons may be used, if desired, to fill in lightly the actual colors obtained at various *p*H. The regio showing the color change may be bracketed for emphasis.

Instructor's approval of chart_____

2. The Hydrolysis of Salts.

Solution	*Indicators Used*	*Color*	(H^+)	(OH^-)	*pH*
1 *M* $NaC_2H_3O_2$					
1 *M* NaCl					
1 *M* NH_4Cl					
1 *M* $NH_4C_2H_3O_2$					
1 *M* Na_2CO_3					

In the case of sodium acetate the hydrolysis is due to the formation of: . . _____

The ion from the sodium acetate involved in the hydrolysis is therefore: . . _____

The net ionic equations for the hydrolysis, if any, of the various salt solutions are given below:

Sodium acetate _____

Sodium chloride _____

Ammonium chloride _____

Ammonium acetate _____

Sodium carbonate _____

3. The Degree of Hydrolysis

A. *Salts of a Strong Base and a Weak Acid*

If a 1 *F* sodium carbonate solution hydrolyzed completely according to the equation given, the concentration of the hydroxide ion would be: . . . . . _____ *M*

A comparison of the actual hydroxide ion concentration with this hypothetical value indicates that the percent of the salt hydrolyzed in this 1 *F* sodium carbonate solution is: _____ %

Method of this calculation:

Similarly the percent of sodium acetate hydrolyzed in a 1 *F* sodium acetate solution is: _____ %

Method of this calculation:

The general principle relating the degree of hydrolysis and the strength of the acid (or base) formed by the hydrolysis reaction is as follows:

Considering both the positive ions and negative ions involved, which of the two salt solutions is hydrolyzed most, 1 *F* sodium acetate, or 1 *F* ammonium acetate? . _____

Explanation:

B. *Salts of a weak base with strong and weak acids.*

(1) *Hydrolysis of ammonium salts.*

My results of smelling the three ammonium salts indicate that the one giving the

(a) strongest odor of ammonia is . . . . . _____.

(b) next strongest odor of ammonia is . . . . . _____

(c) weakest odor of ammonia is . . . . . _____

My explanation of the reason for this order is as follows:

(2) *Hydrolysis of aluminum sulfide.*

The equation for the preparation of aluminum sulfide is:

_____

The net ionic equation for the hydrolysis of this substance is:

_____

List below all the specific factors which you can think of which cause this reaction to go practically to completion:

4. An Application of Hydrolysis

Approximate *p*H of solutions of $Al_2(SO_4)_3$_____, and $NaHCO_3$_____.

The net ionic equation for the hydrolysis reaction involved in the $Al_2(SO_4)_3$ solution is:

_____

Combine this equation with the equation for the neutralization of the sodium bicarbonate:

$$H^+ + HCO_3^- \rightleftarrows H_2O + CO_2,$$

so as to eliminate H^+ and give the final net ionic equation for the whole process:

_____

Application of Principles

(Refer to Table XI in the Appendix, if necessary.)

1. For each of the salts listed, indicate in general whether its water solution would be acidic, basic, or neutral:

$BaCl_2$ _____ $CuSO_4$ _____ $AlBr_3$ _____

$MgSO_4$ _____ K_2S _____ Na_3PO_4 _____

Na_2SO_3 _____ $NaNO_3$ _____ $LiCl$ _____

2. Consider the following list of salt solutions:
1 *F* KNO_3, 1 *F* Na_2S, 1 *F* NH_4Cl, 1 *F* $NH_4C_2H_3O_2$, 1 *F* $KC_2H_3O_2$
Indicate which solution has the characteristic called for:

The highest H^+ concentration _____
The highest OH^- concentration _____
The highest degree of hydrolysis _____
The lowest degree of hydrolysis _____
The two solutions most nearly neutral _____

3. List the solutions given below on the lines at the right, in order of increasing *p*H (highest H^+ concentration at the top):

1 *F* Na_2CO_3 1 *F* $(NH_4)_2SO_4$ _____

1 *F* $NH_4C_2H_3O_2$ 1 *F* HCl _____

1 *F* NaOH 1 *F* $(NH_4)_2CO_3$ _____

_____

_____

4. Experiment: Some magnesium ribbon is placed in a warm solution of aluminum sulfate. Bubbles of a gas are formed.
Write two net ionic equations to explain what you think occurs: _____

_____

5. Write equations for the hydrolysis of ferric ion in steps: _____

_____

_____

6. Consider the two compounds $NaHCO_3$ and $NaHSO_4$. One of these gives an acid reaction in solution, the other a slightly basic reaction. Explain these facts, both by words and by net ionic equations:

7. A 0.5 *F* solution of sodium cyanide, NaCN, has a *p*H of about 12. Write the hydrolysis equation, and calculate the degree of hydrolysis.

_____

_____

Types of Equilibria—Slightly Soluble Substances. Coordination Compounds 35

College Chemistry, Chapters 21, 22

Review of Fundamental Concepts

Thus far, we have studied the equilibria which are established between the undissociated molecule and its ions in the case of pure water, in solutions of weak acids, of weak bases, and of their salts. We also have considered the equilibrium between a slightly soluble solid substance and its ions in solution. In this experiment, we shall review these principles in an experimental study of the solubility of metallic hydroxides. We shall also introduce a new type of equilibrium which involves the formation of "complex ions," as discussed in the following paragraphs.

Coordination Compounds and Complex Ions

Most of the common ions, for which we usually write simple formulas, as Cu^{++}, Zn^{++}, Al^{+++}, H^+, Cl^-, and so forth, in reality are hydrated, both in solution, and in many crystals. In such hydrated ions, a number of water molecules are grouped in a stable configuration about the central ion. The more complex ions permit a greater number of water molecules to be grouped about them. Several examples are: H_3O^+ or $H(H_2O)^+$, $Cu(H_2O)_4^{++}$, $Al(H_2O)_6^{+++}$, and $Fe(H_2O)_6^{+++}$. The formation and stability of such hydrated ions are related to the fact that the water molecule possesses unshared pairs of electrons and is quite polar (see

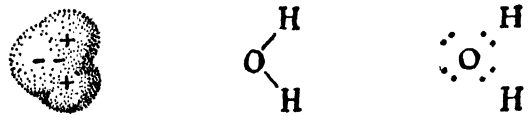


FIG. 35-1. Three ways to represent the polar character of the water molecule. The hydrogen to oxygen to hydrogen bond is not linear, but forms an angle of about 105°. The oxygen side of the molecule is more negative than the hydrogen side.

Fig. 35-1). Water molecules thus tend to group about a cation so that their unshared pairs of electrons form or complete a noble gas electron structure.

These hydrates constitute one example of the type of substances which are called **coordination compounds.** Other neutral, but polar, molecules, such as ammonia, NH_3, and also a number of ions, as OH^-, Cl^-, CN^-, $S_2O_3^{--}$, and $C_2O_4^{--}$, likewise can form similar, very stable, coordination groupings about a central ion. These coordination compounds may form by the replacement of the water molecules from the hydrated ion by these other molecules or ions which are present in the solution at high concentration, to form a more stable bond. The resulting coordination compound may be a positively or negatively charged ion (*a complex ion*), or it may be a neutral molecule, depending on the number and kind of coordinating groups attached to the central ion. A few examples are: NH_4^+ or $H(NH_3)^+$, $Cu(NH_3)_4^{++}$, $AuCl_4^-$, $HgCl_4^{--}$, $Fe(CN)_6^{---}$, and $Ag(CN)_2^-$. Such complex ions may be diagrammed or illustrated in various ways, as shown in Figure 35-2.

The *ammonia complex ions*[1] are formed in the presence of a high concentration of ammonium hydroxide. In this latter solution, we have several substances in equilibrium, as represented by the equation

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

We shall study these ammonia complexes in this experiment and show how we may decide which substance in the above equilibrium is responsible for the formation of the complex.

Hydroxide Complex Ions, or Amphoteric Hydroxides

The hydroxides of most metals are insoluble in water, so that when sodium hydroxide, for example, is added to a metal ion in solution, as lead ion, Pb^{++}, we get a precipitate,

$$Pb^{++} + 2\ OH^- \rightleftharpoons Pb(OH)_2.$$

It would be expected that excess hydroxide ion would give more complete precipitation. Instead, the precipitate dissolves. This is explained by the tendency of lead ion to form a coordination compound with additional hydroxide ion,

$$Pb(OH)_2 + 2\ OH^- \rightleftharpoons Pb(OH)_4^{--}.$$

This may be written as a replacement of the water

[1] See Pauling, *College Chemistry*, page 489, for a table of important ammonia complex ions.

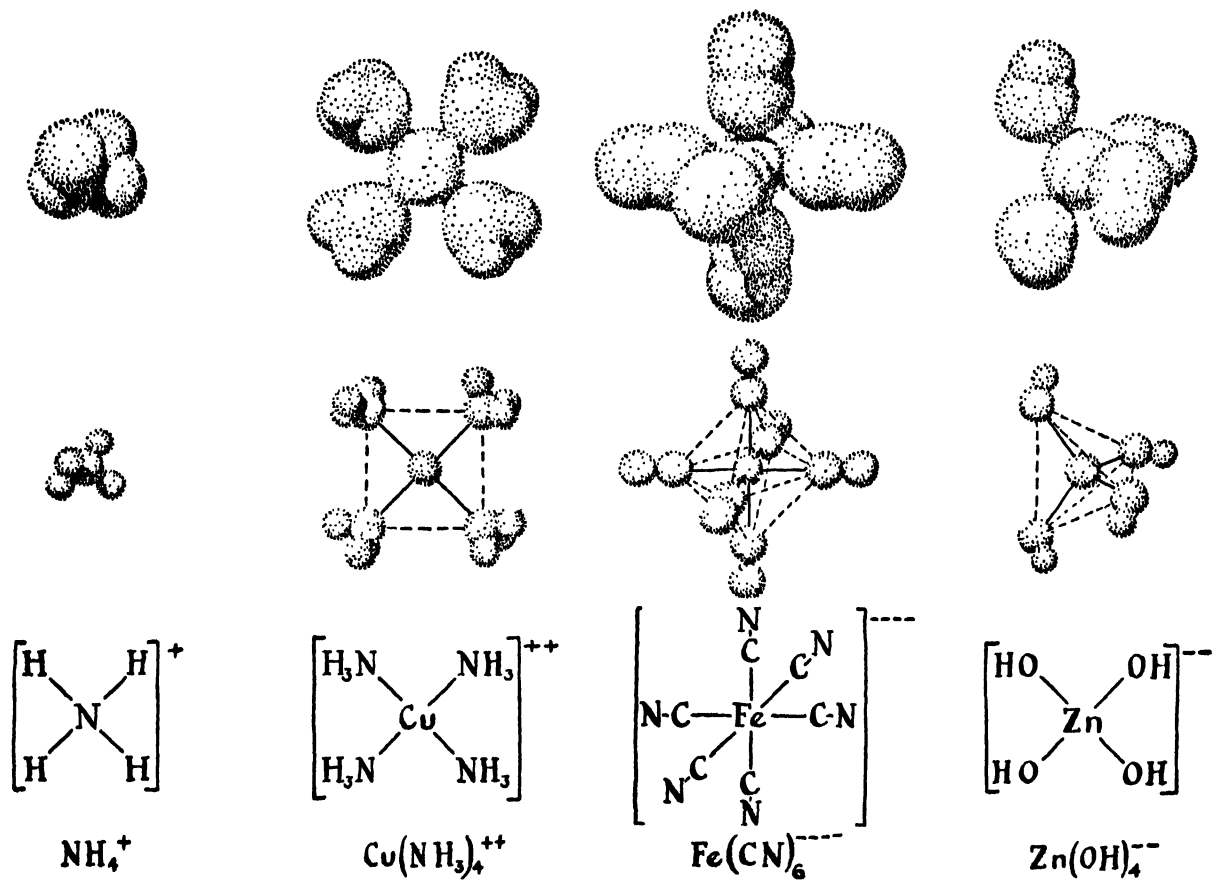
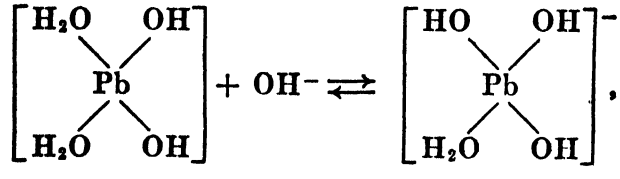
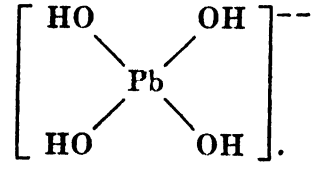


FIG. 35-2. Diagrams showing the spatial arrangement of the coordinating groups about a central ion in the formation of a complex ion. In the bracketed diagrams (immediately above the conventional formulas in each case) the lines represent a bonding pair of electrons. Above these, the groups are represented at the points of tetrahedra or octahedra, or in the case of $Cu(NH_3)_4^{++}$ as a square coplanar structure. In these, the atomic diameters have been reduced to one-third their correct size as compared to the interatomic distances, to show their relative spatial positions. The upper figures show these in their proper relative dimensions.

molecule in the hydrated formula, as follows:[1]



or with 2 OH^-,



A number of metal ions, but not all, behave in a similar manner. Examples of these are indicated in the following table.

Simple Ion	*Precipitate*	*Hydroxide Complex Ion*
Pb^{++}	$Pb(OH)_2$	$Pb(OH)_4^{--}$, plumbite ion
Zn^{++}	$Zn(OH)_2$	$Zn(OH)_4^{--}$, zincate ion
Al^{+++}	$Al(OH)_3$	$Al(OH)_4^-$, aluminate ion
Cr^{+++}	$Cr(OH)_3$	$Cr(OH)_4^-$, chromite ion
Sn^{++}	$Sn(OH)_2$	$Sn(OH)_4^{--}$, stannite ion
Sn^{++++}	$Sn(OH)_4$	$Sn(OH)_6^{--}$, stannate ion

These hydroxide complex ions frequently have been written in the anhydrous form: PbO_2^{--}, ZnO_2^{--}, AlO_2^-, CrO_2^-, SnO_2^{--}, and SnO_3^{--}. (Such formulas may be derived from the hydroxide complex ion formulas simply by subtracting 2 or 3 H_2O.)

[1] There is some uncertainty as to whether $Pb(OH)_3^-$, and also $Sn(OH)_3^-$, will coordinate further with hydroxide ion to form $Pb(OH)_4^{--}$, and $Sn(OH)_4^{--}$.

The reactions to form these hydroxide complex ions are entirely reversible. If an acid is added to the above, we have first the re-precipitation of the hydroxide,

$$Pb(OH)_4^{--} + 2\,H^+ \rightleftarrows Pb(OH)_2 + 2\,H_2O.$$

With an excess of acid, this dissolves as the simple metal ion,

$$Pb(OH)_2 + 2\,H^+ \rightleftarrows Pb^{++} + 2\,H_2O.$$

Such metallic hydroxides, which may be dissolved by an excess of either a strong acid, or a strong base, are called *amphoteric hydroxides*. For example, with aluminum hydroxide, we have, with excess acid:

$$Al(OH)_3 + 3\,H^+ \rightleftarrows Al^{+++} + 3\,H_2O,$$

or with excess base:

$$Al(OH)_3 + OH^- \rightleftarrows Al(OH)_4^-.$$

We shall study the nature of this type of equilibrium experimentally.

Experimental Procedure

Chemicals: 1 *F* NH_4Cl, 1 *F* NH_4OH, 0.1 *F* $CaCl_2$, $Ca(OH)_2$ solid, 0.02 *F* $Ca(OH)_2$, $CuSO_4 \cdot 5H_2O$, 0.1 *F* $CuSO_4$, 0.1 *F* $FeCl_3$, 0.1 *F* $Mg(NO_3)_2$, 0.1 *F* $AgNO_3$, 0.1 *F* $Zn(NO_3)_2$.

1. Slightly Soluble Metallic Hydroxides. The slightly soluble metallic hydroxides give sufficient OH^- concentration in solution to carry out convenient test tube reactions and, thus, determine experimentally the relative concentrations of OH^- in their saturated solutions, as follows:

(a) To 2 or 3 g of solid $Ca(OH)_2$ in a small beaker, add 5 ml of 1 *F* NH_4Cl. Warm the mixture. The solid $Ca(OH)_2$ will, of course, dissolve until a saturated solution is formed. Is there any evidence that this can react with 1 *F* NH_4Cl? What can you conclude as to the relative concentration of OH^- in saturated $Ca(OH)_2$ and 1 *F* NH_4OH? As a further check on your reasoning, test 3 ml samples of saturated $Ca(OH)_2$ (limewater), and 1 *F* NH_4OH with indigo carmine indicator, to discover which has the higher OH^- concentration.

(b) Would you expect to get a precipitate of $Ca(OH)_2$ when 0.1 *F* $CaCl_2$ and 1 *F* NH_4OH are mixed? Try it. Try also 6 ml of 0.1 *F* $CaCl_2$ with 1 ml of 6 *F* NaOH. Note the results.

(c) Try 2 ml of 0.1 *F* $FeCl_3$ with 2 ml of 1 *F* NH_4OH. Which hydroxide furnishes more OH^- to a solution, saturated $Fe(OH)_3$ or 1 *F* NH_4OH?

(d) Prepare two test tubes, one containing 2 ml of 1 *F* NH_4OH + 1 ml of 1 *F* NH_4Cl, and the other containing 2 ml of 1 *F* NH_4OH + 1 ml of H_2O. To each of these, add 1 ml of 0.1 *F* $Mg(NO_3)_2$. Write net ionic equations for any reactions and explain the difference in the two cases. Compare the OH^- concentration in each of the three cases, saturated $Mg(OH)_2$, 1 *F* NH_4OH, and 1 *F* NH_4OH containing NH_4Cl.

(e) To the mixture of NH_4OH and NH_4Cl used in (d), now add a few drops of 0.1 *F* $FeCl_3$. Was there still an appreciable concentration of OH^- in the mixture?

Summarize all your results in this section by arranging all the substances studied in the order of decreasing OH^- concentration, as provided in the table in the report sheet.

2. The Formation of Insoluble Hydroxides and Oxides. When a high concentration of OH^- is added to a metallic ion, either the metallic hydroxide or the corresponding oxide may be precipitated. This depends on the relative insolubility of the hydroxide as compared with the oxide, and on the rate of the decomposition of the hydroxide into the oxide and water. In some cases, the precipitate is of variable and rather indefinite composition, as in the case of ferric hydroxide above, which probably is more properly written $Fe_2O_3 \cdot xH_2O$, and is sometimes called a *hydrous oxide*.

(a) To 3 ml of 0.1 *F* $CuSO_4$ in a large test tube, add 1 ml of 6 *F* NaOH. Note the results at room temperature, then heat the solution and note any changes. (*Caution:* Be very careful never to point a test tube containing hot alkali or hot acid toward anyone.) The black precipitate formed is cupric oxide.

(b) When OH^- is added to silver ion at room temperature, the oxide, not the hydroxide, precipitates. Try it with 1 ml of 0.1 *F* $AgNO_3$ and a drop of 6 *F* NaOH.

3. The Formation of Complex Ions. To 3 ml of 0.1 *F* $CuSO_4$, add a drop of 6 *F* NH_4OH. Note the result. Now continue to add NH_4OH a little at a time, with shaking, until a distinct change has taken place. Is this contrary to the law of Le Chatelier? Since it is obvious that the cupric hydroxide dissolved while the OH^- concentration was increasing, how must the Cu^{++} concentration have changed? Did it increase or decrease?

To learn which of the substances present in

ammonium hydroxide solution is responsible for the change, try adding 1 ml of 1 *F* NH_4Cl to 1 ml of 0.1 *F* $CuSO_4$. Try also the effect of ammonia gas by placing several crystals of solid cupric sulfate in a dry beaker. Also place in the beaker, but not touching the $CuSO_4$ crystals, a piece of filter paper moistened with concentrated ammonia solution. Cover with a watch glass. Observe whether the ammonia gas liberated from the solution has any effect on the crystals. What do you consider to be responsible for the dark blue color, NH_3 or NH_4^+? Write an equation to show the formation of this new substance, when excess ammonium hydroxide solution is added to a cupric salt solution. (To assist you in the writing of correct formulas for this type of complex ion, note the following rule: The number of moles coordinated with one mole of the ion usually is twice the valence of the ion. In this case, the formula is $Cu(NH_3)_4^{++}$.)

To 1 ml of cupric ammonia complex ion solution, add 6 *F* HNO_3 in excess. Explain the result and write the equation.

4. The Formation of Amphoteric Hydroxides. To a 3-ml sample of 0.1 *F* $Zn(NO_3)_2$, add a drop of 6 *F* NaOH. Note the result. Now continue adding NaOH, with shaking, as long as a change occurs (2 to 3 ml may be needed). Is this result contrary to the law of Le Chatelier? Has the concentration of Zn^{++} increased or decreased as more OH^- is added? Write separate equations for each of the two steps of the reaction. Now to this strongly basic solution, add 6 *F* HCl a little at a time. What is the precipitate? Continue to add an excess of HCl. What are the principal substances in the solution now? Write equations for these reactions.

5. Reaction of Zinc Ion with Ammonia. When ammonium hydroxide solution is added to Zn^{++}, zinc hydroxide first forms, then dissolves when excess ammonia is added. Does the zinc hydroxide dissolve as zincate ion $Zn(OH)_4^{--}$, due to the excess base added, or does it dissolve as $Zn(NH_3)_4^{++}$, due to the NH_3 molecules added? To answer this question take 5 ml of 0.1 *F* $Zn(NO_3)_2$, and add 6 *F* NaOH drop by drop, with shaking, until the $Zn(OH)_2$ first precipitated has almost, but not completely, redissolved. Avoid an undue excess of NaOH solution. Find the OH^- concentration in this solution by dividing it into two portions. Test one with alizarin yellow indicator, and the other with indigo carmine.

Now to a second 5-ml sample of 0.1 *F* $Zn(NO_3)_2$, add 6 *F* NH_4OH, drop by drop, until the precipitate of $Zn(OH)_2$ just about dissolves. Again find the OH^- concentrations, this time using phenolphthalein, and alizarin yellow indicators. What is your conclusion as to the possibility of forming zincate ion, $Zn(OH)_4^{--}$, by adding ammonium hydroxide to a zinc salt solution? Explain.

REPORT: Exp. 35

Types of Equilibria—Slightly Soluble Substances. Coordination Compounds

Name _____

Date _____

Section _____

Locker Number _____

1. Slightly Soluble Metallic Hydroxides

(a) The equilibrium equation for a saturated solution of $Ca(OH)_2$, with excess solid, is: _____

The experimental evidence that $Ca(OH)_2(s)$ can react with NH_4Cl solution is: _____

The net ionic equation (above reaction) is: _____

The reason this reaction will take place as indicated is:

_____

Color with indigo carmine: $Ca(OH)_2$ _____, NH_4OH _____

Therefore _____ has the higher OH^- concentration.

(b) to (e) The net ionic equation for any reaction in each of the following mixtures is:

$CaCl_2$ and NH_4OH . . . . . _____

$CaCl_2$ and NaOH . . . . . _____

$FeCl_3$ and NH_4OH . . . . . _____

NH_4OH, NH_4Cl, and $Mg(NO_3)_2$ . . _____

NH_4OH and $Mg(NO_3)_2$ . . . . . _____

NH_4OH, NH_4Cl, and $FeCl_3$ . . . . _____

From the above experimental evidence, list in the chart below, the following hydroxide solutions, in the order of decreasing OH^- concentration: Saturated $Fe(OH)_3$, saturated $Ca(OH)_2$, saturated $Mg(OH)_2$, 1 *F* NaOH, 1 *F* NH_4OH, 1 *F* NH_4OH+NH_4Cl. Optional honor problem: Verify the order you have written down, by calculating the OH^- concentration in each case. Obtain any data needed from a handbook, and from Experiment 26 for the NH_4OH solution. Omit the NH_4OH+NH_4Cl mixture, as you have not yet studied the methods for calculating this case.

List of Hydroxides[1]	*Molarity of OH^-*	*Method of Calculating the OH^- Concentration*
High (OH^-)		
Low (OH^-)		

[1] Note that this list of hydroxides is arranged in such an order that any substance lower down would tend to be formed by the reaction of its positive ion with any substance above it in the list. Compare with the equations you have written.

2. The Formation of Insoluble Hydroxides and Oxides.

Write net ionic equations for the reactions indicated, and give the color of any precipitates formed:

$CuSO_4$ and NaOH (cold) . . . . . _____

$CuSO_4$ and NaOH (hot) . . . . . _____

$AgNO_3$ and NaOH . . . . . _____

3. The Formation of Complex Ions.

Write the net ionic equation for the reaction of $CuSO_4$, in excess, with a small amount of NH_4OH:

_____

From this reaction and from Le Chatelier's theory, would you expect the addition of excess NH_4OH to form more, or less, solid $Cu(OH)_2$?

_____

From the actual result, how must the Cu^{++} concentration have changed as more ammonium hydroxide is added

_____

What is the result of adding NH_4Cl to $CuSO_4$?

_____

What is the result of adding NH_3 gas to $CuSO_4$ crystals?

_____

The equation for the reaction of excess ammonium hydroxide solution on copper sulfate solution is:

_____

What result did you observe, and what is the net ionic equation, for the reaction of HNO_3 on the product formed above?

_____

4. The Formation of Amphoteric Hydroxides.

Write the net ionic equation for the reaction of $Zn(NO_3)_2$ in excess, with a small amount of NaOH:

_____

From this equation, and Le Chatelier's theory, would you expect the addition of excess OH^- to form more, or less, solid $Zn(OH)_2$?

_____

From the actual result, how must the Zn^{++} concentration have changed as more NaOH is added:

_____

Explain in your own words why the $Zn(OH)_2$ solid dissolves with excess OH^-, and write the net ionic equation for the reaction:

Explanation:

Equation: _____

What is the result when a moderate amount of HCl is added to this strongly basic solution?

Observation:

Equation: _____

What further change takes place when an excess of HCl is added?

Observation:

Equation: _____

5. Reaction of Zn^{++} with Ammonium Hydroxide Solution.

Solution	*Indicator Color*	*OH^- Concentration*
$Zn(NO_3)_2$ + NaOH to almost dissolve ppt.	Alizarin yellow R _____ Indigo carmine _____	_____
$Zn(NO_3)_2$ + NH_4OH to almost dissolve ppt.	Phenolphthalein _____ Alizarin yellow R _____	_____

What proof does this experiment give as to the coordination compound [$Zn(OH)_4^{--}$ or $Zn(NH_3)_4^{++}$] which Zn^{++} forms with excess NH_4OH solution? State your reasons clearly.

The net ionic equation for the reaction of Zn^{++} with excess NH_4OH solution is:

Interpretation of Data

1. Will calcium hydroxide, $Ca(OH)_2$, precipitate when saturated barium hydroxide, $Ba(OH)_2$, is mixed with an equal volume of 1 *F* $CaCl_2$? The solubility of barium hydroxide is 3.9 g per 100 g of H_2O at 20°C. See also Table XI in the Appendix. (Show calculations, and explain.)

2. When ammonium hydroxide is added to zinc nitrate solution, a white precipitate forms, which dissolves on the addition of excess ammonia; but when ammonium hydroxide is added to a mixture of zinc nitrate and ammonium nitrate, no precipitate forms at any time. Can you suggest an explanation of this difference in behavior?

3. Suppose you are given the following experimentally observed facts regarding the reactions of silver ion:

(1) Silver ion reacts with chloride ion to give white AgCl,

(2) Silver ion reacts with ammonia to form a quite stable complex ion, $Ag(NH_3)_2^+$,

(3) A black suspension of solid silver oxide, Ag_2O, shaken with sodium chloride solution, changes to white AgCl,

(4) Solid silver chloride will dissolve when ammonia is added, but solid silver iodide does not dissolve under these conditions.

Write equations for any net reactions in each of the above cases:

(1) _____

(2) _____

(3) _____

(4) _____

Arrange each of the substances, AgCl, AgI, Ag_2O, and $Ag(NH_3)_2^+$ in such an order that their solutions with water would give a successively decreasing concentration of Ag^+.

_____

_____

_____

_____

The Ionization Constant of a Weak Acid — 36

College Chemistry, Chapters 19, 20

Review of Fundamental Concepts

The Quantitative Treatment of Chemical Equilibrium

In this experiment an introduction to the quantitative study of equilibrium will be given through a study of the reaction

$$HC_2H_3O_2 \underset{2}{\overset{1}{\rightleftarrows}} H^+ + C_2H_3O_2^-.$$

It is a fundamental concept in all equilibrium situations, as stated in the preceding experiment, that the rates of the forward and of the reverse reactions are equal.

In reactions such as this example (where the coefficient of each constituent in the equation is one), the rate of each reaction, forward and reverse, is proportional to the concentration of the reacting molecules or ions.[1] Thus we have, for the forward reaction,

$$HC_2H_3O_2 \xrightarrow{1} H^+ + C_2H_3O_2^-, \quad \text{Rate}_1 = k_1(HC_2H_3O_2),$$

and for the reverse reaction,

$$HC_2H_3O_2 \xleftarrow[2]{} H^+ + C_2H_3O_2^-, \quad \text{Rate}_2 = k_2(H^+)\,(C_2H_3O_2^-).$$

The symbols k_1 and k_2 are the proportionality constants, or the specific reaction rates. They express the *constant* ratio between the rates of the reaction and the concentrations of the substances involved. Thus, in this case, k_1 is small, since the tendency for acetic acid to ionize is not very great. If the concentration of acetic acid, represented by the bracketed symbol $(HC_2H_3O_2)$, is doubled, rate_1 will be doubled. Similarly, we find that k_2 is relatively large, since the tendency for hydrogen ion and acetate ion to unite is great. Rate_2 will be proportional, both to the concentration of hydrogen ion, written (H^+), and to the concentration of acetate ion, written $(C_2H_3O_2^-)$. Thus, if we double the hydrogen ion concentration, and triple the acetate ion concentration, rate_2 will be increased sixfold. It should be remembered that k_1 and k_2 do not change as the concentrations are varied. They are constants, characteristic of the reactions concerned.

The relative concentrations of the reactants and products will automatically be adjusted as the rates of the forward and of the reverse reactions correspondingly change, until these rates are equal, that is, until

$$\text{Rate}_2 = \text{Rate}_1.$$

The processes do not stop, but there is no further change in the concentration of any of the constituents, since each is being formed as fast as it is being used up. If we equate the concentration expressions, corresponding to rate_2 and rate_1, we have,

$$k_2(H^+)\,(C_2H_3O_2^-) = k_1\,(HC_2H_3O_2).$$

Now transposing the variable concentration factors to one side of the equation, and the constants to the other, we have,

$$\frac{(H^+)\,(C_2H_3O_2^-)}{(HC_2H_3O_2)} = \frac{k_1}{k_2} = K.$$

Since k_1 and k_2 are both constant, their quotient K will also be constant. It is called **the equilibrium constant,** or in this case the ionization constant.[2]

While it is often impossible to measure k_1 and k_2 separately, since the speeds of the reactions of many ionic reactions are immeasurably great, the ratio, k_1/k_2, or K, can be measured easily. A small value of K, (k_1 smaller than k_2), means that the forward reaction is slow, and consequently the equilibrium mixture is largely present as reactants. Conversely, a large value of K means that the products of the reaction are present at relatively high concentration.

Since the numerical values of k_1 and k_2 are not affected by variations in the concentrations of hydrogen ion, acetate ion, or acetic acid molecules, their ratio, k_1/k_2, or K, will also be unaffected by changes in these concentrations. Whether the concentrations of these substances are varied by dilution, by the addition of sodium acetate to supply

[1] The more general case, where the coefficients of the several formulas in the equation are not always one, is considered in Experiment 37 and Study Assignment F.

[2] Equilibrium constant expressions are customarily written so that the products of the reaction (as the equation is written), are in the numerator, and the reactants are in the denominator.

acetate ion, or by the addition of hydrochloric acid to supply hydrogen ion, the same numerical relationship between K and the molar concentrations of the reacting substances in the equilibrium holds:

$$\frac{(H^+)\ (C_2H_3O_2^-)}{(HC_2H_3O_2)} = K.$$

Although a change in the equilibrium concentration of one of the three substances forces the other two concentrations to change, the numerical value of K remains unchanged. This fact makes an ionization constant or equilibrium constant a very useful tool when it is desired to calculate the equilibrium concentrations without actually measuring them experimentally.

In this experiment, the ionization constant of acetic acid will be determined. We shall measure the hydrogen ion concentration by means of indicators. In pure acetic acid solutions, the acetate ion concentration will be equal to the hydrogen ion concentration. The concentration of un-ionized acetic acid molecules (molarity of $HC_2H_3O_2$) can be calculated by subtracting the measured molarity of the hydrogen ion from the formality of acetic acid in the solution, since one acetic acid molecule is used up for each hydrogen ion formed.

We shall also vary the ratio of hydrogen ion to acetate ion by adding excess sodium acetate. In this latter situation, the concentration of acetate ion and of un-ionized acetic acid may be calculated from the formalities of the acid and of the salt in the solution, as suggested in the experimental procedure.

Experimental Procedure

Chemicals: 1 *F* $HC_2H_3O_2$, 0.1 *F* $HC_2H_3O_2$, 1 *F* $NaC_2H_3O_2$, or $NaC_2H_3O_2$ crystals. Methyl violet, methyl orange, and methyl red indicators. H^+ solutions from 10^{-4} to 10^{-6} *M*.

1. The effect of a Common Ion. To 10 ml of 1 *F* $HC_2H_3O_2$ colored with a drop of methyl orange indicator, add a little 1 *F* $NaC_2H_3O_2$, or a few crystals of $NaC_2H_3O_2$. Interpret the change in terms of the equilibrium equation.

2. The Ionization Constant of Acetic Acid

A. Recall from your data for Experiment 26, the H^+ concentration of 1 *F* $HC_2H_3O_2$. If necessary, determine this again, using methyl violet indicator, as in that experiment. Calculate the molarity of $C_2H_3O_2^-$ and of $HC_2H_3O_2$ as described above. Substituting the values found in the equilibrium constant expression, find the numerical value of K for 1 *F* $HC_2H_3O_2$. Tabulate and record the values in the chart in the report sheet.

B. Using the value for the H^+ concentration in 0.1 *F* $HC_2H_3O_2$ (from Exp. 26), calculate the molarity of $C_2H_3O_2^-$, of $HC_2H_3O_2$, and the value of K for 0.1 *F* $HC_2H_3O_2$. Tabulate and record these values.

C. Add 25.0 ml of 1 *F* $NaC_2H_3O_2$ to 10.0 ml of 1 *F* $HC_2H_3O_2$, and mix well. To a 5-ml portion of this in a 10-cm test tube, add a drop of methyl red indicator and estimate the H^+ concentration. To do this, compare the color with color comparison standards made by adding a drop of the indicator to each of 5-ml portions of the standard acid buffer solutions of hydrogen ion concentration 10^{-4} *M* H^+, 10^{-5} *M* H^+, and 10^{-6} *M* H^+.[1] Save these color standards for use in part D. Calculate the molarity of the $C_2H_3O_2^-$ and of the $HC_2H_3O_2$. (Assume that $NaC_2H_3O_2$ is completely ionized, and that all of the $C_2H_3O_2^-$ comes from the $NaC_2H_3O_2$. The amount of $C_2H_3O_2^-$ from the slightly ionized $HC_2H_3O_2$ is negligible in comparison to that from the $NaC_2H_3O_2$. These assumptions simplify the calculations and do not introduce an error as large as the experimental error.) Calculate K for this mixture.

D. Dilute 10 ml of the solution used in C with 40 ml of distilled water and mix well. Again determine the H^+ concentration experimentally, using methyl red indicator. Calculate K for this diluted mixture.

E. Mix 4.0 ml of 1 *F* $NaC_2H_3O_2$ with 22.0 ml of 1 *F* $HC_2H_3O_2$. This time use methyl orange indicator to measure the H^+ concentration. Compare the color with acid solutions of the concentrations: 10^{-3} *M* H^+, 10^{-4} *M* H^+, and 10^{-5} *M* H^+. Calculate the value of K for this mixture.

[1] The color of methyl red indicator changes appreciably toward the red when the H^+ concentration increases only very slightly beyond 10^{-5} *M*. It is almost completely transformed to the red color at $10^{-4.5}$ or 0.00003 *M* H^+.

REPORT: Exp. 36

The Ionization Constant of a Weak Acid

Name _____

Date _____

Section _____

Locker Number _____

1. The Effect of a Common Ion.

The color of methyl orange in 1 *F* $HC_2H_3O_2$ is . . . . . _____

The color of methyl orange in 1 *F* $HC_2H_3O_2$ to which $NaC_2H_3O_2$ has been added is _____

Give a brief explanation of this change in color in terms of the equilibrium equation

$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$.

2. The Ionization Constant of Acetic Acid.

Enter all data, as calculated below, in the chart on the following page and calculate the value of K for each solution.

A. Recall the data from Experiment 26 on the molarity of H^+, $C_2H_3O_2^-$, and $HC_2H_3O_2$, in 1 *F* $HC_2H_3O_2$.

B. Recall the data from Experiment 26 on the molarity of H^+, $C_2H_3O_2^-$, and $HC_2H_3O_2$, in 0.1 *F* $HC_2H_3O_2$.

C. In the mixture of 25.0 ml of 1 *F* $NaC_2H_3O_2$ + 10.0 ml of 1 *F* $HC_2H_3O_2$, the formality of each substance is:

_____ *F* $NaC_2H_3O_2$

_____ *F* $HC_2H_3O_2$

D. In the mixture of 10 ml of mixture C above plus 40 ml of distilled water, the formality of each substance is:

_____ *F* $NaC_2H_3O_2$

_____ *F* $HC_2H_3O_2$

E. In the mixture of 4.0 ml of 1 *F* $NaC_2H_3O_2$ + 22.0 ml of 1 *F* $HC_2H_3O_2$, the formality of each substance is:

_____ *F* $NaC_2H_3O_2$

_____ *F* $HC_2H_3O_2$

Fill in the values in the following table, for the five solutions studied. In the space provided below the table, show the method of calculation of the constant, K, for each trial:

	Formality of $HC_2H_3O_2$	*Formality of* $NaC_2H_3O_2$	*Molarity of* H^+	*Molarity of* $C_2H_3O_2^-$	*Molarity of* $HC_2H_3O_2$	*K*
A	1 *F* $HC_2H_3O_2$	———				
B	0.1 *F* $HC_2H_3O_2$	———				
C						
D						
E						
	Accepted value of K for $HC_2H_3O_2$, from the literature					

Method of calculation of K for each trial:

Problems

1. The H^+ concentration of 0.1 *F* hydrofluoric acid, HF, is 0.0086 *M*. Write the equilibrium equation for its ionization, the equilibrium constant expression, and solve for the value of K.

K_{HF} = _____

2. The OH^- concentration of 0.01 *F* ammonium hydroxide, NH_4OH, is 4.2×10^{-4} *M*. Write the equilibrium equation for its ionization, the equilibrium constant expression, and solve for the value of K.

K_{NH_4OH} = _____

The Solubility Product of Slightly Soluble Salts 37

College Chemistry, Chapter 21

Review of Fundamental Concepts

This experiment extends our quantitative study of chemical equilibrium to the case of saturated solutions. Such equilibria are established every time we form a precipitate of a slightly soluble salt. The study of such equilibria is very important, for it enables us to calculate the experimental conditions (concentration, acidity, etc.), to cause, or to prevent the formation of a given precipitate. In Experiments 24 and 36 we learned the essential characteristics of chemical equilibrium. Let us recapitulate these briefly.

Chemical Equilibrium

When a process has reached a state of equilibrium, we have the following three conditions:

(1) *A dynamic situation*—that is, the forward and the reverse processes continue to take place. The action seems to have stopped only because the relative amounts of the various reactants and products do not change.

(2) *A "balance"*—so that the rate of formation of the products is just equal to the rate at which they are being decomposed again to give the initial substances. Representative equations for equilibria which we have studied are:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-,$$
(ionization)

$$NH_4OH + HC_2H_3O_2 \rightleftarrows NH_4^+ + C_2H_3O_2^- + H_2O,$$
(neutralization and hydrolysis)

$$AgC_2H_3O_2 \text{ (solid)} \rightleftarrows Ag^+ + C_2H_3O_2^-.$$
(solubility of salts)

Chemists frequently generalize the idea of an equilibrium process by the equation

$$A + B \rightleftarrows C + D.$$

(3) *A definite mathematical relationship*—which enables one to calculate the concentrations of the various substances present under any desired situation. This relationship, *the law of chemical equilibrium*, is treated in considerable detail in general chemistry texts. We shall review the essential ideas of this law briefly in the following section.

The Equilibrium Constant

In the generalized reaction

$$A + B \underset{2}{\overset{1}{\rightleftarrows}} C + D$$

the rate of reaction of the substance A with the substance B will depend on the number of collisions between molecules of A and molecules of B, and this will be proportional to the concentration of each of the reactants. Thus, the rate, or speed, of the forward reaction may be expressed by the equation

$$S_1 \propto (A)\,(B), \text{ or } S_1 = k_1\,(A)\,(B),$$

where the bracketed symbols represent the concentration in moles per liter, and k_1 is the proportionality constant. Similarly, the speed of the opposing or reverse reaction is expressed by the equation

$$S_2 \propto (C)\,(D), \text{ or } S_2 = k_2\,(C)\,(D).$$

Changes in concentration will take place until the forward and reverse reaction rates become equal, that is, until

$$S_2 = S_1.$$

Therefore, when equilibrium has been attained, we have the relation

$$k_2\,(C)\,(D) = k_1\,(A)\,(B),$$

or rearranging terms,

$$\frac{(C)\,(D)}{(A)\,(B)} = \frac{k_1}{k_2} = K_{equil.}$$

By custom, we always write the products in the numerator, and the reactants in the denominator.

If more than one molecule of a given substance is involved in the equation for a given reaction, that is, if 1 A reacts with 2 B to form the molecule AB_2, it is evident that the number of collisions per second which occur in the formation of the intermediate substance AB will be proportional to the concentrations of A and of B. The rate of formation of AB_2 must then depend on the chance of collision of this intermediate AB with molecules of B a *second* time. The rate of formation of AB_2 will therefore be proportional to the first power of

A, and to the *square* of B. The equilibrium constant expression for the equilibrium

$$A + 2\,B \rightleftarrows AB_2$$

is, therefore,

$$\frac{(AB_2)}{(A)\,(B)^2} = K.$$

In general, *the concentration of a substance must be raised to the same power as its coefficient in the equation for the reaction.*[1]

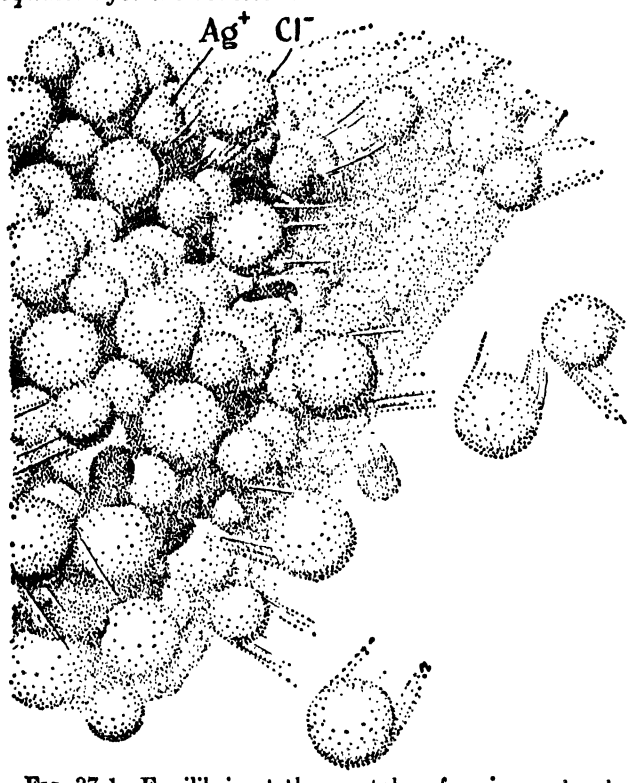


FIG. 37-1. Equilibria at the crystal surface in a saturated silver chloride solution. Silver ions and chloride ions are leaving the crystal surface and returning to it at equal, opposing rates.

The Solubility Product Law

With slightly soluble substances, we have the equilibrium of a solid salt with its ions in solution. In this case, the equilibrium constant expression may be expressed in a simplified form—called the solubility product law. For example, we may write

$$A_2B_3(\text{solid}) \rightleftarrows 2\,A^{+++} + 3\,B^{--}.$$

The equilibrium constant expression for this would be

$$\frac{(A^{+++})^2(B^{--})^3}{(A_2B_3)} = k_1$$

However, the factor (A_2B_3) is practically a constant, for its "activity," which depends on its rate of solution per unit surface, is practically constant. We therefore have the simplified expression

$$(A^{+++})^2(B^{--})^3 = k_1\,(A_2B_3) = K. \quad \text{(At saturation).}$$

The solubility product law thus states that in a saturated solution of a slightly soluble substance, the product of the concentration of the ions of the salt (each raised to its proper power, corresponding to its subscript in the molecular formula) is a constant. A salt is less soluble in the presence of an excess of either of its ions than it is in pure water. This so-called *common ion effect* was observed qualitatively in Experiment 24, paragraph 2A, for a saturated solution of silver acetate.

The Effect of High Ionic Concentration on Equilibrium

The law of chemical equilibrium applies with quantitative precision only in cases where we have a low total concentration of ions in the solution. In a solution which contains many ions, each charged particle mutually affects every other nearby charged particle, with the result that the ions are thus retarded to some extent in their movements. This is sometimes called a "drag effect." As a consequence, the ions are less "active," and behave as if they were at a lower concentration than would be the case if they were largely surrounded by neutral molecules.

A high concentration of *any* ions in the solution therefore affects the solubility of a slightly soluble salt, and, in general, tends to make it more soluble. Thus, as in this experiment, while sodium nitrate contains no ions in common with those of silver acetate, we find that the latter is somewhat more soluble in a sodium nitrate solution than in pure water. Even in a strong sodium acetate solution, where the common ion will cause a decrease in solubility of silver acetate, this decrease is not as great as the solubility product law would predict. This effect was formerly called the "salt effect," and is now explained by the *Debye-Hückel theory*, which applies the law of chemical equilibrium to strong electrolytes by substituting a corrected concentration, known as the "activity," for the molarity. This takes account of the electric charge and the concentration of all ions in the solution.

Supersaturation

The formation of a saturated solution involves

[1] For a discussion of reaction rates and for a more thorough development of the general equation for the equilibrium constant, see also Chapter 19 in your text.

the establishment of an equilibrium between the ions in solution and the crystal surface of the solid. It sometimes happens that, although the concentration of the ions gives an ion-product somewhat greater than the solubility product for that substance, no precipitate forms. This is explained by the fact that there is no solid present to which the ions may attach themselves and also because the formation of the first bit of solid crystal is a more difficult process than the further growth of the crystal. The difficulty usually can be overcome by shaking, or by "seeding" the solution with a small crystal of the solid substance. In this experiment the methods used are favorable for the existence of supersaturated solutions, and it will be instructive to study their behavior.

Experimental Method

We shall test the solubility product relationship quantitatively for the same salt used before, namely silver acetate. As an optional experiment, you may also test the relationship for a saturated solution of lead chloride ($PbCl_2$). This will give opportunity to show the necessity of squaring the chloride ion concentration in order to obtain a constant.

We shall mix measured volumes of 0.2 formal solutions of silver nitrate and of sodium acetate in several different proportions. The concentrations of silver ion and of acetate ion have been arbitrarily chosen so that, in the mixture which results, their product, $(Ag^+) \times (C_2H_3O_2^-)$, is greater than the solubility product for silver acetate. Consequently, solid silver acetate will separate out until the above ion-product is reduced to the value it always has when the equilibrium

$$AgC_2H_3O_2 \text{ (solid)} \rightleftharpoons Ag^+ + C_2H_3O_2^-$$

is established. We shall then determine the silver ion concentration in this solution by titration with 0.1 *N* potassium thiocyanate (KCNS) solution, using a ferric alum indicator. In this titration, the very insoluble silver thiocyanate (AgCNS) is precipitated. As soon as the end-point is reached and an excess of thiocyanate ion (CNS^-) can remain in solution, the blood red ferric thiocyanate ion ($FeCNS^{++}$) is formed. If we know the silver ion concentration at equilibrium, and the total number of moles of silver ion and of acetate ion mixed in a known volume at the start, we can calculate the acetate ion concentration, and hence the solubility product constant

$$(Ag^+)\,(C_2H_3O_2^-) = K_{AgC_2H_3O_2}.$$

Experimental Procedure

Special supplies: 1 burette.

Chemicals: carefully prepared solutions of 0.2 *F* $AgNO_3$, 0.2 *F* $NaC_2H_3O_2$, 0.2 *F* $Pb(NO_3)_2$, and 0.4 *F* NH_4Cl. Standardized solutions of 0.1 *N* KCNS, 0.1 *N* $AgNO_3$. Indicators of ferric alum, and 1 *F* K_2CrO_4.

1. The Solubility Product of Silver Acetate. Obtain about 130 ml each of the specially prepared solutions of 0.2 *F* $AgNO_3$, and 0.2 *F* $NaC_2H_3O_2$, in dry beakers or dry flasks. By *careful* measurement with a graduated cylinder, prepare the four mixtures listed below. In each case, place the solutions in dry, numbered 250-ml flasks. Stopper these to avoid evaporation, especially if they are to be left overnight.

Mixture No.								
1	Use 20.0 ml	0.200 *F*	$AgNO_3$	+ 40.0 ml	0.200 *F*	$NaC_2H_3O_2$
2	" 30.0 "	"	"	+ 30.0 "	"	"
3	" 35.0 "	"	"	+ 25.0 "	"	"
4	" 40.0 "	"	"	+ 20.0 "	"	"

The mixtures, which contain an excess of Ag^+ and $C_2H_3O_2^-$, may remain supersaturated for a while. If necessary, they may be seeded with a small crystal of solid silver acetate to induce crystallization. Mix these, or shake gently at intervals for at least 30 minutes *after the precipitation appears to be complete*, in order to give time for the establishment of the equilibrium. A longer time is desirable. If convenient, it is well to let these mixtures stand overnight, although this is not essential.

Clean a burette, rinse it with tap water, then with a 5-ml portion of distilled water, and finally with two 5-ml portions of a standardized 0.100 *N* potassium thiocyanate solution (KCNS), letting some run through the tip. Finally, fill the burette with the KCNS solution. Use a dry filter and funnel to filter your mixture No. 1 into a dry 250-ml beaker. Accurately measure out 25.0 ml of the filtrate, using a 50-ml graduate which you have rinsed with a little of the solution. Place this solution in a beaker which contains a stirring rod, for

the titration. Add 1 ml of a saturated ferric alum solution as indicator, and 1 ml of 6 *F* HNO_3. If the red color due to the hydrolysis of Fe^{+++} is not dispelled completely, add a little more HNO_3. Titrate the solution to the first permanent appearance of red color due to the formation of $Fe(CNS)^{++}$. You may need to add another drop or two after you have apparently reached the end-point, as the Ag^+ ion is partially absorbed in the precipitated AgCNS, and is slow in reacting. Repeat the titration with a second 25.0-ml sample from this same filtrate if your results seem at all uncertain. Filter and analyze the other three mixtures for the concentration of Ag^+ in a similar manner. You can have the next mixture filtering while titrating the preceding sample.

Calculations. Find the concentration of acetate ion in each mixture by calculating successively the various items called for from (a) to (g) under the calculated data section in the report sheet. Study through these items first, so that you understand what you are calculating, and why each step is needed. Finally, calculate the solubility product, $K_{AgC_2H_3O_2}$, by multiplying the experimentally determined Ag^+ concentration by the calculated $C_2H_3O_2^-$ concentration. Carry out all calculations (a) to (g) to three significant figures, and the final solubility product, $K_{AgC_2H_3O_2}$, to two significant figures.

2. The Solubility Product of Lead Chloride. (Optional.) This experiment provides a more rigorout test of the solubility product law, than the $AgC_2H_3O_2$ equilibrium does, since here we have 2 Cl^- to 1 Pb^{++} and, therefore, the constant involves the square of the Cl^- concentration. The determination may be carried out by the same general method as was used for the silver acetate. Obtain about 130 ml each of the specially prepared 0.2 *F* $Pb(NO_3)_2$ and 0.4 *F* NH_4Cl solutions, in dry beakers. Use these to prepare the following carefully measured mixtures:

Mixture No.									
1	Use 20.0 ml	0.200*F* $Pb(NO_3)_2$	+ 40.0 ml	0.400*F* NH_4Cl	+ 20.0 ml H_2O[1]
2	" 25.0 "	" "	+ 35.0 "	" "	+ 20.0 " "
3	" 30.0 "	" "	+ 30.0 "	" "	+ 20.0 " "
4	" 35.0 "	" "	+ 25.0 "	" "	+ 20.0 " "

[1] Do not add the 20 ml of distilled water until after a precipitate starts to form, thus avoiding the tendency to form a rather stable supersaturated solution in some cases.

The mixtures (80 ml in all) must be kept in stoppered flasks to avoid evaporation, if they are to be left overnight. Shake them gently, at intervals, for at least 30 minutes after the precipitation appears to be complete, to allow time for the establishment of equilibrium.

This time we shall determine the concentration of the Cl^- by titration with a standard 0.1000 *N* $AgNO_3$ solution. Clean, rinse, and fill a burette with this standard $AgNO_3$ solution. Filter the mixtures, using a dry filter paper and dry receiving vessel. Measure 25-ml portions of the filtrates carefully with a graduate, and titrate with the $AgNO_3$ solution. The indicator to be used this time is a 1 *F* K_2CrO_4 solution. The first indicator added will, of course, precipitate the very insoluble $PbCrO_4$, so it is necessary to use enough indicator so that about 1 ml will be present after the Pb^{++} is all precipitated. This will require about 1.5 ml of 1 *F* K_2CrO_4 for mixture No. 1, increasing to 5 ml for mixture No. 4. In the titration AgCl precipitates until the end-point is reached, when, as soon as excess Ag^+ appears, the slightly more soluble Ag_2CrO_4 separates as a red precipitate. The end-point is then the first permanent appearance of a slightly reddish cast to the yellow mixture. If a momentary red color does not appear where the $AgNO_3$ from the burette strikes the solution, insufficient indicator is present.

Calculations. Prepare your own report sheet, in neat order, for this part of the experiment. You can model it after the form given for silver acetate. However, note that we are determining the Cl^- directly by titration this time, not the positive ion. Also note that the number of moles of solid $PbCl_2$ which precipitates out will be one-half the difference between the total moles of chloride in the 80-ml mixture and the moles of Cl^- (dissolved) in the solution. The total moles of Pb^{++} (dissolved) can then be calculated as the difference between the total moles of Pb^{++} in the mixture and the moles of $PbCl_2$ precipitated out. From this the concentration of Pb^{++}, and the solubility product, $(Pb^{++}) \times (Cl^-)^2$, can be calculated. As a comparison, show also on your report sheet the calculation for the simple ion-product, $(Pb^{++}) \times (Cl^-)$. Which calculation shows the best constant?

REPORT: Exp. 37

Equilibria of Slightly Soluble Salts

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. The Solubility Product of Silver Acetate

DATA	*1*	*2*	*3*	*4*
Volume of 0.200 *F* $AgNO_3$ (ml)	20.0	30.0	35.0	40.0
Volume of 0.200 *F* $NaC_2H_3O_2$ (ml)	40.0	30.0	25.0	20.0
Total volume of the mixture (ml)	60.0	60.0	60.0	60.0
Volume of mixture titrated				
Volume 0.100 *N* KCNS required for the titration				

CALCULATIONS[1]					
a) Total moles Ag^+ added in preparing each mixture					
b) Total moles $C_2H_3O_2^-$ added in preparing each mixture					
c) Concentration of Ag^+ at equilibrium with solid $AgC_2H_3O_2$					
d) Total moles Ag^+ (dissolved) in total volume of mixture					
e) Total moles of solid $AgC_2H_3O_2$ precipitated out. (a-d)					
f) Total moles $C_2H_3O_2^-$ (dissolved) in total mixture. (b-e)					
g) Concentration of $C_2H_3O_2^-$ at equilibrium with solid $AgC_2H_3O_2$					
h) The solubility-product, $K_{AgC_2H_3O_2} = (Ag^+) \times (C_2H_3O_2^-)$					

[1] Show details of calculation for the first mixture only, where there is not space for all.

Exercises

1. Look up the solubilities of silver acetate and of lead chloride at 20° C, in grams per 100 ml of water, in a reference source, and record the values below.

Reference source: _____

(a) The solubility of silver acetate, at 20° C, is: _____ g/100 ml
Calculate its solubility product.[1]

$K_{AgC_2H_3O_2}$ = _____

(b) The solubility of lead chloride, at 20° C, is: _____ g/100 ml
Calculate its solubility product.

K_{PbCl_2} = _____

2. How do these values compare with your own experimental values? If your values are slightly larger, can you suggest a reason?

3. Why, in making a qualitative test based on the formation of a precipitate, should one generally allow some time, and shake the test solution, before deciding that the substance tested for is absent?

[1] Remember that concentrations are always expressed in moles per liter in calculating solubility products. Why? See also Examples 1 and 2, Page 280.

The Equilibria of Carbonic Acid and Its Salts

38

College Chemistry, Chapters 21, 7

Review of Fundamental Concepts

This experiment will help you to understand the principles involved in the behavior of a typical weak, dibasic acid, such as carbonic acid, and its salts, and will enable you to apply these principles to similar situations. Our study will be both experimental and theoretical from the equilibrium equations. We shall determine the principal ionic and molecular substances present in solutions of CO_2 and H_2CO_3, $NaHCO_3$ and Na_2CO_3, and $Ca(HCO_3)_2$ and $CaCO_3$.

These are all important substances. Carbon dioxide and carbonic acid are important in the beverage industry and in *p*H control; sodium hydrogen carbonate and sodium carbonate are important as baking soda and washing soda respectively, and as cheap alkaline chemicals for industrial use; calcium hydrogen carbonate and calcium carbonate are important in hard water and its softening, in the formation of limestone caves and other limestone deposits, in the lime and cement industries, and as an alkaline flux in metallurgical processes.

As a basis for this study, we shall give below the fundamental equilibrium relationships involved.

$$CO_2\,(aq) + H_2O \rightleftarrows H_2CO_3\,(aq).$$

The position of this equilibrium in solution is difficult to measure, and is not important here, for the total number of moles of solute, whether as CO_2 or as H_2CO_3, is the same. In the following treatment all the dissolved carbon dioxide is written as carbonic acid.

As a weak acid, carbonic acid ionizes in steps, as follows:

(1) $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 4.5 \times 10^{-7}$$

(2) $HCO_3^- \rightleftarrows H^+ + CO_3^{--}$

$$K_2 = \frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = 6 \times 10^{-11}.$$

More detailed comment on these equations is given in the experimental procedure.

Experimental Procedure

Special supplies: thistle tube.

Chemicals: $CaCO_3$ (marble chips), $NaHCO_3$ solid, $Ca(OH)_2$ (sat. sol.), 0.1 *F* $CaCl_2$, 1 *F* $NaHCO_3$ (freshly prepared), 1 *F* Na_2CO_3, 0.1 *F* NaOH, *p*H 8 and *p*H 11 buffer solutions, and indicator solutions: methyl orange, bromthymol blue, phenol red, phenolphthalein, alizarin yellow R, and indigo carmine.

1. *Carbonic acid.* Prepare a simple carbon dioxide generator, similar to that illustrated in Fig. 13-1. The Erlenmeyer flask contains about 5 grams of marble chips and 10 ml H_2O, and is fitted with a thistle tube and a gas delivery tube to which are attached a length of rubber tubing and a 15-cm length of glass tubing. Add concentrated HCl through the thistle tube, a few milliliters at a time, as needed, when you wish to generate CO_2 gas.

Prepare a saturated CO_2 solution by bubbling the gas through about 20 ml of distilled water in a 15-cm test tube. We shall determine the approximate relative concentrations of H_2CO_3, H^+, HCO_3^-, and CO_3^{--} in this solution, as follows:

(a) From the solubility data in Appendix II, Table IX, calculate the total formality of dissolved CO_2. Record this all as formality of H_2CO_3. (Recall that 1 mole of CO_2 gas at 20° C would equal 22,400 ml × 293/273 = 24,000 ml.)

(b) Determine the approximate H^+ concentration in this saturated solution by testing a 5-ml portion with methyl orange indicator.

(c) Add 3 ml of 0.1 *F* $CaCl_2$ to a 3-ml portion of the saturated CO_2 solution. If you are not satisfied with the result, bubble more CO_2 into the solution to saturate it. From this result, and by calculation from the solubility product for $CaCO_3$ (Table XV in Appendix II), estimate the maximum CO_3^{--} concentration in saturated CO_2 solution. (It is actually considerably less than this.) From the results of paragraphs (a) and (b), and from the ionization equations for H_2CO_3, how will the

HCO_3^- concentration compare with that of H^+ and of CO_3^{--}?

2. *Sodium hydrogen carbonate.* As a salt, this substance will be completely ionized in solution into Na^+ and HCO_3^-. The HCO_3^- can ionize further into H^+ and CO_3^{--}, according to equation 2 for the ionization of H_2CO_3, and it also can hydrolyze, because H_2CO_3 is a weak acid, as experimentally determined in paragraph (a) above.

Determine the approximate *p*H of a freshly prepared 1 *F* $NaHCO_3$ solution, by testing 5-ml portions with bromthymol blue, phenol red, and phenolphthalein indicators (or recall the results of Experiment 34, paragraph 4). You may compare the colors with *p*H 8 buffer solution in case of any doubt. Now utilize this *p*H value and the K_2 value given above for the second step in the ionization of H_2CO_3, to calculate the approximate ratio of (CO_3^{--}) to (HCO_3^-) in 1 *F* $NaHCO_3$. Also estimate the actual approximate concentrations of HCO_3^- and CO_3^{--} in 1 *F* $NaHCO_3$. Would you expect this solution to precipitate $CaCO_3$ when added to 0.1 *F* $CaCl_2$? Try it. (Note the relative amount of any precipitate.)

3. *Sodium carbonate.* This salt will, of course, be completely ionized into Na^+ and CO_3^{--}. The CO_3^{--} will be partially hydrolyzed to HCO_3^-, because HCO_3^- is a very weak acid, as indicated by the second ionization equation for H_2CO_3. In a solution as basic as this, further hydrolysis to H_2CO_3 is practically negligible.

Determine the approximate *p*H of a 1 *F* Na_2CO_3 solution, using alizarin yellow R and indigo carmine indicators (or recall the result of Experiment 34, paragraph 2). In case of any doubt, compare the colors with those obtained from a *p*H 11 buffer and from a *p*H 12 standard prepared by 10-fold dilution of a little 0.1 *F* NaOH. Use this *p*H value and the K_2 value for the ionization of HCO_3^-, to estimate the ratio of (CO_3^{--}) to (HCO_3^-), and the approximate actual concentration of each, in 1 *F* Na_2CO_3. How would you expect the amount of $CaCO_3$ precipitate obtained on mixing 0.1 *F* $CaCl_2$ and 1 *F* Na_2CO_3 to compare with that obtained above with 0.1 *F* $CaCl_2$ and 1 *F* $NaHCO_3$? Try it, using comparable volumes of solutions.

4. *The instability of HCO_3^- solutions.*

(a) Boil about 10 ml of 1 *F* $NaHCO_3$ solution for several minutes. Cool the solution, and again determine the approximate *p*H, using phenolphthalein and alizarin yellow R indicators. Compare this result with that of paragraph 2 above, and explain any change by writing an equation which combines the ionization equation and the hydrolysis equation for HCO_3^-. Consider also the volatility of H_2CO_3.

(b) *Temporarily hard water, and limestone cave formation.* Bubble CO_2 gas from your CO_2 generator through about 10 ml of limewater contained in a 15-cm test tube. Continue this operation as long as any change occurs. Explain fully, by words and by equations: first, why a precipitate forms in this case, when no precipitate resulted from the solution of CO_2 in $CaCl_2$ solution [paragraph 1(c) above]; second, why the precipitate redissolves as the solution becomes saturated with CO_2.

Divide this "temporarily hard water" which you have just prepared into two portions. Boil one portion for several minutes, or until a change occurs; to the other portion add an equal volume of limewater. For each case, explain fully, by words and by equations, the reasons for the changes which you observe.

(c) *Soda ash.* Place 2 or 3 grams of solid $NaHCO_3$ in a test tube which has been fitted with a rubber stopper and a gas delivery tube. Arrange the delivery tube so it is immersed in some limewater contained in a test tube. Heat the $NaHCO_3$ quite hot for a short time.[1] What gas is evolved? Dissolve in distilled water some of the solid which remains, and test it with phenolphthalein indicator. Explain all changes which have occurred and also the significance of the name "soda ash." Much soda ash is manufactured this way by the Solvay soda process.

---

[1] Remove the delivery tube from the limewater before the heating is discontinued.

REPORT: Exp. 38

The Equilibria of Carbonic Acid and Its Salts

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Carbonic Acid

(a) Solubility of CO_2 at 20° C (Appendix II, Table IX) . . . . . _____ l/100 l

Calculation of this as formality:

_____ *F* H_2CO_3

(b) Concentration of hydrogen ion in saturated CO_2 solution:

Methyl orange color_____ _____ *M* H^+

(c) Observed results of adding 0.1 *F* $CaCl_2$ to saturated CO_2 solution . . . _____

Maximum concentration of CO_3^{--} in saturated CO_2 solution, based on the above observation, and the solubility product of $CaCO_3$:

_____ *M* CO_3^{--}

Approximate concentration of HCO_3^- (indicate reasoning):

_____ *M* HCO_3^-

2. Sodium Hydrogen Carbonate

Concentration of hydrogen ion and of hydroxide ion in 1 *F* $NaHCO_3$ (record indicator colors): _____ *M* H^+, _____ *M* OH^-

Rewrite the equation, and the equilibrium constant expression, for the second step in the ionization of H_2CO_3:

_____ $K_2 =$

Concentration of carbonate ion and of hydrogen carbonate ion in 1 *F* $NaHCO_3$ (use this K_2 expression and the above H^+ concentration):

_____ *M* CO_3^{--}

_____ *M* HCO_3^-

_____ *M* Na^+

Comment on your ability to precipitate $CaCO_3$ (and indicate the relative amount of precipitate) from 0.1 *F* $CaCl_2$ and 1 *F* $NaHCO_3$:

3. Sodium Carbonate

Concentration of hydrogen ion and of hydroxide ion in 1 *F* Na_2CO_3 (record indicator colors): _____ *M* H^+, _____ *M* OH^-

Concentration of carbonate ion and of hydrogen carbonate ion in 1 *F* Na_2CO_3 (use this H^+ concentration and the K_2 expression):

_____ *M* CO_3^{--}

_____ *M* HCO_3^-

_____ *M* Na^+

Comment on your ability to precipitate $CaCO_3$ (indicate the relative amount of any precipitate) from 0.1 *F* $CaCl_2$ and 1 *F* Na_2CO_3:

Summarize the data of this experiment by placing, at the appropriate place in the chart at the right, the formulas H_2CO_3, H^+, OH^-, HCO_3^-, CO_3^{--}, and Na^+, for each of the solutions indicated.

	sat. H_2CO_3	*1 F* $NaHCO_3$	*1 F* Na_2CO_3
High conc.			
Mod. conc.			
Low conc.			
Very low conc.			

4. The Instability of HCO_3^-

(a) Approximate concentration of hydrogen ion and of hydroxide ion in 1 *F* $NaHCO_3$ after boiling the solution (record indicator colors):

_____ *M* H^+, _____ *M* OH^-

Explain the above behavior, both by words and by the equations for the ionization and hydrolysis of HCO_3^-:

(b) *Temporarily hard water. Limestone cave formation.* Explain, both by words and by equations, all the results you observe as the limewater solution is saturated with CO_2:

Account for the difference in behavior of CO_2 with $Ca(OH)_2$ solution and with $CaCl_2$ solution:

Explain, both by words and by equations, the results obtained when the "temporarily hard water" is boiled:

is treated with additional $Ca(OH)_2$:

Correlate the above results with the solution of limestone rock and the formation of stalactites in limestone caves:

(c) *Soda ash.* Explain, both by words and by equations, all the results you observe when solid $NaHCO_3$ is heated. Account also for the name "soda ash":

Recapitulation of Problems on Ionic Equilibria

College Chemistry, Chapters 19, 20, 21

A Study Assignment

After studying Experiment 36 on the Equilibrium Constant and Experiment 37 on the Solubility Product, you may have gained the impression that here we have a means of determining by mathematical calculation the exact concentrations of the several substances present in equilibrium with one another. In any solution containing a considerable concentration of ions, this may be far from the truth. Furthermore, it is not always easy to determine the exact concentration of a particular molecular or ionic species because of hydrolysis, complex ion formation, amphoteric behavior, and similar phenomena.

The calculated concentrations, based on the mathematical equations for the equilibrium constant and solubility product, give idealized results which might be expected if the interionic attractions were negligible, and if there were no other complicating equilibria. With very dilute solutions one obtains quite satisfactory agreement between the experimental and the calculated values.

The mathematical equations would be exact if we used "activities" instead of concentrations. The activity is obtained by multiplying the concentration by a corrective factor, called the "activity coefficient." This latter factor is not constant for a given ion but depends on the total concentration of all the ions in the solution, and on their valence type. In this manual we shall simplify our study of the principles involved by using the simple concentrations of the ions.

In spite of these limitations, the quantitative study of equilibrium conditions by means of the theoretical equilibrium constant expressions serves as a very valuable tool in chemical reasoning. You will do well to become familiar with the methods involved in such calculations.

Typical Problems Involving Ionization Constants

Example 1. A 0.01 *F* formic acid ($HCHO_2$) solution is found by electrical conductivity measurements to be 13.2% ionized. What is its ionization constant?

The equilibrium expressions are

$$HCHO_2 \rightleftarrows H^+ + CHO_2^-, \quad \text{and } K = \frac{(H^+)\,(CHO_2^-)}{(HCHO_2)}.$$

The hydrogen ion concentration, (H^+), will be 13.2% of 0.01 *F*, or 0.00132 *M* H^+. The formate ion concentration, (CHO_2^-), will also be 0.00132 *M* CHO_2^-. The un-ionized formic acid concentration, $(HCHO_2)$ will be $0.01 - 0.00132 = 0.00868$ *M* $HCHO_2$. Therefore

$$K = \frac{(H^+)\,(CHO_2^-)}{(HCHO_2)} = \frac{(0.00132)\,(0.00132)}{(0.00868)} = 2 \times 10^{-4}.$$

Example 2. If the ionization constant for formic acid is 2×10^{-4}, what is the hydrogen ion concentration, and what is the degree of ionization, of a 0.1 *F* formic acid solution?

Given

$$\frac{(H^+)\,(CHO_2^-)}{(HCHO_2)} = 2 \times 10^{-4}.$$

Let $x = (H^+) = (CHO_2^-)$. Then $0.1 - x = (HCHO_2)$.

Substituting in the formula, we write

$$\frac{(x)\,(x)}{(0.1 - x)} = 2 \times 10^{-4}.$$

This is a quadratic equation. Our solution will be much simplified if we note that the value of x will be small as compared to the total concentration (0.1), so that $(0.1 - x)$ is approximately equal to (0.1). Making this simplification, we have

$$\frac{(x)\,(x)}{(0.1)} = 2 \times 10^{-4},$$

$$x^2 = 2 \times 10^{-5} = 20 \times 10^{-6},$$

$$x = 4.5 \times 10^{-3}, \text{ or } 0.0045\ M\ H^+.$$

If the 0.1 *F* $HCHO_2$ were completely ionized, the hydrogen ion concentration would have been 0.1 *M* H^+, so that the fraction ionized is

$$\frac{0.0045}{0.1} = 0.045, \text{ or } 4.5\%.$$

Comparing this value with the 13.2% ionization in 0.01 *F* formic acid, we see that the equilibrium constant expression requires that the degree of ionization increase with the dilution. This fact was observed experimentally in Experiment 26.

Example 3. Calculate the hydrogen ion concentration in a buffer mixture which contains 0.1 formula weight of formic acid ($HCHO_2$) and 0.2 formula weight of sodium formate ($NaCHO_2$) in a liter of solution.

Given:

$$HCHO_2 \rightleftarrows H^+ + CHO_2^-, \text{ and } \frac{(H^+)\,(CHO_2^-)}{(HCHO_2)} = 2 \times 10^{-4}.$$

Let $x = (H^+)$, then $(x + 0.2) = (CHO_2^-)$, and $(0.1 - x) = (HCHO_2)$.

Note, in the above expression for the formate ion concentration, that x moles come from the ionization of the formic acid, and 0.2 mole comes from the 100% ionization of the sodium formate.

Substituting these values in the equilibrium constant expression,

$$\frac{(H^+)\,(CHO_2^-)}{(HCHO_2)} = \frac{(x)\,(x + 0.2)}{(0.1 - x)} = 2 \times 10^{-4}.$$

Now, due to the common ion effect, (H^+) will be even smaller than it is in a formic acid solution alone, so we may neglect the x in $(x + 0.2)$, and also in $(0.1 - x)$. The expression then simplifies to

$$\frac{(x)\,(0.2)}{(0.1)} = 2 \times 10^{-4},$$

$$x = 1 \times 10^{-4}\ M\ H^+.$$

Thus, we see that the addition of 0.2 formula weight of sodium formate per liter to the 0.1 *F* formic acid solution reduces the hydrogen ion concentration from 0.0045 *M* to 0.0001 *M* H^+.

Problems Involving Ionization Constants[1]

Note. Be systematic and use a good form in setting up and in solving problems. This is just as important as getting the right answer.

1. Calculate the ionization constant for each of the following from the data given:

(a) 0.1 *F* HNO_2 is 6.5% ionized.

(b) 0.01 *F* NH_4OH is 4.15% ionized.

(c) A 1 *F* solution of H_3PO_4 has a H^+ concentration of about 0.083 *M*. Assuming that this H^+ all comes from the first stage of ionization, calculate K_1.

2. Use the ionization constants given in Table XIV, App. II, to calculate the H^+ concentration in each of the following:

(a) 0.5 *F* H_3BO_3 (eye wash solution)

(b) 0.1 *F* H_2CO_3 (a carbonated beverage at the soda fountain. Use K_1 only.)

(c) Vinegar. Assume it is 5% $HC_2H_3O_2$ and has a density of approximately 1.0. Calculate the molarity first.

3. Use the ionization constant of NH_4OH given in the table to calculate the OH^- concentration and also the degree of ionization, for:

(a) 1 *F* NH_4OH

(b) 0.1 *F* NH_4OH

(c) 0.01 *F* NH_4OH

4. (a) 15 grams of acetic acid is dissolved to make a liter of solution. What is the H^+ concentration, and the $C_2H_3O_2^-$ concentration?

(b) 15 grams of sodium acetate is dissolved in the solution formed in problem 4(a). Now what is the H^+ concentration, and the $C_2H_3O_2^-$ concentration? (Assume no change in volume.)

5. 4 grams of NH_4Cl is added to 100 ml of 0.1 *F* NH_4OH solution. What is the OH^- concentration? (Special problem: Calculate the *p*H of this solution See Exp. 34.)

6. It is desired to make a solution having a H^+ concentration of 10^{-5} *M*. How many grams of sodium acetate must be added to 250 ml of 0.1 *F* $HC_2H_3O_2$ to do this?

7. 400 ml of 0.5 *F* $HC_2H_3O_2$ and 600 ml of 0.2 *F* NaOH are mixed. What is the resulting H^+ concentration? (Hint: First calculate the formality of the $HC_2H_3O_2$, and of the $NaC_2H_3O_2$ formed, in the final mixture.)

Typical Problems Involving Solubility Products

Example 1. The solubility of silver bromide at room temperature is about 1.2×10^{-5} grams per 100 ml H_2O. Calculate its solubility product, $(Ag^+)\,(Br^-) = K_{AgBr}$.

From the formula weight of AgBr, 188, we may first calculate its formality:

$$\frac{(1.2 \times 10^{-5} \times 10)\ g/l}{188\ g/gfw} = 6.4 \times 10^{-7}\ F\ AgBr.$$

Since we regard salts as 100% ionized, thus $AgBr \longrightarrow Ag^+ + Br^-$,

$$(Ag^+) = (Br^-) = 6.4 \times 10^{-7}\ M.$$

The solubility product is, therefore,

$$(Ag^+)\,(Br^-) = (6.4 \times 10^{-7})\,(6.4 \times 10^{-7})$$
$$= 40 \times 10^{-14} = 4 \times 10^{-13} = K_{AgBr}.$$

Example 2. Consider the case of a substance of different valence type, such as $Ca(OH)_2$. For this

[1] Some of these problems, as well as some of those in the following set, may advantageously be left for assignment until similar situations are encountered in the qualitative procedures, Experiments 39–44.

the solubility is 0.161 grams per 100 ml H_2O. Let us calculate the solubility product.[1]

We first calculate the formality of the saturated solution:

$$\frac{(0.161 \times 10)\ g/l}{74\ g/gfw} = 0.0218\ F\ Ca(OH)_2.$$

Noting that the ionization of this would give one Ca^{++}, but *two* OH^-,

$$Ca(OH)_2 \rightleftarrows Ca^{++} + 2\ OH^-,$$

we have

$$(Ca^{++}) = 0.0218\ M$$
$$(OH^-) = 2 \times 0.0218\ M = 0.0436\ M$$

and the solubility product would be calculated thus:

$$(Ca^{++})\ (OH^-)^2 = (0.0218)\ (0.0436)^2 = 4 \times 10^{-5}.$$

Note that to get the (OH^-), we double the total formality of the compound, and then we square the (OH^-) according to the solubility product formula. We do *not* double the (OH^-), and then square that.

Example 3. Suppose we have given the solubility product of $Mg(OH)_2$ as 6×10^{-12}. How many grams of $Mg(OH)_2$ will dissolve in 100 ml of water?

$$(Mg^{++})\ (OH^-)^2 = 6 \times 10^{-12}.$$

Let x = (Mg^{++}) in the saturated solution,
then 2x = (OH^-).

Substituting in the solubility product expression,

$$(x)\ (2x)^2 = 6 \times 10^{-12}$$
$$4x^3 = 6 \times 10^{-12}$$
$$x^3 = 1.5 \times 10^{-12}$$
$$x = 1.14 \times 10^{-4}\ M\ Mg^{++}, \text{ or } 1.14 \times 10^{-4}\ F\ Mg(OH)_2.$$

The weight of $Mg(OH)_2$ = $(1.14 \times 10^{-4} \times 58)$ g/liter, or 7×10^{-3} g/liter
= 7×10^{-4} grams $Mg(OH)_2$ per 100 ml.

Note: The above example is a somewhat complicated type. For a simple univalent salt, such as AgCl, letting x = (Ag^+) = (Cl^-), we would simply have $x^2 = K_{AgCl}$.

Example 4. How many grams of $SrSO_4$ will dissolve in 5.0 liters of 0.01 F $SrCl_2$ solution?

From the Table of Solubility Products,

$$(Sr^{++})\ (SO_4^{--}) = 2.8 \times 10^{-7}.$$

Let x = the formula weights of $SrSO_4$ which dissolve, then x = (SO_4^{--}), and $(0.01 + x) = (Sr^{++})$. Substituting in the solubility product expression, we have

$$(0.01 + x)\ (x) = 2.8 \times 10^{-7}.$$

Since the quantity $(0.01 + x)$ does not differ materially from 0.01, we write as an approximation

$$(0.01)\ (x) = 2.8 \times 10^{-7},$$
$$(x) = 2.8 \times 10^{-5}\ F\ SrSO_4.$$

The weight of $SrSO_4$ in 5.0 liters = $(2.8 \times 10^{-5} \times 183.6)$ g/l $\times 5.01$
= 0.026 g $SrSO_4$.

Example 5. (Theory of Fractional Crystallization). To a solution which contains Cl^- and Br^- each at a concentration of 0.1 M, add silver nitrate solution. Which salt will crystallize first, and under what conditions can the other salt crystallize?

By noting the relative size of the solubility products:

$$(Ag^+)\ (Cl^-) = 1.6 \times 10^{-10}$$
$$\text{and } (Ag^+)\ (Br^-) = 4 \times 10^{-13}$$

it is obvious that only AgBr solid will separate first. The (Ag^+) cannot rise high enough to precipitate AgCl, as long as considerable Br^- remains in solution. For both precipitates to co-exist in equilibrium at the same time, the (Ag^+) would be the same for both (since there is only one solution). We may thus divide one solubility product expression by the other, cancelling out (Ag^+):

$$\frac{(Ag^+)\ (Cl^-)}{(Ag^+)\ (Br^-)} = \frac{(Cl^-)}{(Br^-)} = \frac{1.6 \times 10^{-10}}{4 \times 10^{-13}} = 400.$$

Thus, the chloride ion concentration will be 400 times that of the bromide ion. If the (Cl^-) were 0.1 M, no AgCl would precipitate until the (Br^-) were reduced to

$$\frac{1}{400} \times 0.1\ M = 2.5 \times 10^{-4}\ M\ Br^-,$$

which thus allows the silver ion concentration to increase sufficiently to precipitate AgCl.

Problems Involving Solubility Products[2]

8. Calculate the solubility products for each of the following difficultly soluble salts, from the

[1] For compounds of polyvalent ions such as Ca^{++}, and Mg^{++} in Example 3, it is likely that at least the intermediate ion $Ca(OH)^-$ is poorly ionized, so that the equation, $Ca(OH)_2 \rightleftarrows Ca^{++} + 2\ OH^-$, does not completely describe the equilibrium. Likewise, the activity of the ions is considerably less than their concentration. For reasons of simplicity, such factors are neglected here, and the calculated solubility products are larger than they should be.

[2] Some lack of agreement between your answers and the solubility products or solubility data given in the literature is accounted for in part by the fact that your calculations are based on concentrations, rather than activities.

solubility in grams per 100 ml of water as given below:

(a) AgCl 1.8×10^{-4} (c) PbI_2 6.4×10^{-3}
(b) $PbSO_4$ 4.1×10^{-3} (d) Ag_2CrO_4 2.6×10^{-3}

9. Calculate the solubility of each of the following, in grams per 100 ml of water. See Table XV, Solubility Products, Appendix II, for the necessary data.

(a) AgI (c) $BaSO_4$
(b) Ag_2SO_4 (d) $Fe(OH)_3$

10. How many grams of silver acetate will dissolve in

(a) 100 ml of 0.1 *F* $NaC_2H_3O_2$?
(b) 100 ml of 0.1 *F* $Ca(C_2H_3O_2)_2$?

11. If solid sodium sulfide, Na_2S, is added gradually to a solution containing 0.01 mole of Pb^{++} and 0.01 mole of Zn^{++} per liter,

(a) What is the sulfide ion concentration when solid PbS begins to precipitate?

(b) What is the sulfide ion concentration when solid ZnS begins to precipitate?

(c) What is the concentration of the remaining Pb^{++} when the ZnS begins to precipitate?

12. How many formula weights of $BaSO_4$ will dissolve in a liter of

(a) pure water (d) 0.1 *F* NaCl
(b) 0.01 *F* Na_2SO_4 (e) 10^{-5} *F* Na_2SO_4 (Use
(c) 0.1 *F* $BaCl_2$ the quadratic equation in this case. Why?)

13. Given a 0.1 *F* $MgSO_4$ solution, calculate the hydroxide ion concentration necessary to precipitate $Mg(OH)_2$. Also calculate the *p*H of the solution.

14. What concentration of oxalate ion, $C_2O_4^{--}$, is necessary to precipitate CaC_2O_4 from a saturated solution of $CaSO_4$?

15. A liter of solution contains 0.1 *M* Ag^+ and 0.1 *M* Ba^{++}. If a strong K_2CrO_4 solution is added drop by drop, which will precipitate first, Ag_2CrO_4 or $BaCrO_4$? Show calculations.

16. Suppose the above solution, question 15, contained Ag^+ and Ba^{++}, each at 0.001 *M* concentration. Now, which will precipitate first, Ag_2CrO_4 or $BaCrO_4$, as K_2CrO_4 solution is added? Show calculations.

Problems Involving Both Ionization Constants and Solubility Products

17. A solution contains 1 *F* NH_4OH and 1 *F* NH_4Cl. What is the maximum concentration of Mg^{++} which could be present in such a solution without precipitating $Mg(OH)_2$? (Hint: Calculate the (OH^-) first.)

18. How many grams of NH_4Cl should be added to 50 ml of 0.2 *F* NH_4OH to just prevent precipitation when this solution is added to an equal volume of 0.2 *F* $MgCl_2$?

19. A solution containing cadmium chloride, $CdCl_2$, is saturated with H_2S, and the precipitated CdS is filtered out. The concentration of H^+ is found to be 0.5 *M*. What is the concentration of Cd^{++} which remains in the solution? (Hint: Multiply the equilibrium constant expressions for the first and second stages of ionization of H_2S together, to get the relation for the equilibrium of $H_2S = 2\ H^+ + S^{--}$. See Experiment 41, for a fuller discussion of this. Calculate the sulfide ion concentration, and finally the cadmium ion concentration.)

20. A solution is prepared by dissolving 6.3 grams of oxalic acid crystals (0.05 gfw) in 100 ml of 2 *F* HCl. How many grams of solid $CaCl_2$ could be dissolved in this solution without precipitating calcium oxalate? (See the hint in Prob. 19 above.)

21. To what value must the concentration of the hydrogen ion in a 0.1 *F* $FeCl_2$ solution be adjusted, in order to just prevent the precipitation of ferrous sulfide (FeS) when hydrogen sulfide gas is passed into the solution? (See the hint in Prob. 19.)

The Negative Ions—Qualitative Tests 39

College Chemistry, Chapters 13, 14, 15, 16

Review of Fundamental Concepts

As a background for your study of the behavior of, and of tests for, the common negative ions and their acids and salts, the Appendix II will provide useful information, with which you should become thoroughly familiar: Table XI, on the relative strength of various acids; Table VII, on the relative volatility of various acids; and Table X, on the general solubility rules for salts and hydroxides.

Typical Reactions of Common Anions

The identification of negative ions in a sample generally depends on the establishment of one or more of the several types of equilibria which we have studied. These involve the formation of weak acids, volatile acids, insoluble salts, or complex ions. While we have tested for several of these ions in previous experiments, we must now consider the principles on which these tests are based.

Sulfate Ion. This ion is the anion of a *strong acid:* it forms characteristic precipitates with certain metal ions, as with barium ion:

$$Ba^{++} + SO_4^{--} \rightleftarrows BaSO_4\ (s).$$

Other anions also form insoluble precipitates with barium ion:

$$Ba^{++} + CO_3^{--} \rightleftarrows BaCO_3$$
$$Ba^{++} + SO_3^{--} \rightleftarrows BaSO_3$$
$$3\ Ba^{++} + 2\ PO_4^{---} \rightleftarrows Ba_3(PO_4)_2.$$

However, these are salts of *weak acids* and would all dissolve, or fail to precipitate, in an acid solution. (See the chart on the next page.) In the presence of excess hydrogen ion, the concentration of the free anion is reduced to such a low value that the solubility equilibrium is reversed, and the precipitate dissolves or fails to form in the first place. We may therefore use barium ion in an acid solution as a test reagent for the presence of sulfate ion.

Sulfite Ion, Sulfide Ion, and Carbonate Ion. In each of these anions of *weak, volatile acids,* the free acid is formed by the addition of a strong acid:

$$CO_3^{--} + 2\ H^+ \rightleftarrows H_2CO_3 \rightleftarrows CO_2\ (g) + H_2O$$
$$SO_3^{--} + 2\ H^+ \rightleftarrows H_2SO_3 \rightleftarrows SO_2\ (g) + H_2O$$
$$S^{--} + 2\ H^+ \rightleftarrows H_2S\ (g).$$

The odors of sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) are usually sufficient identification. Sulfite ion (SO_3^{--}) may be oxidized to sulfate ion (SO_4^{--}) by bromine water (Br_2) or hydrogen peroxide (H_2O_2), and then tested as the sulfate ion is tested. Sulfide ion (S^{--}) may be further confirmed by placing it in contact with a lead salt solution on filter paper, thus forming a black deposit of lead sulfide (PbS).

In your study of the oxidation states of sulfur (Study Assignment D and Experiment 21), you have learned that sulfite ion, which is intermediate in its oxidation state, can be reduced to free sulfur by sulfide ion, which in turn is oxidized to sulfur. The equation is

$$SO_3^{--} + 2\ S^{--} + 6\ H^+ \longrightarrow 3\ S + 3\ H_2O.$$

These ions, therefore, are not likely to be found together in the same solution, particularly if it is acid. Likewise, separate solutions of these ions are rather unstable because of their ease of oxidation by atmospheric oxygen:

$$2\ SO_3^{--} + O_2 \longrightarrow 2\ SO_4^{--}$$
$$2\ S^{--} + O_2 + 2\ H_2O \longrightarrow 2\ S + 4\ OH^-$$

In the carbonate ion test, the evolution of a colorless, almost odorless gas when an acid is added to the sample is an indication, but not proof, that the gas is carbon dioxide. The sample must be reprecipitated as an insoluble carbonate salt, such as calcium carbonate ($CaCO_3$). When the slightly soluble carbon dioxide gas is bubbled into a neutral solution *containing calcium ion,* the weak acid which is formed, carbonic acid (H_2CO_3),

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows 2\ H^+ + CO_3^{--},$$

does not furnish a high enough concentration of carbonate ion to precipitate calcium carbonate. What would be the effect on the carbonate ion concentration if the carbon dioxide gas were bubbled into an alkaline solution instead of into the neutral one? This is the reason for using limewater, $Ca(OH)_2$, although the hydroxide is only slightly soluble, rather than some soluble calcium

salt, in the carbonate ion test. The over-all net ionic equation is

$$CO_2 + Ca^{++} + 2\ OH^- \rightleftharpoons CaCO_3 + H_2O.$$

Sulfite ion, if also present in the unknown, will interfere with the carbonate ion test, as it will liberate sulfur dioxide gas (SO_2) along with the carbon dioxide gas when the sample is acidified, and will form a calcium sulfite ($CaSO_3$) precipitate when the gases are absorbed in the limewater. (Sulfide ion, S^{--}, would not interfere, as CaS is soluble.) To overcome this, it is necessary first to oxidize any sulfite ion to sulfate ion, and thus prevent the formation of any sulfur dioxide gas.

Chloride Ion, Bromide Ion, and Iodide Ion. These ions are, like the sulfate ion, the anions of *strong acids*. Their salts with silver ion are insoluble, whereas the silver salts of most other anions, which are also insoluble in neutral solution, will dissolve in acid solution. Silver sulfide (Ag_2S), however, is so very insoluble that the presence of hydrogen ion does not reduce the sulfide ion concentration sufficiently to dissolve it.

We may test for the presence of *chloride ion* in the mixed precipitate of AgCl, AgBr, and AgI by dissolving the AgCl from the still more insoluble AgBr and AgI by adding ammonium hydroxide solution, thus forming the complex ion $Ag(NH_3)_2^+$ and Cl^-. When the filtrate is again acidified, the AgCl is reprecipitated:

$$AgCl + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$
$$Ag(NH_3)_2^+ + Cl^- + 2\ H^+ \longrightarrow AgCl + 2\ NH_4^+.$$

It is thus possible, by carefully controlling the NH_4OH and Ag^+ concentrations, to redissolve the AgCl without appreciably redissolving the more insoluble AgBr and AgI. Furthermore, AgCl is white, AgBr is cream-colored, and AgI is light yellow.

The distinctive differences which enable us to separate and test for *bromide ion* and *iodide ion* in the presence of chloride ion depend on differences in their ease of oxidation. Iodide ion is easily oxidized to iodine (I_2) by adding ferric ion (Fe^{+++}), which does not affect the others. After adding carbon tetrachloride (CCl_4) to identify (purple color) and remove the iodine, we may next oxidize the bromide ion with potassium permanganate or chlorine water solutions, absorb the bromine (Br_2) formed in carbon tetrachloride, and identify it by the brown color produced.

Phosphate Ion. This is the anion of a moderately weak, nonvolatile acid, phosphoric acid (H_3PO_4). It is tested by the typical method of forming a characteristic precipitate. The reagent used is ammonium molybdate solution, to which

	Ag^+	Ba^{++}	Ca^{++}	Pb^{++}
NO_3^-	Soluble	Soluble	Soluble	Soluble
Cl^-, Br^-, I^-	AgCl, white; AgBr, cream; AgI, yellow. All insoluble in HNO_3. AgCl soluble, AgBr slightly soluble, and AgI insoluble, in NH_4OH.	Soluble	Soluble	$PbCl_2$ and $PbBr_2$, white, soluble in hot water. PbI_2, yellow, slightly soluble in hot water.
SO_4^{--}	Moderately soluble	$BaSO_4$, white, insoluble in HNO_3	$CaSO_4$, white, slightly soluble	$PbSO_4$, white, insoluble in HNO_3
SO_3^{--}	Ag_2SO_3, white, soluble in NH_4OH and in HNO_3	$BaSO_3$, white, soluble in HNO_3	$CaSO_3$, white, soluble in HNO_3	$PbSO_3$, white, soluble in HNO_3
S^{--}	Ag_2S, black, soluble in hot, conc HNO_3	Soluble	Soluble	PbS, black, soluble in HNO_3
PO_4^{---}	Ag_3PO_4, yellow, soluble in NH_4OH and in HNO_3	$Ba_3(PO_4)_2$, white, soluble in HNO_3	$Ca_3(PO_4)_2$, white, soluble in HNO_3	$Pb_3(PO_4)_2$, white, soluble in HNO_3
CO_3^{--}	Ag_2CO_3, white, soluble in NH_4OH and in HNO_3	$BaCO_3$, white, soluble in HNO_3	$CaCO_3$, white, soluble in HNO_3	$PbCO_3$, white, soluble in HNO_3

an excess of ammonium ion is added in order to shift the equilibrium further to the right. An acid solution is necessary. The equation is

$$3\,NH_4^+ + 12\,MoO_4^{--} + H_3PO_4 + 21\,H^+ \rightleftarrows (NH_4)_3PO_4 \cdot 12\,MoO_3 + 12\,H_2O.$$

The yellow precipitate is a mixed salt, ammonium phosphomolybdate. Sulfide ion interferes with this test but may be removed first by acidifying the solution with HCl and boiling it.

Nitrate Ion. In this case, since all nitrates are soluble, we cannot use a precipitation method as the test. Two other facts are utilized. First, nitrate ion is a good oxidizing agent in an acid solution when a reducing agent such as ferrous ion (Fe^{++}) is added:

$$4\,H^+ + NO_3^- + 3\,Fe^{++} \longrightarrow 3\,Fe^{+++} + NO + 2\,H_2O.$$

Second, the nitric oxide (NO) formed readily unites with excess ferrous ion present to form a brown complex ion:

$$NO + Fe^{++} \longrightarrow Fe(NO)^{++}.$$

It is essential that an excess of ferrous ion be used, or the test will fail.

Summary. The preceding chart may be of assistance to you in summarizing the behavior of the above negative ions with the metallic ions: silver ion, barium ion, calcium ion, and lead ion.

Experimental Procedure

Chemicals: 0.5 *F* $(NH_4)_2MoO_4$, 0.1 *F* $BaCl_2$, saturated Br_2 water, saturated Cl_2 water, 0.02 *F* $Ca(OH)_2$, 0.1 *F* $FeCl_3$, $FeSO_4 \cdot 7\,H_2O$, 3% H_2O_2, $Pb(C_2H_3O_2)_2$ paper, 0.1 *F* KBr, 0.1 *F* KI, 0.1 *F* KNO_3, $Ag(C_2H_3O_2)$, 0.1 *F* $AgNO_3$, 1 *F* Na_2CO_3, 0.1 *F* NaCl, 1 *F* KH_2PO_4, 1 *F* Na_2SO_4, 0.1 *F* Na_2SO_3 (freshly prepared), 0.1 *F* Na_2S (freshly prepared).

First familiarize yourself with the test procedures by performing tests on known solutions of the ions to be tested: S^{--}, SO_4^{--}, SO_3^{--}, CO_3^{--}, Cl^-, Br^-, I^-, PO_4^{---}, and NO_3^-. Then obtain two unknown solutions from the instructor, and perform analyses on these for each of the ions. Use a fresh portion of the unknown for each test.

Test for Sulfide Ion. To about 2 ml of the test solution add a slight excess of 6 *F* HCl. Note any odor of H_2S, and, as a more sensitive test, place a piece of moistened lead acetate paper over the mouth of the test tube. Heat the tube gently. A darkening of the paper indicates S^{--} in the original solution. (If S^{--} is found to be present, SO_3^{--} cannot be present [why?], and the SO_3^{--} test may then be omitted. Note also the modification of the PO_4^{---} test when S^{--} is present.)

Test for Sulfate Ion. To 2 ml of the test solution add 6 *F* HCl drop by drop until the solution is slightly acid. Then add 1 ml of 0.1 *F* $BaCl_2$ solution, or more as needed to complete the precipitation. A white precipitate of $BaSO_4$ proves SO_4^{--}. (Save for the sulfite test.)

Test for Sulfite Ion. If the solution from the previous sulfate ion test had a sharp odor of SO_2 when it was made acid with HCl, SO_3^{--} is present. If in doubt, filter or centrifuge the solution to obtain a clear filtrate, add a drop or more of 0.1 *F* $BaCl_2$ to be sure all SO_4^{--} was precipitated, and if necessary add more $BaCl_2$; then refilter or recentrifuge. To the clear solution add 1 to 2 ml of bromine water to oxidize any SO_3^{--} to SO_4^{--}. A second white precipitate of $BaSO_4$ now proves the presence of SO_3^{--}.

Test for Carbonate. Fit a 15-cm test tube with a 1-hole rubber stopper and bent delivery tube (see Fig. 3-1). Place about 3 ml of the test solution in this test tube. If sulfite ion (SO_3^{--}) is present in the unknown, add 1 ml of 3% H_2O_2 to oxidize it to sulfate ion. Now insert the delivery tube into some clear limewater, $Ca(OH)_2$, in another test tube. When ready, remove the stopper just enough to add a little 6 *F* HCl to the test solution. Immediately close the stopper again, and heat the tube gently to boiling to drive any CO_2 gas into the limewater. Be careful not to let any of the boiling liquid escape through the delivery tube into the limewater. A white precipitate in the limewater indicates CO_3^{--} or HCO_3^- in the test solution.

Test for Chloride Ion. To a 2-ml portion of the test solution add a few drops of 6 *F* HNO_3, as needed, to make the solution slightly acid. (Test with litmus paper.) Any sulfide ion present may be removed by boiling the solution a moment. The free sulfur formed does not interfere. Add 1 ml of 0.1 *F* $AgNO_3$. (No precipitate here proves the absence of Cl^-, Br^-, or I^-.) Centrifuge the mix-

ture. (See Fig. F-1, in the following study assignment, on the use of the centrifuge.) Test the clear filtrate with a drop of 0.1 *F* $AgNO_3$, for complete precipitation. If necessary, centrifuge again. Discard the filtrate. Wash the precipitate (see Fig. F-2 on washing precipitates) with distilled water to remove excess acid and silver ion. Now to this precipitate in the test tube add 3 ml of distilled water, four drops of 6 *F* NH_4OH, and a half ml of 0.1 *F* $AgNO_3$. (The proportions are important, as we wish to dissolve only the AgCl from any mixture of AgCl, AgBr, AgI, and Ag_2S.) $Ag(NH_3)_2^+$ and Cl^- will form. Shake the mixture well. Centrifuge. Transfer the clear solution to a clean test tube, and acidify with 6 *F* HNO_3. A white precipitate of AgCl confirms Cl^-.

Test for Iodide Ion. To 2 ml of the test solution add 6 *F* HCl to make the solution acid. If S^{--} or SO_3^{--} is present, boil the solution to remove the ion. Add 1 ml of 0.1 *F* $FeCl_3$ to oxidize any I^- to I_2. (Br^- is not oxidized by Fe^{+++}.) Add 1 ml of carbon tetrachloride (CCl_4), and agitate the mixture. A purple color proves I^-. (Save this for the Br^- test.)

Test for Bromide Ion. *If no I^- was present,* add 2 ml of chlorine water to the above I^- test mixture, and agitate it. A brown color in the CCl_4 layer proves Br^-. *If I^- was present,* separate, by means of a medicine dropper, as much as possible of the solution above the CCl_4 layer which contains the I_2, and place it in a clean test tube. Again extract any remaining I_2 by adding 1 ml of CCl_4, agitating the mixture, and separating the solution. The solution may be boiled a moment to remove any remaining trace of I_2. Then add 2 ml of chlorine water and 1 ml of CCl_4, and agitate the mixture. A brown color proves Br^-.

Test for Phosphate Ion. First mix about 1 ml of 0.5 *F* $(NH_4)_2MoO_4$ reagent with 1 ml of 6 *F* HNO_3. (If a white precipitate forms here, dissolve it by making the solution basic with NH_4OH, and then re-acidify with HNO_3.) If S^{--} has been found in the unknown, first make a 2-ml sample of it distinctly acid with HCl, boil it a moment to remove all H_2S, then add this, or a 2-ml sample of the original unknown if no S^{--} is present, to the above clear molybdate solution. A yellow precipitate of $(NH_4)_3PO_4 \cdot 12\ MoO_3$, appearing at once or after warming a few minutes to about 40° C, proves PO_4^{---}.

Test for Nitrate Ion. *If Br^- and I^- are absent,* use 2 ml of test solution acidified with 3 *F* H_2SO_4. Add 1 ml of freshly prepared saturated $FeSO_4$. Incline the test tube at about a 45° angle, and pour about 1 ml of concentrated H_2SO_4 slowly down the side of the test tube. Be careful to avoid undue mixing. A brown ring of $Fe(NO)^{++}$ at the interface

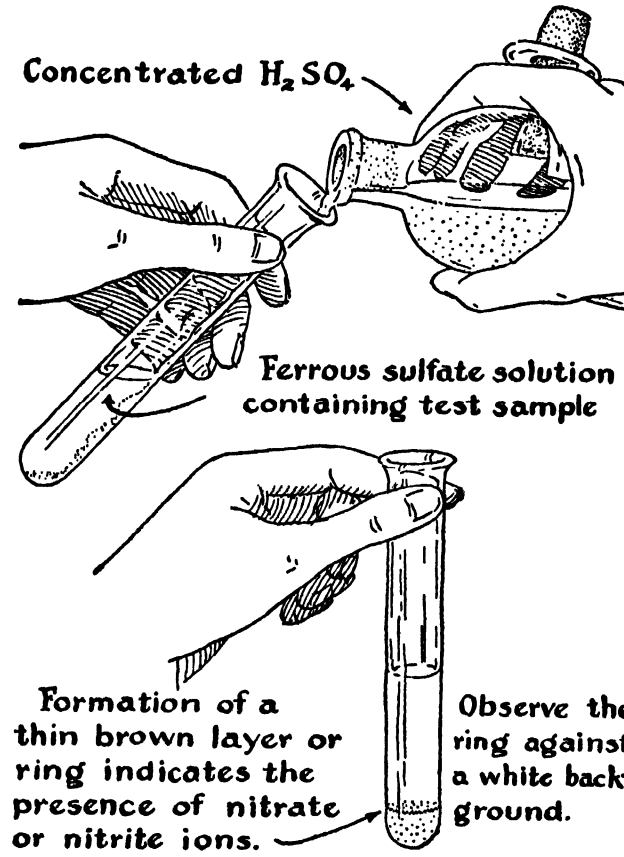


Fig. 39-1. The nitrate test.

of the two liquids proves NO_3^-. A faint test may be observed more easily by holding the test tube against white paper and looking toward the light. (See Fig. 39-1.)

If Br^- and I^- are present, free Br_2 or I_2 may form at the interface with the concentrated H_2SO_4 and invalidate the test. In this case, place a fresh 2-ml sample of the test solution in a clean mortar, add about 10 mg of solid silver acetate, and grind the mixture together for a couple of minutes to metathesize it to solid AgBr and AgI. Decant the liquid into a test tube, and centrifuge. Treat the clear solution with $FeSO_4$ and conc H_2SO_4, as above.

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

REPORT: Exp. 39

The Negative Ions— I. Qualitative Tests

1. Review Questions

(1) In the tests for Cl^- and SO_4^{--}, explain fully why the addition of acid will dissolve other insoluble silver salts and barium salts, respectively, which would interfere with the tests if the solutions were neutral. (See the chart in the preceding discussion.)

(2) Suppose a white precipitate is obtained on adding $BaCl_2$ reagent to a neutral unknown solution. What might the precipitate be? Write as many formulas as you can of possible substances, considering both positive and negative ions as given in the preceding chart.

(3) A moderate test for SO_4^{--} is to be expected whenever you have SO_3^{--} or S^{--} in an unknown solution, even when no SO_4^{--} has been placed in the solution. Why?

(4) Why cannot both S^{--} and SO_3^{--} be present in the same solution?

(5) Why is an excess of Fe^{++} necessary in the test for NO_3^-, if the test is to be successful?

(6) Suppose you have two solutions, one a carbonate, CO_3^{--}, and the other a bicarbonate, HCO_3^-. Give specific procedures by which you could distinguish between the two. (Hint: Consider the *p*H of the solution.)

2. Report of Unknown Solutions

Write in the correct formula for each ion found, for each unknown. (The ions, if added at all in these unknowns, are present in more than traces.)

Unknown No._____ Ions found_____

Unknown No._____ Ions found_____

3. Supplementary Drill

(1) Give the formulas of all new characteristic molecules or ions formed when solutions of the following are mixed. (Indicate any cases of no action.)

Cl^-, Br^-, I^-, Fe^{+++}_____ Ag^+, Cl^-, NH_4OH (excess)_____

Cl^-, Br^-, I^-, Cl_2 water_____ Ag^+, I^-, NH_4OH (excess)_____

Fe^{++}, Br_2 water_____ SO_2 bubbled in $Ca(OH)_2$_____

SO_3^{--}, H_2O (acid)_____ CO_2 bubbled in $CaCl_2$_____

S^{--}, SO_3^{--} (acid)_____ $Pb(C_2H_3O_2)_2$, H_2S gas_____

(2) An unknown solution is to be tested for the ions, or their derivatives,[1] listed at the right. The following tests are performed on *separate* portions of the unknown:

(a) Phenolphthalein added to a test portion gives a red color.

(b) When a test portion is warmed, red litmus held in the mouth of the test tube turns blue.

(c) When a test portion is acidified with HCl, and lead acetate paper is held in the mouth of the test tube, the paper turns black.

(d) A test portion is acidified with HCl, boiled, cooled, then Cl_2 water and CCl_4 added. After shaking the mixture, the CCl_4 layer is reddish-brown.

(e) Addition of dilute H_2SO_4 in excess to a test portion results in a white precipitate.

On the basis of these tests, considered as a whole, mark, in the column headed (2), a plus sign (+) for each ion or its derivative, in the original solution, which is definitely present, a minus sign (−) if the ion is definitely absent, or a question mark (?) if there is no evidence to prove the ion present or absent.[2]

	(2)	(3)
Na^+	____	____
NH_4^+	____	____
Ag^+	____	____
Pb^{++}	____	____
Ca^{++}	____	____
Ba^{++}	____	____
Cl^-	____	____
Br^-	____	____
I^-	____	____
SO_4^{--}	____	____
SO_3^{--}	____	____
S^{--}	____	____
NO_3^-	____	____
CO_3^{--}	____	____
PO_4^{---}	____	____

(3) A second unknown solution is to be tested for the same list of ions given above. The following tests are performed:

(a) The solution is basic to phenolphthalein, and smells of ammonia.

(b) The addition of excess HNO_3 to a test portion results in the formation of a white precipitate.

(c) If the mixture from (b) above is filtered, and ammonium molybdate reagent added to the clear filtrate, a yellow precipitate results.

On the basis of these tests, considered as a whole, mark, in the column headed (3), a plus sign, a minus sign, or a question mark for each of the ions in the list, as you did for the preceding unknown solution.

[1] By "derivative" is meant, for example, PO_4^{---} or H_3PO_4, Ag^+ or $Ag(NH_3)_2^+$, NH_4^+ or NH_4OH, etc.

[2] Take account of the insolubility of certain salts. For example, if an acid solution is known to contain Pb^{++}, then SO_4^{--}, S^{--}, etc., cannot be present.

An Introduction to the Qualitative Analysis of the Metal Ions

F

A Study Assignment

Qualitative analysis is concerned with the identification of the particular substances present in a given sample of material. In the analysis of inorganic substances, this involves separate analyses for the metallic constituents or cations, and for the non-metallic constituents or anions. We have given a brief consideration of the latter in the preceding experiment. We now must turn our attention, for the following series of experiments, to the analytical procedures by which we separate and identify the cations.

You should recognize at the outset that the methods we shall use are not the procedures generally adopted in industrial laboratories. In the latter, the investigator usually is concerned with the determination of the presence or absence of only a very few metals in a given sample. Furthermore, the problem often is simplified because the nature and source of the sample make it unnecessary to consider many metals. The methods used in industry naturally involve the shortest and most direct procedures that will give the information desired. Such observations as the ignition of the material to form characteristic decomposition products, the use of specific organic reagents for the various metal ions, or the microscopic study of crystalline form, may be used. Frequently, the identification and the quantitative determination as well are based on purely physical properties, such as the measurement of characteristic spectral lines. Such specialized tools as the spectrophotometer, which measures the absorption of various wavelengths of light in passing through a solution of the sample, and the mass spectrograph, which measures the masses of the various kinds of molecules in the sample, have recently come into widespread use. These latter tools are particularly useful in the analysis of organic mixtures.

Grouping the Metal Ions for Qualitative Separation

In a systematic analysis, a solution of the unknown sample is prepared, using nitric acid or other reagents, if needed. Then, by the successive addition of specific reagents, insoluble salts of the metal ions are precipitated in groups. Each group can be subdivided further and tested for each metal ion in that group. The most commonly used scheme of analysis involves the separation into major groups of the twenty-four ions usually considered, as indicated in the accompanying outline.

As would be expected, there is some correlation

THE SEPARATION OF THE METAL IONS INTO GROUPS

Nitric Acid Solution of the Sample
Reagent: HCl or NH_4Cl

Precipitate	*Solution (Ions of Groups 2–5)* Reagent: H_2S in 0.3 *M* H^+		
AgCl Hg_2Cl_2 $PbCl_2$ (partly) *(Group 1)*	*Precipitate* CuS PbS Bi_2S_3 CdS HgS As_2S_3 Sb_2S_3 SnS_2 *(Group 2)*	*Solution (Ions of Groups 3–5)* Reagent: $(NH_4)_2S$ in NH_4OH solution	
		Precipitate $Al(OH)_3$ FeS ZnS CoS NiS $Cr(OH)_3$ MnS *(Group 3)*	*Solution (Ions of Groups 4–5)* Reagent: $(NH_4)_2CO_3 + NH_4Cl$
			Precipitate $BaCO_3$ $CaCO_3$ $SrCO_3$ *(Group 4)*
			Solution Mg^{++} Na^+ K^+ NH_4^+ *(Group 5)*

between the groups of elements as precipitated for qualitative analysis and the groups which constitute the families of elements in the periodic table. Periodic sub-group 1 is represented by silver and mercury in qualitative Group 1. The alkaline earths, as precipitated by ammonium carbonate, constitute qualitative Group 4. With some change in procedure, magnesium would also precipitate here. The alkali metals (periodic group 1), nearly all of whose salts are soluble, constitute qualitative group 5.

It will be profitable, if time is available, for you to prepare a solution containing one ion from each of these groups, for example Ag^+, Cu^{++}, Zn^{++}, Ca^{++}, and K^+, and by the successive addition of the group reagents given in the scheme, to remove each ion in turn as a precipitate until only potassium ion remains. The instructor may wish to demonstrate this.

In this course, we shall study a limited number of these ions, including all the ions of qualitative Groups 1 and 5, but omitting several ions from Groups 2, 3, and 4. No fundamental principles of qualitative separation will be omitted, however.

Instructors who wish to consider all the ions usually studied in a course in qualitative analysis, as outlined in the preceding chart on the Separation of the Metal Ions into Groups, are referred to the following Study Assignment G for the inclusion of the optional ions.

Laboratory Techniques for Qualitative Analysis

The volumes of solutions used in these qualitative procedures are rather small and approach the semimicro scale of work. While the experimental operations are, in general, similar to those we have been using, the reminders and suggestions which follow and the accompanying figures will help you to attain better technique, to save time, and to be more accurate in your analyses.

The oft-repeated admonition—*keep your desk neat and orderly*—will pay big dividends. Keep your working space on the table top and in front of the sink clear of unnecessary equipment. Keep dirty test tubes and other articles in one place. Clean and rinse these at the first opportunity, so that a stock of clean equipment is always ready. Label any solutions which are to be kept some time. Do

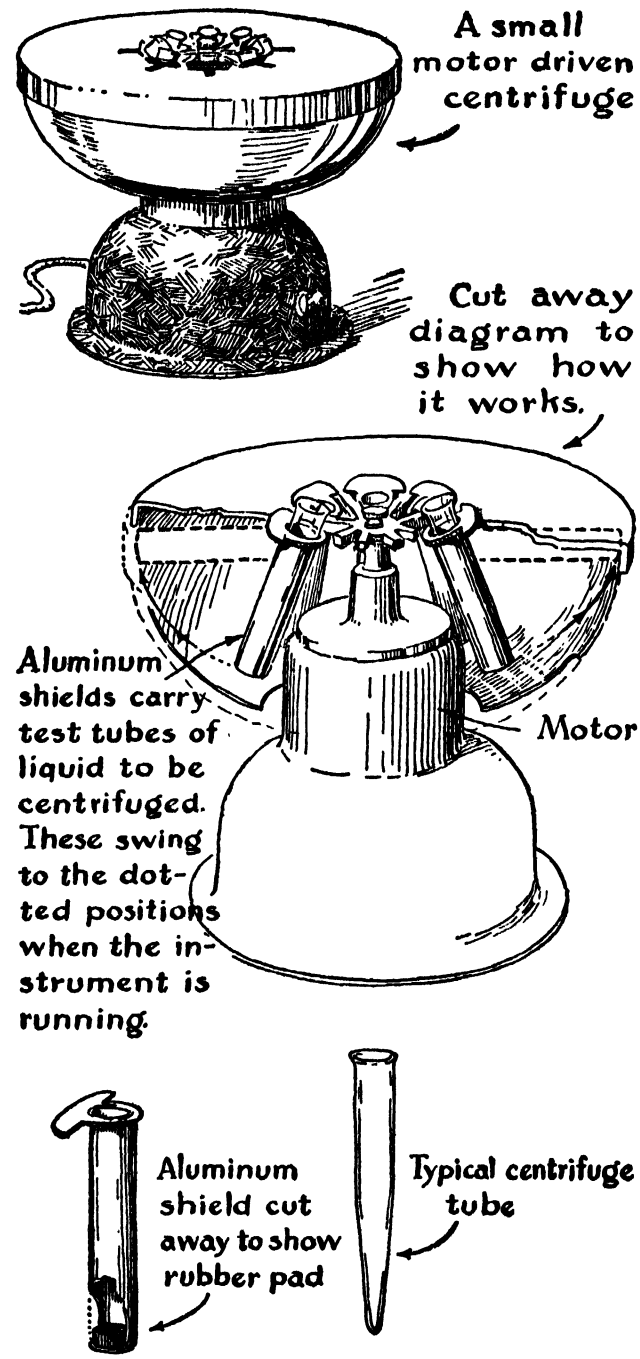


FIG. F-1. The centrifuge and its use.

your thinking and keep your laboratory record up to date as you work.

The Separation of Precipitates. Either the *centri-*

fuge (see Fig. F-1) or the *vacuum filtration* technique (see Fig. 20-2b) may be used. The former process is faster (about 2 minutes centrifuging time usually is sufficient) and has been specified in most instances throughout these procedures. Filtration may be substituted if centrifuges are not available. When you filter a small volume (1 to 5 ml) of liquid, use a small filter paper so that all the liquid is not lost by absorption in the paper. Note the detailed techniques for each process, as illustrated. In particular, be sure you know how to *wash a precipitate* properly, as this generally is essential in qualitative work (see Fig. F-2).

The Evaporation of a Solution. When you boil down a solution in a 10-cm test tube, it is very easy to "boil it over" or suddenly eject some of the contents, especially if there is much precipitate present. With more than 2 ml of liquid, it usually is advisable to transfer the sample to a 15-cm test tube, and shake it sidewise while heating it (see Fig. F-3). If more than 10 ml of liquid is being evaporated, use a small beaker, casserole, or evaporating dish.

The Preparation and Use of Hydrogen Sulfide. Because of the frequency with which we use this gas, it is advisable to make the best possible preparation for handling it. If hydrogen sulfide is not piped directly into a well-ventilated hood for your use, generate it by one of the methods illustrated in Figure F-4, as directed by your instructor. A ready-prepared commercial mixture, called "Aitch-tu-ess,"[1] is available for method (a). **Always work in a hood, as hydrogen sulfide is very poisonous. A pronounced odor of the gas in the laboratory can and must be prevented.**

Thioacetamide, CH_3CSNH_2, may be used to generate hydrogen sulfide, without contaminating the atmosphere. The reagent is rather expensive. To use this method, add 5 to 15 drops of 1 *F* CH_3CSNH_2, as needed, directly to the test solution, after adjustment of the H^+ ion concentration. Heat the test tube in a small beaker of hot water to promote hydrolysis, according to the equation:

$$CH_3CSNH_2 + 2\,H_2O \longrightarrow H_2S + NH_4^+ + C_2H_3O_2^-.$$

[1] "Aitch-tu-ess" is supplied by The Hengar Co., 1833 Chestnut St., Philadelphia, Pa., or by various laboratory supply houses.

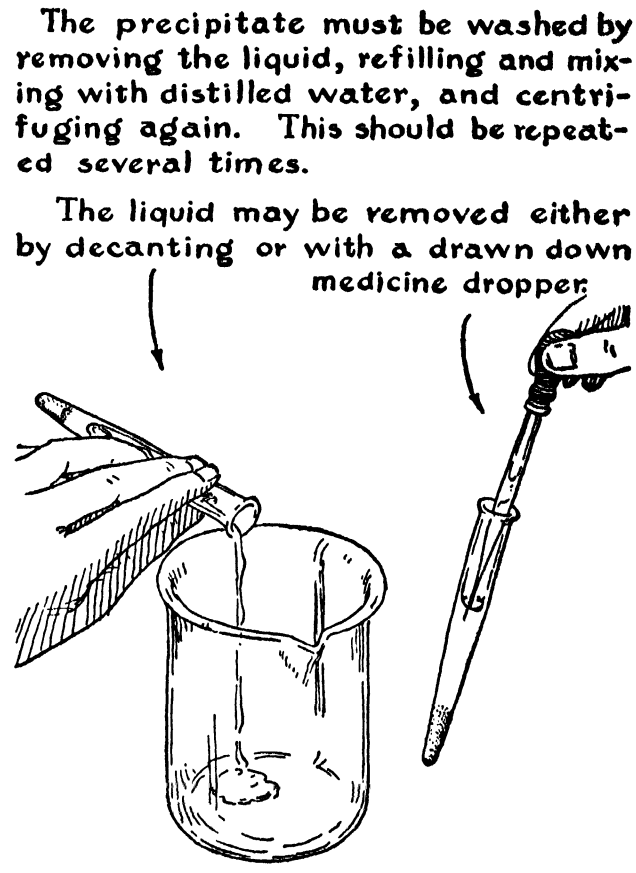


FIG. F-2. How to wash a precipitate which has been centrifuged.

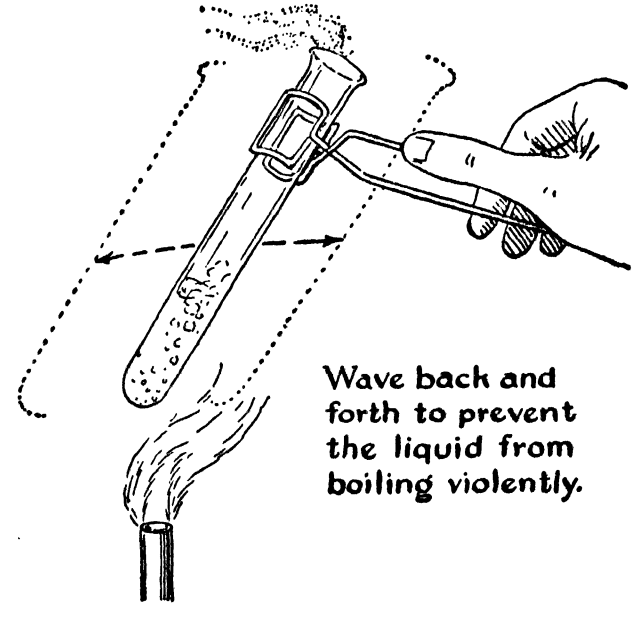


FIG. F-3. This will improve your technique when you evaporate a solution in a test tube.

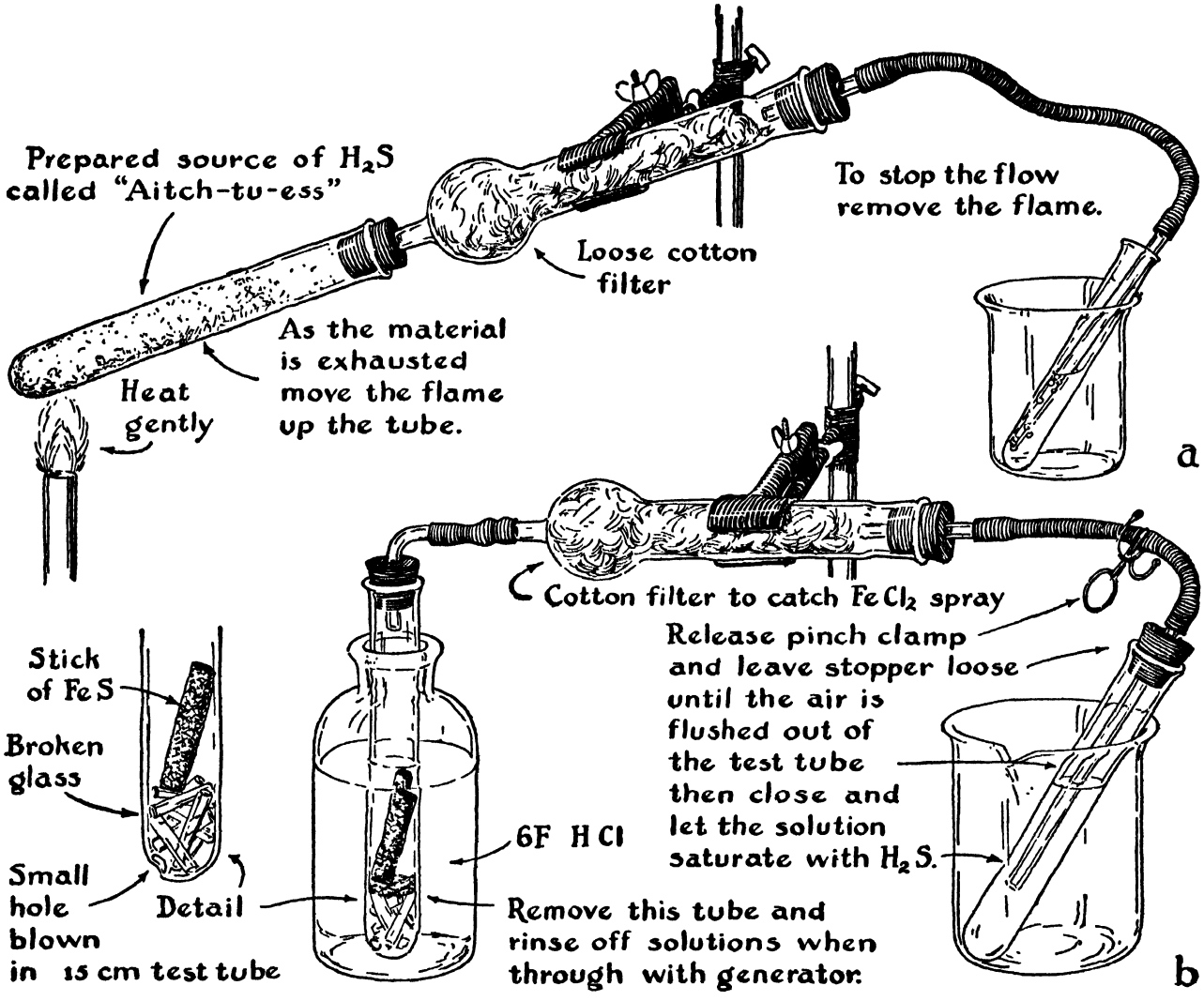


FIG. F-4. Methods for the generation of hydrogen sulfide gas for individual use: (a) by heating a mixture of sulfur, paraffin, and asbestos, (b) by the reaction of HCl on FeS in a small automatic generator.

The Silver Group 40

College Chemistry, Chapters 26, 28

Review of Fundamental Concepts

The precipitating reagent for the group is chloride ion in an acid solution. Only three of all the twenty-four metal ions form a precipitate on the addition of this reagent, namely silver ion (Ag^+), mercurous ion (Hg_2^{++}), and lead ion (Pb^{++}). The mercurous ion is not the simple ion, Hg^+, but consists of two atoms held together by a covalent bond, with a double positive charge. Since lead chloride is somewhat soluble, it is not completely precipitated here, and hence lead ion appears also in Group 2.

Ammonium hydroxide solution gives different results with each of the three metal ions, as shown by the preliminary experiments which follow. The behavior of mercury salts is peculiar and needs some explanation. Mercury exhibits three oxidation states, zero in free mercury, Hg°, +1 in mercurous ion, Hg_2^{++}, and +2 in mercuric ion, Hg^{++}. In some situations, the intermediate mercurous ion, Hg_2^{++}, is unstable, part of the mercury being reduced to the metal, and part oxidized to Hg^{++}, thus:

$$Hg_2^{++} \rightleftarrows Hg^\circ + Hg^{++}.$$

When ammonia is added to mercur*ic* chloride solution, a white "ammonolysis" product, $HgNH_2Cl$, is formed. This is analogous to the partial hydrolysis of $HgCl_2$ to form a basic salt. Compare the two equations

$$HgCl_2 + HOH \longrightarrow Hg(OH)Cl + HCl,$$
and $$HgCl_2 + HNH_2 \longrightarrow Hg(NH_2)Cl + HCl.$$

If mercur*ous* chloride is treated with ammonia, part of it is oxidized to the white mercur*ic* aminochloride above, while part is reduced to black finely divided mercury:

$$Hg_2Cl_2 + 2\ NH_3 \longrightarrow Hg(NH_2)Cl + Hg + NH_4^+ + Cl^-.$$

The mixed precipitates appear jet black.

Experimental Procedure

Chemicals: 1 *F* NH_4OH, 0.1 *F* $Pb(NO_3)_2$, 0.1 *F* $HgCl_2$, 0.05 *F* $Hg_2(NO_3)_2$, 0.1 *F* KBr, 1 *F* K_2CrO_4, 0.1 *F* KI, 0.1 *F* $AgNO_3$, 0.1 *F* NaCl, 1 *F* $Na_2S_2O_3$.

A. Typical Reactions of the Silver Group

1. *Solubility of the Chlorides.* Prepare a sample of each of the three chlorides by adding 2 ml of 0.1 *F* NaCl to 2 ml of test solutions of $AgNO_3$, $Hg_2(NO_3)_2$, $Pb(NO_3)_2$. If a precipitate fails to form in any of these (why?), add 1 ml of 6 *F* HCl. Let the precipitates settle, decant and discard the supernatant liquid. Add to each about 2 ml of distilled water. Heat each nearly to boiling and shake. Results? Cool under the cold water tap. Results? Save for the next paragraph.

2. *Behavior with Ammonia.* To each of the three precipitates, add 1 ml of 6 *F* NH_4OH. Shake to see if they will dissolve. Compare the behavior of the Hg_2Cl_2 precipitate with ammonia with that of $HgCl_2$. To do this, add 1 ml of 6 *F* NH_4OH to 1 ml of 0.1 *F* $HgCl_2$ solution. Divide the ammoniacal solution of AgCl into two unequal portions. To the smaller, add a slight excess of 6 *F* HNO_3. Result?

3. *Relative Solubility of Silver Salts.* To the larger portion of the ammoniacal AgCl solution, add 1 ml of 0.1 *F* KBr. Result? Now, to this add 1 ml of 1 *F* $Na_2S_2O_3$ (sodium thiosulfate) and shake. The complex ion formed is $Ag(S_2O_3)_2^{---}$. (This is the reaction of "hypo" in fixing the developed film in photography.) To this solution, add a little 0.1 *F* KI. Compare the results with the solubility data for AgCl, AgBr, and AgI.

4. *Stability of* $Ag(NH_3)_2^+$. The formation and dissociation of silver ammonia complex ion is governed by the equilibrium

$$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2\ NH_3,$$

and the corresponding equilibrium constant expression is

$$\frac{(Ag^+)\ (NH_3)^2}{(Ag(NH_3)_2^+)} = K.$$

We can get a fairly accurate value of this constant and therefore of the stability of this complex ion by the following simple experiment.

Place 3.0 ml of 0.1 *F* $AgNO_3$ (measure it accurately in a 10-ml graduate) in a 15-cm test tube. Add 3.0 ml (also carefully measured) of 1 *F* NH_4OH. Now, prepare some 0.02 *F* NaCl by diluting 2.0 ml of 0.1 *F* solution to 10.0 ml in your 10-ml graduate. Mix thoroughly, note the exact volume, and then add this from a medicine dropper, about a half milliliter at first and then drop by drop until a very faint permanent milky precipitate of AgCl

OUTLINE—THE SILVER GROUP

<table>
<tr><td colspan="3">To the solution to be tested, add 6 F HCl.
Filter. Wash the precipitate.</td></tr>
<tr><td colspan="2">Res. 11[1] AgCl, Hg₂Cl₂, PbCl₂
Pour boiling water over the precipitate on the filter.</td><td rowspan="2">Sol. 11
Cations of Groups 2-5. Save for Group 2 analysis.</td></tr>
<tr><td>Sol. 12 Pb^{++}
Add K_2CrO_4 solution.
Yellow $PbCrO_4$ proves Pb^{++}.</td><td>Res. 12 AgCl, Hg₂Cl₂
Add NH_4OH on the filter.

Res. 13.
Hg, $HgNH_2Cl$
Black, proves Hg_2^{++}.</td><td>Sol. 13.
$Ag(NH_3)_2^+$, Cl^-
Acidify, HNO_3
White AgCl, proves Ag^+.</td></tr>
</table>

[1] The first number in a residue or solution indicates the group, the second number indicates sequence in the group.

remains after shaking. Return any excess NaCl from the medicine dropper to the graduate, and note the exact volume of the 0.02 *F* NaCl used. From these data, calculate the concentrations of $Ag(NH_3)_2^+$, Ag^+, and NH_3 in the final mixture, and the value of K, as outlined in the report sheet.

B. Analysis of the Silver Group (Group 1)

For each group, we shall present first a brief outline of the method of separation, which will enable you to visualize and learn the general steps in the analysis. This is followed by the "Procedure," which gives detailed directions for the actual analysis. (*Note*: You first should prepare a "known" solution containing the three ions and analyze it to gain practice in technique, and then analyze one or two unknown solutions supplied by the instructor.)

Procedure for the Analysis of the Silver Group Ag^+, Hg_2^{++}, Pb^{++}:

Precipitation of the Group. To 4 ml of the solution to be tested, add a half ml of 6 *F* HCl (or about 10 drops added by a medicine dropper) and mix well for a minute or two. (No precipitation indicates absence of Ag^+, Hg_2^{++}, and of much Pb^{++}.) Filter[2] into a 15-cm test tube, and test the filtrate for complete precipitation with 1 drop of HCl. After the liquid has all drained through the filter, spray the precipitate (Res.11) with 1-3 ml of distilled water from your wash bottle to wash it. Let drain. Reserve the filtrate (label it S11) for the analysis of Groups 2-5 if you are analyzing for these. If not, discard it.

Test for Lead Ion. Heat 10 - 15 ml of water to boiling, and pour 3-4 ml of this boiling water over the residue R11 on the filter, catching the hot filtrate S12 in a small test tube. (Wash the remaining residue by pouring 10 ml of boiling water in portions over it, discarding these washings.) Add several drops of 1 *F* K_2CrO_4 to the filtrate. A yellow precipitate indicates Pb^{++}.

Test for Mercurous Ion. To residue R12 on the filter, add 1 ml of 6 *F* NH_4OH and then 2 ml of water,[3] collecting the filtrate S13 in a small test tube. A black residue on the filter indicates Hg_2^{++}.[4]

Test for Silver Ion. If the filtrate S13 is not perfectly clear, it may be due to colloidal Pb(OH)Cl coming through the filter. In this case, refilter the solution as often as necessary through the same filter, until a perfectly clear filtrate is obtained. Then, acidify the filtrate with a little 6 *F* HNO_3 and mix. (If in doubt, test for acidity with litmus.) A white precipitate, AgCl, proves Ag^+.

[2] It probably is simpler in this experiment to use the usual filtration procedure (vacuum is unnecessary), rather than the centrifuge, although the centrifuge may be used, if desired, with a corresponding modification of the directions which follow.

[3] Small volumes may be estimated by noting that a 10-cm test tube holds about 8 or 9 ml, and using the appropriate portion. Measure, by means of a 10-ml graduate, 1 ml, then 2 ml, of H_2O into a 10-cm test tube. Remember the resulting height of liquid as a guide for future use, as directions frequently call for 1 or 2 ml of a reagent.

[4] If a large amount of Hg_2^{++} was present (heavy black precipitate), a small amount of Ag^+ in the unknown may escape detection in the regular Ag^+ test, due to the fact that free Hg will reduce Ag^+ to Ag, thus retaining it with this black residue, instead of leaving it in solution as $Ag(NH_3)_2^+$.

This silver may be detected by opening out the filter on a watch glass, and pouring over the residue a mixture of 1 ml of 6 *F* HNO_3 and 1 ml of 12 *F* HCl, catching the solution in a small beaker or test tube. Evaporate off most, but not all the acid, and dilute with 3 ml H_2O, adding a drop of 6 *F* HCl if no white precipitate of AgCl forms without it. Further identification may be made by noting if the suspected AgCl dissolves on the addition of excess NH_4OH.

*Name*_____

REPORT: Exp. 40 *Date*_____

The Silver Group

*Section*_____

*Locker Number*_____

A. Typical Reactions of the Silver Group

1, 2. In the proper space in the following chart, note the characteristic behavior, if any (solubility, color, etc.) and write the formula(s) of all new substances formed by the reaction:

	AgCl	*$PbCl_2$*[1]	*Hg_2Cl_2*
Hot water			
NH_4OH (Excess)			

[1] Look up the relative solubilities to help you decide whether a reaction takes place between $PbCl_2$ and NH_4OH.

3. Write net ionic equations for the successive reactions that take place when AgCl is treated with ammonium hydroxide, and then each product, in turn, is treated with potassium bromide, sodium thiosulfate, and potassium iodide. Also look up the solubilities of the silver halides and list these.

_____

_____

_____

_____

Solubility (g/100g H_2O):

AgCl _____

AgBr _____

AgI _____

Explain and correlate these reactions with the solubility data given:

4. The stability of silver ammonia complex ion, $Ag(NH_3)_2^+$.

Indicate your calculations for each step, in the spaces provided.

a) Volume of 0.02 *F* NaCl used . . . . . _____

b) Total volume of the final mixture . . . . . _____

c) Concentration of $Ag(NH_3)_2^+$
(Assume all the silver to be present as this complex ion, neglecting the small amount of free Ag^+ formed) . . . . . _____

d) Concentration of Cl^-
(Neglect any trace of Cl^- removed as AgCl) . . . . . _____

e) Concentration of Ag^+
(Use the value for Cl^- obtained above, and the solubility product relationship, $(Ag^+)(Cl^-) = 1.6 \times 10^{-10}$.) . . . . . _____

f) Concentration of free NH_3
(Assume that 1 *F* NH_4OH is 1 *M* in NH_3. First calculate the NH_3 concentration as if none combined with Ag^+, then subtract from this twice the concentration of $Ag(NH_3)_2^+$ found above.) . . . . . _____

g) Use the values found in e), f), and c) to calculate the value of the constant for silver ammonia complex ion: . . . . . _____

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = K$$

h) Accepted value for this constant in the literature (See the Appendix, Table XIV.)_____

B. Analysis of the Silver Group

Summary, Unknown No._____ Ions found_____

Unknown No._____ Ions found_____

Indicate, for each unknown, each essential step of the procedure, identifying each succeeding stage in the analysis by its Sol. or Res. No.

Sample	*Reagent(s)*	*Observations*	*Conclusions*

Precipitation With Hydrogen Sulfide. The Analysis of the Hydrogen Sulfide Group 41

College Chemistry, Chapters 26, 28

Review of Fundamental Concepts

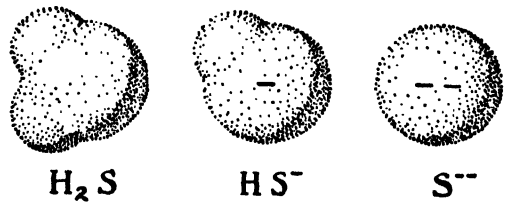


FIG. 41-1. The hydrogen sulfide molecule, the hydrosulfide ion, and the sulfide ion.

Hydrogen Sulfide—a Weak Dibasic Acid

When hydrogen sulfide is bubbled into water at ordinary atmospheric pressure, it dissolves to give a saturated solution which is about 0.1 *F* H_2S. This behaves as a weak acid, and since there are two replaceable hydrogen atoms we may represent its ionization in steps, thus:

$$H_2S \rightleftarrows H^+ + HS^- \qquad (1)$$
$$HS^- \rightleftarrows H^+ + S^{--}. \qquad (2)$$

The extent of the ionization of hydrosulfide ion, step (2) above, is much less than that of step (1), since it involves the removal of a positive hydrogen ion from the negative particle HS^-, while the first hydrogen ion only has to be separated from a neutral molecule, H_2S.

The corresponding equilibrium constant expressions for these stepwise ionizations are

$$\frac{(H^+)\,(HS^-)}{(H_2S)} = K_1 = 1.1 \times 10^{-7} \qquad (3)$$
$$\frac{(H^+)\,(S^{--})}{(HS^-)} = K_2 = 1.0 \times 10^{-15}. \qquad (4)$$

Note that K_2 is about 100,000,000 times smaller than K_1, corresponding to the much smaller extent of ionization in step (2). The expression (H^+) refers to the same value, of course, in both equations (3) and (4), since both equilibria are present in the same solution. Most of the H^+ comes from the first stage. Likewise the HS^- concentration (from the first stage) is about equal to the H^+ concentration and is not nearly so small as the S^{--} concentration which results from the second stage. If we multiply equation (3) by equation (4), cancelling out the common factor (HS^-), we get

$$\frac{(H^+)^2(S^{--})}{(H_2S)} = K_1K_2 = (1.1 \times 10^{-7})\,(1.0 \times 10^{-15}) = 1.1 \times 10^{-22} \qquad (5)$$

Furthermore, in any solution saturated with hydrogen sulfide at atmospheric pressure, the concentration of molecular H_2S remains sensibly constant, and equals about 0.1 *M*. We may, therefore, simplify equation (5) thus:

$$\frac{(H^+)^2(S^{--})}{(0.1)} = 1.1 \times 10^{-22}$$

or

$$(H^+)^2(S^{--}) = 1.1 \times 10^{-23}. \qquad (6)$$

This is a very important relationship, as it shows us, for instance, that if the hydrogen ion concentration in a solution is increased tenfold, the sulfide ion concentration in the solution is thereby reduced a hundredfold. That is, the sulfide ion concentration in a solution saturated with hydrogen sulfide gas is inversely proportional to the square of the hydrogen ion concentration in that solution. We may thus control the maximum sulfide ion concentration in a solution by controlling the hydrogen ion concentration.

For example, in a 10^{-2} *M* H^+ solution, such as we may have in an acetic acid solution, we can calculate the maximum sulfide ion concentration resulting when hydrogen sulfide is bubbled into the solution, by substituting in equation (6) above:

$$(10^{-2})^2(S^{--}) = 1.1 \times 10^{-22}$$
$$(S^{--}) = \frac{1.1 \times 10^{-22}}{10^{-4}} = 1.1 \times 10^{-18}\ M.$$

Similarly, in a 0.3 *M* H^+ solution, such as is used when precipitating the hydrogen sulfide group in acid solution, we may calculate the maximum sulfide ion concentration, as follows:

$$(0.3)^2\,(S^{--}) = 1.1 \times 10^{-22}$$
$$(S^{--}) = \frac{1.1 \times 10^{-22}}{0.09} = 1.2 \times 10^{-21}\ M.$$

Note that in these two examples increasing the hydrogen ion concentration 30 times (from 10^{-2} to 0.3 *M*) has resulted in a decrease of about 1000-fold in the sulfide ion concentration. What effect does this large difference in sulfide ion concentration have on the ability of hydrogen sulfide to

precipitate a metallic sulfide? The next section will discuss this point.

The Precipitation of Metallic Sulfides

In a saturated solution of cupric sulfide, we have the equilibrium

$$CuS \rightleftarrows Cu^{++} + S^{--}. \qquad (7)$$

According to the solubility product principle, the product of the concentrations of the ions in the solution cannot be greater than a certain value, namely,

$$(Cu^{++})\,(S^{--}) = K_{CuS} = 10^{-40}. \qquad (8)$$

The amount of cupric ion which can remain in solution depends, therefore, on the sulfide ion concentration, and as we have seen, this in turn depends on the hydrogen ion concentration. For a 0.3 M H^+ solution, the sulfide ion concentration cannot be greater than 1.2×10^{-22} M. (See the above examples.) From this, we may calculate the maximum cupric ion concentration which could remain in such a solution. Substituting in equation (8), we have

$$(Cu^{++})(1.2 \times 10^{-22}) = 10^{-40}$$

$$(Cu^{++}) = \frac{10^{-40}}{1.2 \times 10^{-22}} = 10^{-18}\ M \text{ (approximately).}^1$$

The precipitation of cupric ion from such a solution is, therefore, practically complete.

Compare this with the somewhat more soluble ferrous sulfide, for which, in a saturated solution

$$(Fe^{++})\,(S^{--}) = 10^{-22}.$$

Again, calculating for a 0.3 M H^+ solution, in which $(S^{--}) = 1.2 \times 10^{-22}$,

$$(Fe^{++})\,(1.2 \times 10^{-22}) = 10^{-22}$$

$$(Fe^{++}) = \frac{10^{-22}}{1.2 \times 10^{-22}} = 1\ M \text{ (approximately).}^2$$

A high concentration of ferrous ion, thus, can remain in solution without being precipitated at all. However, if the solution is made basic with ammonium hydroxide, in which the sulfide ion concentration is about 10^{-7} M when treated with hydrogen sulfide, we calculate

$$(Fe^{++})\,(10^{-7}) = 10^{-22}$$

$$(Fe^{++}) = 10^{-15}\ M.$$

Thus, ferrous ion will be almost completely precipitated in a slightly basic solution, but not at all in a 0.3 M H^+ solution.

The very insoluble metallic sulfides are precipitated along with cupric sulfide in the hydrogen sulfide group, while those which are slightly more soluble may be precipitated along with ferrous sulfide by ammonium sulfide. The readily soluble sulfides will not be precipitated in either case. This is the basic principle of the separation of Groups 2 and 3 in the qualitative scheme.

The Separation of the Hydrogen Sulfide Group into Sub-Groups. Amphoteric Sulfides.

As we have just seen, the hydrogen sulfide group includes all those sulfides which are so insoluble as to be almost completely precipitated in 0.3 M H^+ solution by hydrogen sulfide. This includes eight of the twenty-four metal ions commonly studied. For convenience, these may be subdivided into two smaller groups for individual tests of the ions. This is accomplished by the treatment of the mixed sulfide precipitate with a high sulfide ion concentration. Using a sodium sulfide solution, we find that the sulfides of mercury, arsenic, antimony, and tin dissolve as the corresponding sulfosalts. (If ammonium sulfide, which gives a lower sulfide ion concentration due to hydrolysis, is used, the mercuric sulfide remains undissolved with the "copper" sub-group.) The theory of such separations is as follows.

Just as the hydroxides of certain metals are amphoteric, dissolving in an excess of hydroxide ion to form hydroxide complex ions (see Exp. 35), so also the sulfides of some of the metals will dissolve in a high concentration of sulfide ion to form sulfide complex ions. The addition of only a slight excess of hydroxide ion, or of sulfide ion, to a stannic salt solution forms the expected precipitates:

$$Sn^{++++} + 4\ OH^- \rightleftarrows Sn(OH)_4.^3$$

$$Sn^{++++} + 2\ S^{--} \rightleftarrows SnS_2.$$

[1] The solubility products of the metallic sulfides in many cases are not known more precisely than to the nearest power of 10. Such calculations as this, and those which follow, should be regarded as only approximate. They do serve, however, to show the principles on which the separation of metallic sulfides is based.

[2] The corresponding calculation with zinc ion (solubility product for ZnS = 10^{-24}) would indicate that only 0.01 M Zn^{++} could remain in a 0.3 M H^+ solution saturated with H_2S. ZnS does not precipitate readily, however, from quite concentrated Zn^{++} solutions under these conditions, due, in part at least, to the tendency of ZnS to delay precipitation and form supersaturated solutions. Zn^{++}, therefore, is not precipitated with the H_2S group, but precipitates with the ammonium sulfide group when the solution is made basic.

[3] An ion with such a high positive charge as +4 will have a very strong tendency to coordinate with any negative ions in solution, and will seldom, if ever, be present as the simple ion. In a hydro-

but with a high concentration of these ions, the precipitates redissolve:

$$Sn(OH)_4 + 2\ OH^- \rightleftarrows Sn(OH)_6^{--},$$
$$SnS_2 + S^{--} \rightleftarrows SnS_3^{--}.$$

The addition of hydrogen ion to the above strongly basic solutions will decrease the concentration of hydroxide ion, or of sulfide ion, and reprecipitate stannic hydroxide, or stannic sulfide, respectively. In a high concentration of hydrochloric acid, both precipitates redissolve again, due not only to the action of the hydrogen ion in forming water and hydrogen sulfide, respectively, but also to the high chloride ion concentration, which forms the complex ion $SnCl_6^{--}$.

A very interesting situation is the fact that stannic sulfide dissolves readily in a sulfide ion solution, while stannous sulfide will not dissolve. It should be remembered that sulfide ion is a base[1] and stannic sulfide is acting as an acid as it dissolves. Stannous sulfide is not a sufficiently strong acid to react with sulfide ion. This behavior is in accord with the more acidic character of an element in its higher oxidation state. Likewise, nitrous acid (HNO_2) and sulfurous acid (H_2SO_3) are weak acids, while the corresponding acids in which the elements are more highly oxidized, nitric acid and sulfuric acid, are strong acids. It is for this reason that, in the analytical procedure, an oxidizing agent, hydrogen peroxide, is added to oxidize any tin to stannic ion before adding sulfide ion.

The Oxidation of Hydrogen Sulfide and Metallic Sulfides

Thus far, we have dealt with hydrogen sulfide only as a weak acid. It contains sulfur in its lowest oxidation state, namely minus 2, and is a good reducing agent, reacting readily with any strong oxidizing agents present. The sulfide is nearly always oxidized to free sulfur, together with some sulfate ion which forms by further oxidation.

Nitric acid, or nitrates in acid solution, are nearly always present in the solution to be tested for Group 2 ions. If the solution is quite dilute, and not too hot, these nitrates do not interfere as oxidizing agents. In stronger solution, especially when heated, sulfur will always form when hydrogen sulfide gas is passed into the solution. The reaction is

$$3\ H_2S + 2\ H^+ + 2\ NO_3^- \longrightarrow 3\ S + 2\ NO + 4\ H_2O.$$

This also explains why nitric acid is a better solvent than hydrochloric acid for most metallic sulfides. To dissolve cupric sulfide, we must decrease the concentration of either the cupric ion or the sulfide ion, so as to shift the equilibrium

$$CuS \rightleftarrows Cu^{++} + S^{--}$$

to the right. The sulfide ion concentration is decreased more completely by oxidizing it to free sulfur with nitric acid, than it is by forming the weak acid hydrogen sulfide with hydrochloric acid. The reaction is

$$3\ CuS + 8\ H^+ + 2\ NO_3^- \longrightarrow 3\ Cu^{++} + 3\ S + 2\ NO + 4\ H_2O.$$

Some few sulfides, particularly mercuric sulfide, are so extremely insoluble that they will not dissolve even in concentrated nitric acid. Hot aqua regia, however, is able to dissolve mercuric sulfide quite readily. This reagent owes its powerful solvent action to the fact that, in addition to the oxidizing action of nitric acid, there is a high concentration of chloride ion which readily forms complex ions with a number of metallic ions. With mercuric sulfide, we have the reaction

$$HgS + 4\ H^+ + 2\ NO_3^- + 4\ Cl^- \longrightarrow HgCl_4^{--} + S + 2\ NO_2 + 2\ H_2O.$$

Experimental Procedure

Chemicals: 6 *F* $HC_2H_3O_2$, 3 *F* $NH_4C_2H_3O_2$, saturated Br_2 water, 0.1 *F* $Cu(NO_3)_2$, 0.1 *F* $FeCl_3$, 3% H_2O_2, 30% H_2O_2, Fe (1-cm wire pieces), 0.1 *F* $Pb(NO_3)_2$, 0.1 *F* $HgCl_2$, 0.1 *F* $Hg(NO_3)_2$, 1 *F* K_2CrO_4, 0.1 *F* $K_4Fe(CN)_6$, 1 *F* Na_2SO_4, 2 *F* NaHS, 0.1 *F* $SnCl_4$, 0.1 *F* $SnCl_2$, 0.1 *F* $Zn(NO_3)_2$.

A. Typical Reactions of the Hydrogen Sulfide Group

1. *The Precipitation of Metallic Sulfides.* Dilute 3 ml of 6 *F* HCl to 9 ml with distilled water and mix, to make a 2 *M* H^+ solution. Dilute 1 ml of this to 10 ml to make a 0.2 *M* solution. Use 1 ml of this latter solution to prepare 10 ml of 0.02 *M* H^+, and 10 ml of 0.002 *M* H^+, by successive tenfold dilutions. Mix 2 ml of each of these with an equal volume of 0.1 *M* Cu^{++} to give four solutions varying in H^+ concentration from 1 *M* to 0.001 *M*.

chloric acid solution, stannic salts form the chloride complex ion, $SnCl_6^{--}$, so that the reactions with hydroxide or sulfide ions really constitute replacements:

$$SnCl_6^{--} + 4\ OH^- \rightleftarrows Sn(OH)_4 + 6\ Cl^-,$$
$$SnCl_6^{--} + 2\ S^{--} \rightleftarrows SnS_2 + 6\ Cl^-.$$

[1] This is in accord with the definition of a base as any substance which can react with protons, H^+. Thus, sulfide ion, carbonate ion, acetate ion, etc., as well as hydroxide ion, are bases.

OUTLINE—THE HYDROGEN SULFIDE GROUP

Sol. 11 Cations of Groups 2-5
Adjust the H^+ concentration to 0.3 *M*. Warm, and saturate with H_2S gas. Centrifuge. Wash residue.

Res. 21 HgS, PbS, CuS, SnS, SnS_2, S
Add 6 *F* NaOH, H_2O. Warm and agitate. Cool, if dark residue remains add 3% H_2O_2. Agitate. Heat to decompose excess H_2O_2. Add 2 *F* NaHS reagent. Warm and mix for 2-3 minutes. Dilute with H_2O. Centrifuge. Wash any dark residue with 2 ml H_2O containing NaHS and NaOH. Discard washings.

Sol. 21 Cations of Groups 3-5.
At once boil out H_2S, and save for Group 3 analysis

Res. 22 PbS, CuS, (HgS?)
Add 3 *F* HNO_3, heat almost to boiling for 2 minutes only. Centrifuge. (Combine any dark residue with Res. 24.) To the filtrate add 3 *F* H_2SO_4; evaporate to dense white fumes. Cool. Add H_2O (caution). Centrifuge.

Sol. 22 HgS_2^{--}, SnS_3^{--}
Add 3 *F* H_2SO_4 to just neutralize the solution, noting the volume, and add ⅓ volume in excess. Boil to remove H_2S. Cool. Centrifuge, discarding filtrate. Treat the *residue* (*HgS*, *SnS_2*, *S*) with 6 *F* NaOH, H_2O and special 30% H_2O_2. Warm, then boil to decompose excess H_2O_2. (If yellow color of S_2^{--} persists, repeat H_2O_2 treatment.) Centrifuge.

Res. 23 $PbSO_4$
Dissolve in $NH_4C_2H_3O_2$. Add 1 *F* K_2CrO_4. Yellow precipitate of $PbCrO_4$ proves lead.

Sol. 23 Cu^{++}
Make basic with NH_4OH. Blue $Cu(NH_3)_4^{++}$ indicates copper. To confirm, acidify with $HC_2H_3O_2$. Add 0.1 *F* $K_4Fe(CN)_6$. Maroon precipitate of $Cu_2Fe(CN)_6$, proves copper.

Res. 24 HgS
Add aqua regia, heat, evaporate, add H_2O. To the *clear* solution, add 0.1 *F* $SnCl_2$. Hg_2Cl_2 (white), or Hg (black), proves mercury.

Sol. 24 $Sn(OH)_6^{--}$
Acidify with 6 *F* HCl. Add Fe wire. Evaporate almost to dryness. Add H_2O. Decant. To the *clear* solution add 0.1 F $HgCl_2$. Hg_2Cl_2 (white), proves tin.

Prepare a similar set of solutions using 0.1 *M* Zn^{++}. Pass H_2S gas (see Fig. F-4) into each of the eight solutions to saturate them with the gas. Note the formation of any precipitate, in the chart provided in the report sheet, and explain the results in the light of the differences in solubility and of the ionization of H_2S.

2. *The Oxidation of Hydrogen Sulfide.* Into 2-ml samples each of warm 6 *F* HNO_3, of Br_2 water, and of 0.1 *F* $FeCl_3$ acidified with about 5 drops of 6 *F* HCl, pass H_2S gas. Note, and explain any changes in color, or formation of precipitates.

3. *The Solution of the Sulfides in Acid.* First prepare a little CuS and HgS by passing H_2S into 1-ml samples of 0.1 *M* Cu^{++} and 0.1 *M* Hg^{++} solutions. Add an equal volume of 6 *F* HNO_3 to each to give 3 *F* solutions, and heat just about to boiling for two minutes only. Results? If either precipitate fails to dissolve, let it settle, decant, and to the residue add 10 drops of 12 *F* HCl and 5 drops of 16 *F* HNO_3. Warm, and note results.

4. *Amphoteric Sulfides.* Prepare a little CuS and SnS_2 by adding 2 drops of 2 *F* NaHS solution to 1-ml samples of 0.1 *M* Cu^{++} and 0.1 *M* Sn^{++++} solutions. Let the precipitate settle, decant, and to the residue add 1 ml of 2 *F* NaHS and 0.5 ml of 6 *F* NaOH. Warm, if necessary, and note any difference in behavior of the two precipitates. To the one which dissolved, now add 3 *F* H_2SO_4 drop by drop to just make it acid. Results?

5. *The Behavior of Lead Salts.* Prepare a little $PbSO_4$ precipitate by mixing 1 ml of 0.1 *F* $Pb(NO_3)_2$ and 2 drops of 1 *F* Na_2SO_4. Divide the mixture in two test tubes. To one, add 1 ml of 6 *F* $HC_2H_3O_2$. To the other, add 1 ml of 3 *F* $NH_4C_2H_3O_2$. Note and explain the results. To the one which dissolved, add a few drops of 1 *F* K_2CrO_4. Results?

6. *The Reduction of Mercuric Ion by Stannous Chloride.* To 1 ml of 0.1 *F* $HgCl_2$, add several drops of 0.1 *F* $SnCl_2$. Then, add 2 ml of additional $SnCl_2$. Let stand and observe the change. The black coloration is due to free mercury.

B. Analysis of the Hydrogen Sulfide Group. (Group 2)

We shall include only the ions Cu^{++}, Pb^{++}, Hg^{++}, Sn^{++} and Sn^{++++} in our study of this group. For practice, analyze a known solution containing these ions by the following procedure. Then, obtain an unknown from the instructor. If you have time, analyze an unknown containing ions of both Groups 1 and 2 for both groups.

Procedure for the Analysis of the Hydrogen Sulfide Group, Cu^{++}, Pb^{++}, Hg^{++}, Sn^{++}, Sn^{++++}.

To 4 ml of the solution to be analyzed (or Sol.

11 from the silver group, if a general unknown), add 6 *F* NH_4OH, or 6 *F* HCl, drop by drop, as needed, to adjust to 0.3 *M* H^+. (This acidity may be determined with methyl violet paper, which may be prepared by soaking filter paper with methyl violet indicator solution and drying. Touch a drop of your solution on a stirring rod to the indicator paper. This may be matched with the blue-green color produced by a drop of 0.3 *F* HCl.) An alternate method of adjusting to 0.3 *M* H^+ is to neutralize[1] your solution to the nearest drop by drop-wise addition of NH_4OH and HCl, then add 1 drop of 6 *F* HCl for each milliliter of solution. (Not valid if anions of weak acids are present.)

Precipitation of the Group. Heat the solution, and saturate it with H_2S gas by slowly bubbling the gas into the solution for several minutes. Be sure the gas delivery tube, which should preferably be drawn down to a coarse capillary, is clean. To clean it, immerse it in warm 6 *F* HCl in a 10-cm test tube and rinse. Filter, or centrifuge, the mixture. (Get instructions on the use of the centrifuge. The solution in a 5-ml centrifuge tube or 10-cm test tube must always be carefully balanced with an equal amount of water in a similar tube placed opposite in the centrifuge. A larger amount of solution may be divided equally in two similar tubes to centrifuge it.) Decant the clear solution carefully into a clean test tube and test for complete precipitation[2] by again bubbling in H_2S for a moment. If the solution is to be saved for further analysis, boil it for a moment to expel H_2S completely, label it S21, and set it aside for Group 3. Wash the precipitate (R21) by adding 1 to 2 ml of water. Centrifuge again and discard the wash solution.

Separation of the Copper and Tin Sub-Groups. To Res. 21, add 1 ml of 6 *F* NaOH, and dilute to 2 ml with water. Warm and agitate the mixture gently for a moment. Cool it, and, if a dark residue remains (which might be stannous sulfide), add 1 ml of 3% hydrogen peroxide to oxidize any tin to the stannic state. Agitate again, and finally heat to decompose any excess H_2O_2.[3] Now, add 2 ml of 2 *F* NaHS reagent. Warm and mix for several minutes, then centrifuge. Save the filtrate (S22) for analysis for Hg^{++} and Sn^{++++}. Wash any dark residue (R22) with 2 ml H_2O containing several drops of 2 *F* NaHS and a drop of 6 *F* NaOH, and discard the washings.

Test for Lead Ion. To Res. 22, add 1 ml of H_2O and an equal volume of 6 *F* HNO_3, and heat almost to boiling, with shaking, for 2 minutes, but no longer. Centrifuge, and if a dark residue remains (which might possibly be HgS),[4] save it and combine it later with Res. 24. To the filtrate, contained in a small beaker, add 2 ml of 3 *F* H_2SO_4, and evaporate until almost dry and very dense white choking fumes of SO_3 are evolved. (*Hood*: The excessive escape of these fumes into the room can be prevented by covering the beaker with a watch glass, after the evaporation. The purpose of this heating is to remove all HNO_3, in which lead sulfate is more soluble.) Cool, then cautiously add 3 ml H_2O. Cool, and let stand 5 minutes. A white precipitate, settling readily, is probably $PbSO_4$. Centrifuge, and decant the clear solution (S23) and save for the cupric ion test. Wash the white precipitate (R23) with a little water, let settle or centrifuge, and discard the washings. To the residue, add 1 ml of 3 *F* $NH_4C_2H_3O_2$ and warm to dissolve any $PbSO_4$. Add 1 ml of 1 *F* K_2CrO_4. A yellow precipitate proves lead.

Test for Cupric Ion. To Sol. 23, add 6 *F* NH_4OH to make it distinctly basic. A deep blue color, $Cu(NH_3)_4^{++}$, indicates copper. This is quite distinctive, but if desired Cu^{++} may be confirmed by acidifying with 6 *F* $HC_2H_3O_2$, and adding 0.1 *F* $K_4Fe(CN)_6$. A maroon coloration or precipitate of $Cu_2Fe(CN)_6$ proves copper.

Precipitation of the Tin Group. To the filtrate (S22) which is strongly basic and contains much S^{--}, add 3 *F* H_2SO_4 drop by drop just enough to neutralize it, testing with litmus and noting the

[1] In using litmus paper to test for neutrality, it is best not to put the paper in the solution, as the absorption of ions renders it less sensitive, and also because the litmus dissolves in the solution. Rather, touch a drop of the solution, held on the end of a stirring rod, to the litmus paper.

[2] In case a very large amount of precipitate has formed, the solution may have become too acid due to a reaction of the type:

$$M^{++} + H_2S \longrightarrow MS + 2\,H^+.$$

In this case, boil the solution to remove H_2S, cool it, and readjust to 0.3 *M* H^+ before passing in H_2S a second time.

[3] A black residue, possibly PbS or CuS, may remain at this point.

[4] Since HgS is not too readily dissolved by the previous NaHS treatment, it is wise to test a dark residue here for Hg. However, this dark residue may be simply a trace of CuS or PbS, encrusted over with free S formed by oxidation, and hence rendered insoluble.

volume of acid used. (Mix it well, but be cautious, or the H_2S may be evolved too rapidly. Work under the *hood*. As long as H_2S is evolved rapidly on the addition of each drop of H_2SO_4, the solution is still basic.) When the solution is neutral, add about ⅓ this volume of H_2SO_4, in excess.[1] Centrifuge, or let settle, and discard the solution. A dark or colored residue indicates the presence of the tin group. If the residue is white or very pale yellow, it is sulfur, formed by the decomposition of the S_2^{--} present:

$$S_2^{--} + 2\,H^+ \rightleftharpoons H_2S + S.$$

Test for Mercuric Ion. Treat any colored residue formed above with 1 ml H_2O, heat to boiling to expel H_2S, add 0.5 ml 6 *F* NaOH, and 0.5 ml of 30% (not 3%) H_2O_2.[2] Transfer this to a 15-cm test tube and boil it to decompose excess H_2O_2.[3] If the yellow color of S_2^{--} persists, cool, and repeat the H_2O_2 treatment. Centrifuge, and save the filtrate, Sol. 24, for the Sn^{++++} test.

Confirm mercury by dissolving the residue (R24), to which has been added any dark residue from the treatment of Res. 22, in a little aqua regia made by mixing 1 ml 12 *F* HCl with 0.5 ml 16 *F* HNO_3. Heat this mixture and evaporate almost, but not quite, to dryness. Add 2 ml of H_2O, and filter or centrifuge, if necessary. The solution must be perfectly clear. Add 2-3 drops of 0.1 *F* $SnCl_2$. A white silky precipitate slowly turning dark when an excess of about 1 ml of $SnCl_2$ is added, proves mercury.

Test for Tin. Acidify Sol. 24 with 6 *F* HCl, using a slight excess of acid so that any Sn^{++++} will remain in solution. Add a 1-cm piece of iron wire and evaporate the solution until only 1 or 2 drops of liquid remain. The iron reduces any Sn^{++++} to Sn^{++}. Add 1 ml of H_2O. Decant this clear solution into a clean test tube, and add 5 to 10 drops of 0.1 *F* $HgCl_2$. A white precipitate of Hg_2Cl_2, or black Hg, proves tin.

[1] Since HSO_4^- is a weak acid ($K = 1.2 \times 10^{-2}$), a slight excess of H_2SO_4 reacts with some of the SO_4^{--} formed

$$H_2SO_4 + SO_4^{--} \rightleftharpoons 2\,HSO_4^-,$$

so that the acidity is repressed by a buffering action. With ⅛ excess acid, the SO_4^{--} and HSO_4^- concentrations will be about equal, so that

$$\frac{(H^+)\,(SO_4^{--})}{(HSO_4^-)} = 1.2 \times 10^{-2}, \text{ or } (H^+) = 1.2 \times 10^{-2} M.$$

This is not sufficient H^+ to dissolve the SnS_2 precipitate. See the explanation of buffer action in Experiment 32.

[2] Any SnS_2 will dissolve as $Sn(OH)_6^{--}$ and S^{--}. This S^{--}, unless destroyed by oxidation with H_2O_2, might dissolve some HgS, which is otherwise insoluble in OH^-, and thus render the separation ineffective.

[3] Shake the tube while heating it to minimize the chance of loss of material by the rapid evolution of oxygen. Continue heating until the excessive frothing subsides and the mixture boils gently, and on removal from the flame, no more oxygen gas is evolved.

REPORT: Exp. 41

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

The Hydrogen Sulfide Group

A. Typical Reactions of the Hydrogen Sulfide Group

1. Precipitation of Metallic Sulfides.

	Cu^{++}	Zn^{++}
1 *M* H^+		
0.1 *M* H^+		
0.01 *M* H^+		
0.001 *M* H^+		

Explanation of the above results:

2. The Oxidation of Hydrogen Sulfide.

Write net ionic equations for the reactions of H_2S with each of the three substances, HNO_3, Br_2, $FeCl_3$ in acid solution. Note any changes in the appearance of the solutions.

	Observations

List the two different types of chemical reactions exhibited by hydrogen sulfide (in pars. 1 and 2).

(1) _____

(2) _____

3. Solution of Sulfides in Acid.

Observed results of any action of 3 *F* HNO_3 on CuS and HgS:

The equation is_____

If HCl, instead of HNO_3, is added to CuS, the equation is_____

Why does a mixture of HCl and HNO_3 exert a greater solvent action on HgS than does HNO_3 alone?

The equation is_____

4. Amphoteric Sulfides.

The net ionic equation for the reaction of NaOH and NaHS is:_____

Explain the difference in behavior of CuS and SnS_2 with S^{--}, including any equations needed:

What happens on acidifying the resulting solution? Write equation.

5. Behavior of Lead Salts.

Observed results on treating $PbSO_4$ with

(1) $HC_2H_3O_2$_____ (2) $NH_4C_2H_3O_2$_____

What conclusion can you draw from this as to the solubility and extent of ionization of $Pb(C_2H_3O_2)_2$?

The net ionic equation is_____

When K_2CrO_4 is added, the net ionic equation for the reaction is_____

6. The Reduction of Mercuric Ion by Stannous Chloride.

Write net ionic equations for the reaction of mercuric chloride with (1) a small amount of $SnCl_2$, (2) an excess of $SnCl_2$, recording also the color of any precipitates formed:

(1) _____

(2) _____

B. Analysis of the Hydrogen Sulfide Group[1]

Summary, Unknown No._____ Ions found_____

Unknown No._____ Ions found_____

[1] For these, and each succeeding group, prepare on a separate sheet (with your name at the top) a form similar to that used for the silver group, as on the report sheet for Experiment 40, and hand in with your experiment report.

The Ammonium Sulfide Group 42

College Chemistry, Chapters 26, 27, 28, 29

Review of Fundamental Concepts

Precipitation with Ammonium Sulfide

An ammonium sulfide solution is rather difficult to keep, since such a high concentration of sulfide ion is readily oxidized by the air to free sulfur. This dissolves in the ammonium sulfide solution to form a yellow ammonium polysulfide solution,

$$S^{--} + S \longrightarrow S_2^{--}.$$

This latter ion gives a bothersome precipitate or colloid of free sulfur every time the solution is acidified,

$$S_2^{--} + 2\,H^+ \longrightarrow H_2S + S.$$

We therefore prepare the ammonium sulfide reagent as we use it, by making the test solution basic with NH_4OH, and then passing in H_2S gas,

$$2\,NH_4OH + H_2S \longrightarrow 2\,NH_4^+ + S^{--} + 2\,H_2O.$$

Actually, the reaction does not proceed much past the first stage of neutralization

$$NH_4OH + H_2S \longrightarrow NH_4^+ + HS^- + H_2O,$$

since both ammonium hydroxide and hydrogen sulfide are so poorly ionized that ammonium sulfide, $(NH_4)_2S$, is largely hydrolyzed to ammonium hydrogen sulfide, NH_4HS. The net ionic equation for the precipitation of a metallic sulfide in ammonia solution, therefore, is principally

$$NH_4OH + Zn^{++} + HS^- \longrightarrow ZnS + NH_4^+ + H_2O.$$

However, for such reactions, we shall usually write the simpler equation

$$Zn^{++} + S^{--} \longrightarrow ZnS.$$

The Hydrolysis of Sulfides of Weak Bases

The precipitation of sulfides has been discussed in the preceding experiment. The student will notice, however, that two of the ions in this group are precipitated as hydroxides, not as sulfides, on the addition of ammonium sulfide solution. This fact is due to the large extent to which salts of weak bases and weak acids hydrolyze. (Review Exp. 34 on hydrolysis.) Aluminum hydroxide is such a weak base that when ammonium sulfide is added to Al^{+++} solution, we have the reactions

$$2\,Al^{+++} + 6\,HOH \longrightarrow 2\,Al(OH)_3 + 6\,H^+$$
$$3\,S^{--} + 6\,HOH \longrightarrow 3\,H_2S + 6\,OH^-$$
$$2\,Al^{+++} + 3\,S^{--} + 6\,HOH \longrightarrow 2\,Al(OH)_3 + 3\,H_2S$$

The hydrolysis of both the aluminum ion and the sulfide ion is shifted completely to the right, since the products of the reaction, hydrogen ion and hydroxide ion, neutralize one another, and also because aluminum hydroxide separates as a precipitate and hydrogen sulfide is evolved as a gas. Chromic ion, Cr^{+++}, behaves in a similar fashion. Likewise, the addition of carbonate ion to a metallic ion whose hydroxide is a weak base, as aluminum ion or ferric ion, results in the precipitation of a hydroxide instead of a carbonate, inasmuch as carbonic acid is very poorly ionized.

Buffer Action

Frequently, in chemical processes, it is desirable to maintain the *p*H, or relative acidity and basicity of a solution, at an approximately constant value, even when considerable quantities of base or acid are added. In life processes, the *p*H of the blood must be kept practically constant at a value of about 7.4. This is accomplished by the bicarbonate and acid phosphate ions HCO_3^-, HPO_4^{--}, and $H_2PO_4^-$, which are present. In general, such control of the *p*H of a solution is attained by having present a weak acid together with a salt of that acid, or a weak base together with a salt of the base. Such a combination, which resists change in *p*H, is called a *buffer mixture.*

In the precipitation of the ammonium sulfide group from Solution 21, ammonium hydroxide is added to make the solution basic before passing in hydrogen sulfide gas. It is important, however, that the solution does not become too basic, or magnesium ion from the alkaline earth group may precipitate as magnesium hydroxide. Also, a strong ammonium hydroxide solution has a hydroxide ion concentration almost high enough to redissolve aluminum hydroxide as the amphoteric hydroxide complex ion, $Al(OH)_4^-$. These situations are avoided by having present a moderate concentration of ammonium ion (added as ammonium chloride), which maintains the hydroxide ion concentration at a value somewhat less than that of ammonium hydroxide alone. The buffer action may be explained as follows.

In a mixture of ammonium hydroxide and ammonium ion, with a strong acid added, the hydrogen ion is reacted on by the ammonium hydroxide present; or if a strong base is added, the hydroxide ion is reacted on by the ammonium ion present:

$$NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O,$$

or $$NH_4^+ + OH^- \longrightarrow NH_4OH.$$

The mixture thus does not change its *p*H greatly with the addition of either acid or base. This is further explained by the equilibrium expressions for the ionization of ammonium hydroxide:

$$NH_4OH \rightleftarrows NH_4^+ + OH^-,$$

$$\frac{(NH_4^+)\,(OH^-)}{(NH_4OH)} = K = 1.8 \times 10^{-5}.$$

If we rewrite this in the following manner,

$$\frac{(NH_4^+)}{(NH_4OH)} \times (OH^-) = 1.8 \times 10^{-5},$$

we see that the hydroxide ion concentration depends on the *ratio* of ammonium salt, i.e. NH_4^+, to free ammonium hydroxide, NH_4OH. So long as there is a considerable amount of both salt and base present, the ratio will not change greatly on the addition of moderate amounts of acid or base. The hydroxide ion concentration will be correspondingly constant.

We shall also make use of another buffer, a mixture of sodium sulfate and sodium hydrogen sulfate. The hydrogen sulfate ion is a weak acid, as is represented by its equilibrium expressions:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--},$$

$$\frac{(H^+)\,(SO_4^{--})}{(HSO_4^-)} = K = 1.2 \times 10^{-2}.$$

The addition of hydrogen ion shifts the above equilibrium to the left, and the addition of hydroxide ion shifts it to the right. However, so long as there is a considerable amount of both sulfate ion and hydrogen sulfate ion present, the ratio of $(SO_4^{--})/(HSO_4^-)$ does not change rapidly on the addition of acid or base, and the hydrogen ion concentration, as shown by the above equation, should remain about 10^{-2} *M*.[1]

In Experiment 41 we used this buffer to prevent the re-solution of the stannic sulfide formed when SnS_3^{--} is acidified (footnote 1, p. 302). We shall use it here to prevent the solution of zinc sulfide while dissolving all other sulfides and hydroxides of the group.

[1] Actually, in the buffer mixture which we use in this experiment, 0.5 *F* Na_2SO_4 and 0.5 *F* $NaHSO_4$, the *p*H is nearer a value of one. This fact is to be explained by the effect of such high concentrations on the activities of the ions present.

Oxidation States of Chromium and Manganese

While these elements are metals, they quite readily coordinate with oxygen to form oxides or negative complex ions in which they have higher oxidation states. These are very important substances. (Consult your textbook and review the charts in Study Assignment D on principal oxidation states of chromium and manganese, and the amphoteric character of chromium hydroxide. Also review the chart on the oxidation states of oxygen so as to understand the behavior of hydrogen peroxide. We shall use this substance both as a powerful oxidizing agent and, under different conditions, as a reducing agent. *You should know all these facts well.*)

We make use of the great change in properties of the ions of chromium and manganese with change in oxidation state in order to separate and test for these elements. The properties of chromic ion (Cr^{+++}) are very similar to those of the trivalent ions of aluminum (Al^{+++}) and iron (Fe^{+++}). However, when the chromium is oxidized to chromate ion (CrO_4^{--}), it behaves very differently and is readily separated and tested. The oxidation is accomplished by hydrogen peroxide in a basic solution.[2] The peroxide ion in basic solution is HO_2^-.

[2] The *p*H of the solution has a great deal to do with the action of hydrogen peroxide on the ions of chromium and manganese. While hydrogen peroxide is not nearly so strong an oxidizing agent in basic solution, the potentials for the oxidation of chromic hydroxide and manganous hydroxide to chromate ion and manganese dioxide, respectively, are also much lower, so the oxidation takes place readily. Compare the oxidation potentials from Latimer, *Oxidation Potentials* (Second Edition), Prentice-Hall, 1952.

Acid Solution			*Basic Solution*		
H_2O_2	$-O_2$	−0.67 volt	$Cr(OH)_3$	$-CrO_4^{--}$	+0.13 volt
Mn^{++}	$-MnO_2$	−1.23	HO_2^-	$-O_2$	+0.076
Cr^{+++}	$-Cr_2O_7^{--}$	−1.33	$Mn(OH)_2$	$-Mn(OH)_3$	−0.1
Mn^{++}	$-MnO_4^-$	−1.51	$Mn(OH)_3$	$-MnO_2$	−0.50
MnO_2	$-MnO_4^-$	−1.695	MnO_2	$-MnO_4^-$	−0.60
H_2O	$-H_2O_2$	−1.77	H_2O	$-HO_2^-$	−0.88

In acid solution, $Cr_2O_7^{--}$ is *reduced* by H_2O_2 (potential difference 1.33 − 0.67 or 0.66 volt) to Cr^{+++}. While the H_2O_2 is also a very powerful *oxidizing* agent, and could certainly oxidize Cr^{+++} to $Cr_2O_7^{--}$ (potential difference 1.77 − 1.33 or 0.44 volt), the former reaction predominates. When Cr^{+++} is oxidized to CrO_4^{--} in the basic solution, it is therefore necessary to destroy any excess H_2O_2 completely before the solution is acidified, in order to prevent the subsequent reduction of the $Cr_2O_7^{--}$ back to Cr^{+++} again.

Likewise, while H_2O_2 is sufficiently powerful, either in acid or in basic solution, to oxidize Mn^{++} or $Mn(OH)_2$ to MnO_4^-, in acid solution H_2O_2 does not react on Mn^{++} because it *more rapidly* reduces MnO_4^- or MnO_2 to Mn^{++} and liberates O_2. In basic solution, the peroxide ion reduces MnO_4^- to the very insoluble MnO_2, but no further. Also, the basic peroxide ion oxidizes Mn^{++} to MnO_2, but no further.

The excess hydrogen peroxide is readily decomposed into water and oxygen gas by boiling the solution. (Note that no oxygen gas is formed, however, by the hydrogen peroxide which is used to oxidize the chromic ion.)

Any manganous ion which is present in the above treatment with hydrogen peroxide in basic solution, is precipitated by oxidation to manganese dioxide (MnO_2 or more probably a hydrated form $MnO(OH)_2$). After the separation of the manganese dioxide precipitate, it is redissolved by hydrogen peroxide in a nitric acid solution. In this case, the manganese dioxide is reduced to manganous ion by the hydrogen peroxide, which, in turn, is oxidized to oxygen. Finally, the very characteristic purple permanganate ion (MnO_4^-) is produced by adding the powerful oxidizing agent, sodium bismuthate ($NaBiO_3$),[1] which is reduced to the trivalent bismuth ion (Bi^{+++}). These changes in the oxidation state of manganese are indicated in Figure 42-1.

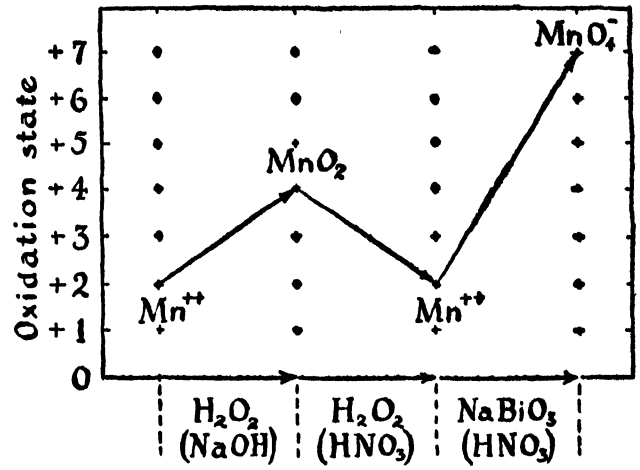


FIG. 42-1. Changes in oxidation state in the separation of manganese.

Experimental Procedure

Chemicals: 1 *F* $HC_2H_3O_2$, Aluminon reagent, 0.1 *F* $Al(NO_3)_3$, 1 *F* $NH_4C_2H_3O_2$, 3 *F* NH_4Cl, saturated Br_2 water, 0.1 *F* $Cr(NO_3)_3$, 0.1 *F* $FeCl_3$, $FeSO_4 \cdot 7H_2O$, 3% H_2O_2, 30% H_2O_2, Fe (filings), 0.1 *F* $Pb(C_2H_3O_2)_2$, 0.1 *F* $Mn(NO_3)_2$, 0.1 *F* $K_3Fe(CN)_6$, 0.1 *F* $K_4Fe(CN)_6$, 0.1 *F* KCNS, $NaHCO_3$ (powdered), $NaBiO_3$ (solid), 1 *F* Na_2CO_3, 1 *F* $NaHSO_4$, 1 *F* Na_2SO_4, 0.1 *F* $Zn(NO_3)_2$.

A. Typical Reactions of the Ammonium Sulfide Group

1. *Behavior of Al^{+++}, Fe^{+++}, Cr^{+++}, Mn^{++}, and Zn^{++} with Typical Reagents.* In the report sheet, is a chart form on which you may enter pertinent data as to any reaction of the above ions with NH_4OH, NaOH, Na_2CO_3, H_2S, and $(NH_4)_2S$, respectively. For any reactions with which you are already thoroughly familiar, fill in the chart without wasting time to repeat the experiment. For each reagent, take about 2-ml samples of 0.1 *F* solutions of the five ions, and add first only 1 to 3 drops of the reagent. Where an excess is called for, add more (up to 2 ml if needed) to the same solution to determine if this produces a different kind of product. Review Experiment 35 in this connection on the formation of complex ions and amphoteric hydroxides. Before testing with H_2S gas, add a drop of 6 *F* HCl to the 2-ml samples of each ion. Then, to test with $(NH_4)_2S$, make these same solutions slightly basic with 6 *F* NH_4OH and pass in more H_2S if necessary.

If you cannot decide the nature of a given precipitate, for example, whether the reaction of sodium carbonate with ferric ion gives a carbonate or a hydroxide, devise a simple experiment to test the point. (In this case, note the evolution of a gas. *After washing* the precipitate, what reagent would you add to cause effervescence of CO_2, if a carbonate were present?)

2. *Red Lake Formation with Aluminum Hydroxide.* The light flocculent precipitate which forms when ammonium hydroxide is added to aluminum ion is often difficult to observe. The dye called "aluminon" (ammonium aurin tricarboxylate), if added to the mixture, is adsorbed by the precipitate to form a characteristic red "lake" which renders the identification of the aluminum hydroxide easier. To 1 ml of water, add a few drops of 0.1 *M* Al^{+++} solution. Add 2 drops of aluminon reagent, and then 3 to 5 drops of 6 *F* NH_4OH to precipitate the $Al(OH)_3$. Note the color. Now make the solution acid with about 0.5 ml 6 *F* HCl, and again make *just* basic by dropwise addition of 6 *F* NH_4OH. After letting the mixture stand a minute, note the color, both of the precipitate (which now should be red), and of the solution. A good red color is not obtained if the solution is too basic. Explain how the above treatment guarantees a

[1] The commercial product here called sodium bismuthate, $NaBiO_3$, is probably quite complex, consisting essentially of B_2O_4 (bismuthyl bismuthate, $BiO \cdot BiO_3$) as the oxidizing agent, which in strong acid easily oxidizes Mn^{++} to MnO_4^-.

very slightly basic solution.

3. *Reactions of Fe^{++} and Fe^{+++}.* You will need to make your own solution of ferrous ion, since such solutions are too easily oxidized by the air to be very stable. For this purpose, dissolve a very small amount of ferrous sulfate, or ferrous ammonium sulfate crystals in 6 to 8 ml of distilled water, for use in the following experiments.

a. *Tests for Fe^{++} and Fe^{+++}.* To very dilute samples of each ion (1 to 2 drops in 1 ml H_2O), add several drops of 0.1 *F* $K_4Fe(CN)_6$ solution. Repeat, using 0.1 *F* $K_3Fe(CN)_6$ solution. Note, in particular, the cases which give dark blue precipitates or colors. Which reagent, then, would you use to test for Fe^{++}? For Fe^{+++}? (Note that we get the intense blue colors when opposite valences are present, i.e., ferr*ous* ion with ferr*i*cyanide ion, and vice versa.)

To 1 ml of very dilute samples of each ion, add 1 ml of 0.1 *F* KCNS. Was your ferrous ion solution entirely free from ferric ion?

b. *Changes in the Oxidation State of Iron.* Add several drops of 6 *F* NaOH to a 2-ml sample of the Fe^{++} solution. Result? Divide the mixture into two portions. To one, add a few drops of 3% H_2O_2 and mix for a moment. Result? Pour the other portion of this mixture over a filter paper and expose to the air for 10 to 15 minutes. Result?

To 1 ml of Fe^{++} solution, add 1 ml of Br_2 water, boil this to remove any excess free bromine, cool the solution and test it for Fe^{+++}.

Shake 2 ml of 0.1 *F* $FeCl_3$ with some iron filings for about 5 minutes. Filter, or decant, and test the resulting solution for Fe^{++}.

4. *Higher Oxidation States of Chromium and Manganese.*

a. *Oxidation with Hydrogen Peroxide.* To 1-ml samples of 0.1 *F* $Cr(NO_3)_3$ and of 0.1 *F* $Mn(NO_3)_2$ in 15-cm test tubes, add 2 drops of 30% H_2O_2, then 5 drops of 6 *F* NaOH. Mix, and after a moment boil the mixture to decompose excess H_2O_2.[1] Results? (Save the solutions for parts b and c.)

b. *Chromates and Dichromates.* To the yellow Na_2CrO_4 solution prepared above, add 3 *F* H_2SO_4 to make it acid. Result? Now again make it basic with 6 *F* NaOH. Result?

c. *Manganese Dioxide, Manganous and Permanganate Ions.* Divide the manganese dioxide mixture prepared above into two portions. To one, add 1 ml of 6 *F* HNO_3; and to the other, add 1 ml of 6 *F* HCl. Warm each. Compare and explain the results. To the one which did not dissolve, add 3 drops of 3% H_2O_2, and mix. Explain the result. Boil the solution to decompose the excess H_2O_2, then cool it and add a small amount (a fourth the volume of a pea) of solid sodium bismuthate, $NaBiO_3$. Result? What would happen if you add 1 ml of 6 *F* HCl to this? Try it.

5. *A Study of Buffer Action*

a. *Ammonium Acetate as a Buffer.* Since acetic acid and ammonium hydroxide have about the same value for their respective ionization constants, a solution of ammonium acetate will be practically neutral, and have the same *p*H as water. Place 5 ml of 1 *F* $NH_4C_2H_3O_2$ in a 15-cm test tube; add 5 ml of distilled water in a second 15-cm test tube. Add 2 drops of methyl orange indicator to each. Prepare a little 1 *F* HCl by a sixfold dilution of the 6 *F* HCl, mix well, and fill your 10-ml graduate to the mark. Now to the 5-ml sample of water, add first a drop of the HCl, and more if needed, until the red methyl orange endpoint is reached, i.e., until the neutral water has been changed to about 10^{-3} *M* in H^+. What volume of the 1 *F* HCl was needed to do this? Now repeat the experiment using the 5-ml sample of 1 *F* $NH_4C_2H_3O_2$ instead of water. What volume of 1 *F* HCl was required this time to make the neutral solution 10^{-3} *M* in H^+?

Let us also test the buffering action of ammonium acetate against the addition of a base. Prepare 2 more 5-ml samples of H_2O and of 1 *F* $NH_4C_2H_3O_2$, respectively. To each, add 2 drops of indigo carmine indicator. (Alizarin yellow R may be used instead.) Prepare a little 1 *F* NaOH by sixfold dilution of the 6 *F* NaOH. Add a drop of this, and more if needed, to the water sample until the indicator color changes, (about 10^{-2} *M* OH^-). Also add the base, from a 10-ml graduate, a little at a time to the ammonium acetate sample, until the hydroxide ion concentration has been increased to 10^{-2} *M* OH^-. Note the respective volumes of 1 *F* NaOH needed. Explain why the ammonium acetate solution is able to neutralize both acids and bases.

b. *Sodium Hydrogen Carbonate as a Buffer.* As an

[1] Any H_2O_2 which is not decomposed will reduce the CrO_4^{--} back to Cr^{+++} when the solution is acidified. See also Footnote 2, p. 306.

instance of the use of an acid salt of a weak acid as a buffer, prepare a dilute sodium hydrogen carbonate solution by dissolving an estimated half gram of solid $NaHCO_3$ in 10 ml of distilled water. Divide into two 5-ml portions. To one add 2 drops of indigo carmine, then 1 *F* NaOH a little at a time until the indicator color change is reached (10^{-2} *M* OH^-). To the other add 2 drops of methyl orange, then 1 *F* HCl until red methyl orange color appears permanently throughout the liquid (10^{-3} *M* H^+). Compare the volumes of base and acid added with the similar data for water. Explain how sodium hydrogen carbonate acts as a buffer.

c. *Control of the Precipitation of Sulfides by Buffer Action.* Dissolve 1 or 2 small crystals of ferrous sulfate in 2 ml of 0.1 *F* $Zn(NO_3)_2$. Acidify this by adding about 0.5 ml of 1 *F* $HC_2H_3O_2$, and saturate the solution with H_2S gas. After noting the color of the precipitate which forms, make the solution just basic by adding 3 to 5 drops of 6 *F* NH_4OH. Explain the result in terms of the relative solubilities of zinc sulfide and ferrous sulfide. Centrifuge the mixture, and discard the solution. To the precipitate, add 1 ml of 1 *F* Na_2SO_4, and then 1 ml of 1 *F* $NaHSO_4$. Shake the mixture, and explain the result.

B. The Analysis of the Ammonium Sulfide Group.

For practice, analyze a known solution containing Al^{+++}, Fe^{+++}, Zn^{++}, Cr^{+++}, and Mn^{++}, by the following procedure. Then, obtain two unknowns from the instructor for analysis. If time permits, an unknown containing ions of both Groups 2 and 3 may be analyzed for both groups. This will give practice in the separation of the sulfides based on their differences in solubility in acid and basic solution.

Procedure for the Analysis of the Ammonium Sulfide Group, Al^{+++}, Fe^{++}, Fe^{+++}, Cr^{+++}, $Cr_2O_7^{--}$, Mn^{++}, MnO_4^-, Zn^{++}.

To 4 ml of the solution to be analyzed (or Solution 21 from the H_2S group, if a general unknown), add 2 ml of 3 *F* NH_4Cl or 1 ml of 6 *F* HCl, and then add just enough 6 *F* NH_4OH to neutralize it, and about 0.5 ml in excess.[1] The absence of a precipitate here (it will flocculate more on standing for several minutes) indicates the absence of which ions? Without filtering off any precipitate, saturate the solution thoroughly with H_2S gas. Again add

[1] Any Fe^{+++}, $Cr_2O_7^{--}$, or MnO_4^- would have been reduced to Fe^{++}, Cr^{+++}, and Mn^{++}, respectively, by the H_2S treatment in acid solution, when Group 2 was precipitated from a general unknown.

If phosphate ion were present in the unknown, the ions of the alkaline earth group of metals (Ca^{++}, Sr^{++}, Ba^{++}, Mg^{++}) would precipitate here as phosphates, when the solution is made basic. This complication will not be introduced into our limited study of qualitative analysis.

OUTLINE—THE AMMONIUM SULFIDE GROUP

Sol. 21 Cations of Groups 3-5.
Add 3 *F* NH_4Cl, or 6 *F* HCl, then 6 *F* NH_4OH to make basic. Saturate with H_2S gas. Add NH_4OH. Warm. Centrifuge, and wash the residue.

Res. 31 $Al(OH)_3$, $Cr(OH)_3$, FeS, Fe_2S_3, MnS, ZnS.
Add 1 *F* Na_2SO_4, 1 *F* $NaHSO_4$, as a buffer. Agitate the mixture. Centrifuge, and wash any residue. White to gray residue indicates zinc.

Sol. 31 Cations of Groups 4-5.
At once add HCl and boil out H_2S. Save for Groups 4-5 analysis.

Res. 32 ZnS.
To confirm, add 6 *F* HCl, evaporate almost to dryness. Add 1 *F* Na_2SO_4, and 1 *F* $NaHSO_4$. Add 1 *F* $NH_4C_2H_3O_2$. Pass in H_2S. White ZnS proves zinc.

Sol. 32 Al^{+++}, Cr^{+++}, Fe^{++}, Fe^{+++}, Mn^{++}.
Boil to remove H_2S. Cool. Add 6-8 drops 30% H_2O_2, and add this to H_2O + NaOH. Let stand. Boil to decompose excess H_2O_2. Centrifuge and wash the residue.

Res. 33 $Fe(OH)_3$, MnO_2.
Add 6 *F* HNO_3 and H_2O_2. Boil. Two portions:
(*1*) *Test for Fe^{+++}.*
Add NH_4OH, HCl, then 0.1 *F* KCNS. A red color of $FeCNS^{++}$ proves iron.
(*2*) *Test for Mn^{++}.*
Add $NaBiO_3$. Purple MnO_4^- proves manganese.

Sol. 33 $Al(OH)_4^-$, CrO_4^{--}.
Acidify, 5 drops excess HCl, then NH_4OH. Flocculent precipitate indicates aluminum. Centrifuge and wash residue.

Res. 34 $Al(OH)_3$.
To confirm, add excess HCl, then aluminon reagent. Add NH_4OH. Flocculent precipitate, $Al(OH)_3$, dyed red, proves aluminum.

Sol. 34 CrO_4^{--}.
Acidify with 1 *F* $HC_2H_3O_2$. Add 0.1 *F* $Pb(C_2H_3O_2)_2$. Yellow precipitate of $PbCrO_4$ proves chromium.

0.5 ml of 6 *F* NH_4OH and warm the mixture slightly. Centrifuge the mixture. (Divide into two tubes to centrifuge it if there is too large a volume for one tube.) Save the solution (S31), acidifying it with HCl and boiling out H_2S at once, if analyses for Groups 4-5 are to be made. Otherwise, discard it. Wash the residue (R31) with 5 ml of distilled water and centrifuge. Discard the washings. Do not let Residue 31 dry; continue *at once* to the separatation of zinc ion.

Separation and Test for Zinc Ion. To Residue 31, add first 2 ml of 1 *F* Na_2SO_4, and then 2 ml of 1 *F* $NaHSO_4$. Agitate the mixture for 2 to 3 minutes. Centrifuge it, and save the solution (S32). Wash and centrifuge any residue (R32).[1] Add 5 drops of 6 *F* HCl to the solid, and evaporate this just to dryness. (Avoid overheating.) Redissolve the residue with 1 ml each of 1 *F* Na_2SO_4, 1 *F* $NaHSO_4$, and 1 *F* $NH_4C_2H_3O_2$. Saturate this with H_2S. Additional $NH_4C_2H_3O_2$ may be added, drop by drop, to promote precipitation. A white precipitate of ZnS proves zinc.

Separation of the Iron and Aluminum Sub-groups. Boil Solution 32 to remove all H_2S gas. Cool it, add 6 to 8 drops of special 30% H_2O_2, and add this mixture to a 15-cm test tube containing a solution of 2 ml of water and 0.5 ml of 6 *F* NaOH.[2] Mix the solution and let it stand for 1 to 2 minutes, then boil it cautiously. (Recall Footnote 3, P. 302, as to the precautions to be observed to prevent loss of material when decomposing H_2O_2.) Centrifuge, and save the solution (S33) for the tests for aluminum and chromium.

Test for Iron (Ferrous or Ferric Ion). Treat Residue 33 with 1 ml of 6 *F* HNO_3. If solution is not complete,[3] add 3 drops of 3% H_2O_2 to reduce any MnO_2 to Mn^{++}, and boil the solution to decompose excess H_2O_2. Cool the solution, dilute it to 2 ml with water, and divide it into two portions. To one, add 6 *F* NH_4OH to neutralize excess acid, and then add 6 *F* HCl dropwise to make the solution slightly acid again. Add 1 ml of 0.1 *F* KCNS. A deep red color of $FeCNS^{++}$ proves iron.[4]

Test for Manganous Ion. To the other portion of the above solution, add a small amount (about a fourth of the volume of a pea) of solid sodium bismuthate ($NaBiO_3$). A purple color of permanganate ion (MnO_4^-) proves manganese.

Test for Aluminum Ion. Acidify Solution 33 with 6 *F* HCl (test by a drop of the mixed solution on litmus paper), and add about 5 drops in excess. Then make the solution just basic with 6 *F* NH_4OH (faint ammonia odor after mixing). An almost invisible, flocculent precipitate indicates aluminum. Centrifuge, and wash the residue. Save the solution (S34) for the test for chromium.

To confirm, dissolve Residue 34 in 1 ml of 6 *F* HCl, add 2 drops of aluminon reagent, and then make the solution just basic by dropwise addition of 6 *F* NH_4OH. A red precipitate, which flocculates as the mixture stands, or on gentle warming, and which is suspended in an otherwise colorless solution, proves aluminum.[5] If in doubt, observe the test tube against a white background. If a good red color, which is completely absorbed in the precipitate, is not obtained, the solution is probably too basic. In this case, re-acidify with HCl, and again make just basic with NH_4OH.

Test for Chromate Ion. To Solution 34, add 1 *F* $HC_2H_3O_2$ to make it slightly acid, and then add 1 ml of 0.1 *F* $Pb(C_2H_3O_2)_2$. A yellow precipitate of $PbCrO_4$ proves chromium. If necessary, centrifuge the mixture to obtain a better observation of the precipitate.

[1] The dark color may be due to some undissolved iron sulfide. If cobalt and nickel salts were present, black CoS and NiS would remain here, due to the slow rate at which they dissolve at this *p*H.

[2] The order of addition of reagents is important as it assures an adequate mixing with the H_2O_2 and opportunity for complete oxidation, before the H_2O_2 is decomposed by the basic solution. 2 to 3 ml of 3% H_2O_2 may be used instead. However, failure to obtain a good test for chromium is often due to incomplete oxidation of Cr^{+++} to CrO_4^{--}.

[3] A separation of the Fe^{+++} solution and the MnO_2 precipitate can be made here, but it is unnecessary as the tests for Fe^{+++} and for Mn^{++} do not interfere with each other.

[4] Do not report iron if only a slight coloration results, which may be due to impurities of iron in the reagents used, or more likely to rust particles carelessly introduced into the sample from test tube clamps, wire gauze, etc. If in doubt, test a sample of the original unknown with 0.1 *F* KCNS.

[5] This precipitate is quite characteristic. Silica, often present as an impurity from the NaOH used, gives a white precipitate. $Cr(OH)_3$, which might be present from any unoxidized Cr^{+++}, gives a precipitate somewhat similar to that of $Al(OH)_3$, but may be distinguished as it will redissolve on the addition of 0.5 ml of 3 *F* $(NH_4)_2CO_3$. Any Fe^{+++} which failed to be completely separated from Solution 32 would give a reddish color to the original $Al(OH)_3$ precipitate before the aluminon reagent is added. In this case, treat this precipitate with a little 6 *F* NaOH, centrifuge the undissolved $Fe(OH)_3$, and acidify the solution with 6 *F* HCl. Then follow the aluminon reagent treatment as above.

*Name*_____

REPORT: Exp. 42

*Date*_____

The Ammonium Sulfide Group

*Section*_____

*Locker Number*_____

A. Typical Reactions of the Ammonium Sulfide Group

1. Behavior of Al^{+++}, Fe^{+++}, Cr^{+++}, Mn^{++}, and Zn^{++}.

In the spaces provided, write the formulas of the precipitates formed, or new ions formed in solution, if any, and indicate also any characteristic colors, etc. when each ion of the group is treated with the reagent in the left hand column.

	Al^{+++}	Fe^{+++}	Cr^{+++}	Mn^{++}	Zn^{++}
6 *F* NH_4OH					
6 *F* NH_4OH (excess)					
6 *F* NaOH					
6 *F* NaOH (excess)					
1 *F* Na_2CO_3					
H_2S (acid solution)					
$(NH_4)_2S$					

2. Red Lake Formation with Aluminum Hydroxide.

The equation for the reaction of Al^{+++} with NH_4OH is . . . . . _____

Explain how the addition, first of an excess of HCl, then of a slight excess of NH_4OH, insures that the solution will not become too basic to form a satisfactory red adsorption compound of the dye with the precipitate.

3. Reactions of Ferrous and Ferric Ions.

a. *Tests for Fe^{++} and Fe^{+++}.* Indicate the characteristic colors of the precipitates or solutions formed when Fe^{++} and Fe^{+++} are treated with the reagents listed.

	$K_4Fe(CN)_6$	$K_3Fe(CN)_6$	$KSCN$
Fe^{++}			
Fe^{+++}			

Summarizing, then, the best reagent to use in testing for:

Fe^{++} would be_____, giving a_____color,

Fe^{+++} would be_____, giving a_____color,

or_____, giving a_____color.

b. *Changes in the Oxidation State of Iron.* Write net ionic equations and indicate colors of any precipitates or solutions formed when the following reactions were carried out:

NaOH is added to ferrous ion . . . . _____

H_2O_2 is added to the above product . . _____

Action of moist air on ferrous hydroxide . . _____

Br_2 water is added to ferrous ion . . . _____

Iron filings are shaken with $FeCl_3$ solution . _____

4. *Higher Oxidation States of Chromium and Manganese.*

Write net ionic equations and indicate colors of any precipitates or solutions formed when the following substances are mixed in solution, (indicate if there is no action):

Hydrogen peroxide and manganous nitrate (basic) . . . . . _____

Hydrogen peroxide and chromic nitrate (basic) . . . . . _____

Hydrogen peroxide, heated in a basic solution. . . . . _____

Chromate ion and sulfuric acid . . . . _____

Above product, and sodium hydroxide . . _____

Manganese dioxide and hydrochloric acid (warm) . . . . . _____

Manganese dioxide and nitric acid (warm) . _____

Above mixture, and hydrogen peroxide . . _____

Manganous ion and sodium bismuthate (acidic) . . . . . _____

5. *A Study in Buffer Action.*

a. *Ammonium Acetate as a Buffer.* The volume of 1 *F* HCl needed to increase the acidity from neutral (*p*H 7) to 10^{-3} *M* H^+ for:

5 ml water was_____, and for 5 ml 1 *F* $NH_4C_2H_3O_2$ was_____. The volume of 1 *F* NaOH needed to increase the basicity from neutral (*p*H 7) to 10^{-2} *M* OH^- for:

5 ml water was_____, and for 5 ml 1 *F* $NH_4C_2H_3O_2$ was_____.

Suppose the same volume of 1 *F* HCl which you added to the 5 ml of 1 *F* $NH_4C_2H_3O_2$ to change it to 10^{-3}*M* H^+, were added to the 5 ml of H_2O instead. What would the H^+ concentration of this solution now be? Show calculations.

_____

*Name*_____

Explain, by discussion and equations, how ammonium acetate is able to buffer the solution against the addition of both acids and bases.

b. *Sodium Hydrogen Carbonate as a Buffer.* The volumes of the following reagents required for reaction with 5-ml samples of an $NaHCO_3$ solution were:

1 *F* HCl_____ml, 1 *F* NaOH_____ml.

Explain, by discussion and equations, how $NaHCO_3$ is able to buffer the solution against the addition of both acids and bases.

c. *Control of the Precipitation of Sulfides by Buffer Action.*

The addition of H_2S to a solution of Zn^{++}, Fe^{++}, and $HC_2H_3O_2$ gave a precipitate of . . . . . _____

The subsequent addition of NH_4OH to the above mixture, which was saturated with H_2S, gave a precipitate of . . . . . _____

Explain these results, considering the relative solubilities of the precipitated salts, and the effect of any buffer formed.

Explain, by discussion and equation, how a mixture of 1 *F* Na_2SO_4 and 1 *F* $NaHSO_4$ is able to separate a mixture of ZnS and FeS:

B. The Analysis of the Ammonium Sulfide Group[1]

Summary, Unknown No._____ Ions found_____

Unknown No._____ Ions found_____

[1] Hand in, also, with each analysis, a summary of the steps in the procedure, as given for the preceding unknowns.

The Alkaline Earth and Alkali Groups — 43

College Chemistry, Chapter 26

Review of Fundamental Concepts

The elements comprising the alkaline earth and alkali groups are quite similar and have many properties in common. Their compounds exhibit only one stable oxidation state; they do not form amphoteric hydroxides, being distinctly basic; and they do not readily form complex ions. The separation of the alkaline earth elements depends almost entirely on differences in the solubilities of their salts, which show a regular gradation through the periodic table. The salts of the alkali metals are almost all readily soluble. The following table will be useful in interpreting the analytical procedure.

Solubilities of Alkaline Earth Salts
(g/100 g H_2O, at room temperature)

	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}
OH^-	0.001	0.16	1.74	3.89
CO_3^{--}	0.09	0.0015	0.001	0.0018
SO_4^{--}	35.5	0.2	0.01	0.00024
CrO_4^{--}	138.	18.6	0.12	0.00037
$C_2O_4^{--}$	0.015	0.0007	0.005	0.01

We shall include the ions Ba^{++}, Ca^{++}, Mg^{++}, Na^+, K^+, and NH_4^+ in our study of these groups. Strontium ion (Sr^{++}) will be omitted, as its inclusion would introduce no new principles of separation and analysis. While ammonium ion is not an alkali ion, its salts, likewise, are nearly all soluble, so it is convenient to consider it at this time. The test for ammonium ion must always be carried out with a separate portion of the original unknown, since ammonium hydroxide and ammonium salts are used as reagents in the general group separations.

Precipitation with Ammonium Carbonate

The group reagent used to precipitate the alkaline earth ions is ammonium carbonate. (It is really an approximately equimolal mixture of ammonium hydrogen carbonate [NH_4HCO_3] and ammonium carbamate [$NH_4CO_2NH_2$], but we shall speak of it simply as ammonium carbonate, $(NH_4)_2CO_3$). Since this is a salt of a weak base and of a weak acid, it will hydrolyze in solution to a marked extent, forming the hydrogen carbonate ion,

$$NH_4^+ + CO_3^{--} + HOH \rightleftarrows HCO_3^- + NH_4OH.$$

This results in a lower concentration of the carbonate ion, on which the precipitation of insoluble carbonates depends. To prevent this, and thereby increase the carbonate ion concentration, the precipitation is carried out in a strong ammonium hydroxide solution. The hydrogen carbonates of the alkaline earth ions are quite soluble. (Recall that calcium and magnesium hydrogen carbonates are the principal substances present in temporarily hard water.)

The Separation of Magnesium

Magnesium carbonate, being fairly soluble, is not precipitated readily unless the solution is concentrated and the carbonate ion concentration is very high. Furthermore, it tends to form supersaturated solutions and does not precipitate promptly. Since magnesium hydroxide is even less soluble than the carbonate, the magnesium ion might precipitate as this compound when the ammonium carbonate and ammonium hydroxide reagent is added. This can be prevented by buffering the solution with a high concentration of ammonium ion so as to repress the hydroxide ion concentration. In the analysis of a general unknown, sufficient ammonium chloride for this purpose will be present from the previous treatment of the solution in the separation of the Group 3 ions.

While in some schemes of analysis, all excess ammonium ion is removed and the carbonate ion concentration is made as high as possible so as to precipitate magnesium ion with the alkaline earth group, we shall leave it in solution and test for it in the solution containing the alkali ions.

Experimental Procedure

Chemicals: 6 *F* $HC_2H_3O_2$, 3 *F* $NH_4C_2H_3O_2$, 3 *F* $(NH_4)_2CO_3$, 3 *F* NH_4Cl, 1 *F* NH_4Cl, NH_4Cl solid, 15 *F* NH_4OH, 0.1 *F* $BaCl_2$, 0.1 *F* $CaCl_2$, 0.1 *F* $Mg(NO_3)_2$, "Magnesium Reagent" (p-nitrobenzene-azoresorcinol), 0.1 *F* KBr, 1 *F* K_2CrO_4, 1 *F* KH_2PO_4, 1 *F* $K_2C_2O_4$, 0.1 *F* NaCl, $Na_3Co(NO_2)_6$ reagent.

A. Typical Reactions of the Alkaline Earth and Alkali Groups.

For this experiment, instead of performing a number of separate, prescribed tests to learn the properties of the ions, study the procedure for Analysis of the Groups, and answer the questions in the report sheet. You may wish to try out various test tube reactions on your own initiative, such as the flame tests for sodium and potassium ions, illustrated in Figure 20-5; or refer to previous experiments such as Experiment 35, where the behavior of magnesium hydroxide in ammonium hydroxide and ammonium chloride solutions is considered.

B. The Analysis of the Alkaline Earth and Alkali Groups (Groups 4 and 5)

Prepare a known solution containing all or some of the ions in the groups, and analyze it according to the Procedure. Then obtain one or more unknown solutions from the instructor for analysis.

Procedure for the Analysis of the Alkaline Earth and Alkali Groups, Ba^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, and NH_4^{+}.

Test for Ammonium Ion. Place 3 ml of the solution to be tested in an evaporating dish, and make it basic with 6 *F* NaOH. Cover the dish with a watch glass, on the under side of which is attached a moist strip of red litmus paper. Warm the solution gently to liberate any ammonia present as the gas. (Avoid boiling, which would contaminate the litmus with spray droplets of the NaOH solution.) An even, unspotted blue color proves ammonium ion. The characteristic odor of ammonia, observed soon after the solution is warmed, would also serve as a positive test. (**Be very cautious** in bringing your nostrils close to a hot sodium hydroxide solution, however, as it might be superheated, and splatter in your face or eyes.)

Precipitation of the Alkaline Earth Group. If the unknown is being analyzed for this group only, evaporate a 4-ml sample of it to 2 ml, add 2 ml of 3 *F* NH_4Cl, and reheat it almost to boiling. If the sample is Solution 31 from a general unknown analysis, evaporate it to 3 to 4 ml, but omit the addition of ammonium chloride as this is already present. To either of these hot samples, add 2 ml of 3 *F* $(NH_4)_2CO_3$ reagent, and agitate the mixture at intervals for 5 minutes. Centrifuge. Save the solution (S41) for the analysis of magnesium ion and the alkali ions.

Test for Barium Ion. To Residue 41, add 6 *F* $HC_2H_3O_2$, a few drops at a time, and warm the mixture to dissolve it. (Avoid much excess, or partially neutralize the excess with NH_4OH.) Buffer the solution with 0.5 ml of 3 *F* $NH_4C_2H_3O_2$, dilute it to 2 ml with water, and add 1 ml of 1 *F* K_2CrO_4. Heat the mixture, and centrifuge. Yellow $BaCrO_4$ (R42) indicates barium. The solution (S42) will contain any Ca^{++}. To confirm barium, add 3 to 5 drops of 6 *F* HCl to Residue 42 to dissolve the yellow precipitate, dilute to 2 ml with H_2O, and add 2 drops of 3 *F* H_2SO_4. A white precipitate of $BaSO_4$ proves barium. (It may be necessary to centrifuge to show whether the precipitate is white, in the yellow solution.)

Test for Calcium Ion. To Solution 42, add 0.5 ml of 1 *F* $K_2C_2O_4$ and then make slightly basic with

OUTLINE—THE ALKALINE EARTH AND ALKALI GROUPS

Test the original unknown for NH_4^{+}.

Sol. 31 Cations of Groups 4-5.

Add 3 *F* NH_4Cl, if not present from previous treatment. Add 3 *F* $(NH_4)_2CO_3$. Agitate. Centrifuge and wash the residue.

Res. 41 $BaCO_3$, $CaCO_3$.
Add 6 *F* $HC_2H_3O_2$, 3 *F* $NH_4C_2H_3O_2$, 1 *F* K_2CrO_4. Heat. Centrifuge.

Res. 42 $BaCrO_4$.	*Sol. 42 Ca^{++}.*
Yellow precipitate indicates barium. To confirm: add HCl, then H_2SO_4. White $BaSO_4$ proves barium.	Add 1 *F* $K_2C_2O_4$, then NH_4OH. White CaC_2O_4 proves calcium.

Sol. 41 Mg^{++}, Na^{+}, K^{+}. Divide into two portions:

(1) *Test for Mg^{++}.*	(2) *Test for Na^{+}, K^{+}.*
Add NH_4OH, 1 *F* KH_2PO_4. White $MgNH_4PO_4$ indicates magnesium. To confirm: centrifuge, to the residue add HCl, "magnesium reagent," then NaOH. Blue lake in $Mg(OH)_2$ proves magnesium.	Evaporate, add HNO_3, evaporate and ignite to remove NH_4^{+} salts. Moisten residue with HCl. Flame tests: Yellow proves sodium, violet proves potassium. To confirm K^{+}: add H_2O, $Na_3Co(NO_2)_6$. Yellow precipitate of $K_2NaCo(NO_2)_6$ proves potassium.

6 *F* NH_4OH. Let stand 10 minutes if a precipitate does not appear before that time. White CaC_2O_4 proves calcium. It may be necessary to centrifuge, to show that the precipitate is white in the yellow solution. Further confirmation may be made, if desired, by decanting the yellow solution. Then to the precipitate add a few drops of 6 *F* HCl to dissolve it, add 1 ml of water, 2 drops of 1 *F* $K_2C_2O_4$, and again make basic with NH_4OH. The white precipitate of CaC_2O_4 will reappear.

Test for Magnesium Ion. Divide Solution 41 into two portions. To one portion, add 1 ml of 6 *F* NH_4OH and then 0.5 ml of 1 *F* KH_2PO_4. Agitate at intervals for 5 to 10 minutes. A white precipitate of magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) indicates magnesium.[1] Let the solution stand at least a half hour and observe, before deciding that Mg^{++} is absent, as this precipitate is often slow in forming. To confirm magnesium, centrifuge the mixture, discard the solution, and dissolve the precipitate by adding several drops of 6 *F* HCl. Dilute this to 1 ml with water, add 1 drop of "Magnesium Reagent" (para-nitrobenzeneazoresorcinol), and then make the solution alkaline with 6 *F* NaOH. Mix, and let stand for 1 to 5 minutes. Observe against good light for a characteristic blue "lake." This is a flocculent precipitate of $Mg(OH)_2$, colored blue by the adsorbed dye.

Test for Sodium and Potassium Ions. Evaporate the second portion of Solution 41 almost to dryness in a porcelain evaporating dish, cool it, add ml of 6 *F* HNO_3, and evaporate to dryness. Continue to heat the evaporating dish intensely with the bare flame, without using the wire gauze, so that all portions of the dish are hot and all ammonium salts have been vaporized, i.e., until white fumes cease to be evolved. (This process is called "igniting" the precipitate.) Let the dish cool. Any solids remaining are probably salts of sodium or potassium. Moisten these with about 5 drops of 6 *F* HCl. Carry out flame tests for sodium and potassium ions, using a clean nichrome wire, and two pieces of blue cobalt glass for observation of the potassium flame if much sodium is present.[2] Review Figure 20-5 for the method of cleaning the nichrome wire, and the proper manner in which to carry out these tests.

If the potassium flame test is not definite, add 1 ml of H_2O to the salt residue, transfer this solution to a 10-cm test tube, and add 0.5 ml of sodium cobaltinitrite reagent $Na_3Co(NO_2)_6$. Let stand and observe after 5 to 10 minutes if necessary, to see the yellow precipitate of $K_2NaCo(NO_2)_6$, which proves potassium.[3]

[1] If Ba^{++} and Ca^{++} were not removed completely before, they would give insoluble phosphate precipitates here.

[2] Since sodium salts are so widely distributed and occur as traces in many salts and reagents, do not report sodium unless it gives a flame test as pronounced as a 0.005 *M* Na^+ solution.

[3] If NH_4^+ salts were not completely removed by the above ignition, a very similar yellow precipitate of ammonium cobaltinitrite would be formed. As a comparison, add 1 ml of $Na_3Co(NO_2)_6$ reagent to 1 ml of H_2O which contains 2 drops of 1 *F* NH_4Cl.

REPORT: Exp. 43

The Alkaline Earth and Alkali Groups

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

A. Typical Reactions of the Alkaline Earth and Alkali Groups

Refer to the Solubility Chart and to the Outline for the Analysis, given in the discussion on this experiment, in answering the following. Try any experimental tests necessary to be certain of the results.

1. Write net ionic equations for any reactions occurring when dilute solutions of the following are mixed:

$MgCl_2$, $CaCl_2$, and NH_4OH . . . . . _____

$CaCl_2$, $BaCl_2$, and K_2CrO_4 . . . . . _____

$MgCl_2$, $BaCl_2$, and H_2SO_4 . . . . . _____

$CaCl_2$, $K_2C_2O_4$, and NH_4OH. . . . . _____

$MgCl_2$, NH_4Cl, K_2HPO_4, and NH_4OH . . . . _____

2. On the basis of the periodic table relationships, what would you predict as to the general solubility (indicate as soluble, slightly soluble, or insoluble) of each of the following:

$Be(OH)_2$_____ $Ra(OH)_2$_____

$BeSO_4$_____ $RaSO_4$_____

3. Why does the addition of HCl dissolve such insoluble salts as $BaCrO_4$ and CaC_2O_4?

4. Why is there a difference in the behavior of a magnesium salt solution with (a) NH_4OH, and (b) $NH_4OH + NH_4Cl$?

5. What happens when a solid ammonium salt, as NH_4Cl, is heated intensely in an evaporating dish?

6. What happens when HNO_3 is added to an ammonium salt solution, and the mixture evaporated and heated? Equation.

B. Analysis of the Alkaline Earth and Alkali Groups[1]

Summary, Unknown No._____ Ions found_____

Unknown No._____ Ions found_____

[1] Summarize the procedure as before.

The Qualitative Analysis of Cd^{++}, Bi^{+++}, AsO_3^{---}, Sb^{+++}, Ni^{++}, and Sr^{++} G

A Study Assignment

In the qualitative analysis scheme which has been presented in this manual, several cations were omitted. In general, the separation and detection of these ions require the application of the same principles which are illustrated by the analytical scheme as given. Therefore, for students who have the time to study the properties of these ions, the following data are included. These data will give the information necessary for the analysis of these ions in the analytical scheme.

Properties of the Ions

In the acid hydrogen sulfide group the additional ions are cadmium, Cd^{++}, and bismuth, Bi^{+++}, in the copper subgroup, and antimonous ion, Sb^{+++}, and arsenite ion, AsO_3^{---}, in the tin subgroup.

Cd^{++}. The nitrate, acetate, sulfate, chloride, bromide, and iodide salts of bivalent cadmium are soluble, colorless compounds. The white, slightly soluble hydroxide is not amphoteric, but is soluble in excess ammonium hydroxide because of the formation of the complex $Cd(NH_3)_4^{++}$ ion. The sulfide is yellow and has a K_{sp} of approximately 10^{-28}. It does not dissolve in alkali sulfides, but is soluble in fairly concentrated hydrochloric acid and in hot, dilute nitric acid. The cadmium ion often forms complex ions, such as $CdCl_4^{--}$ and $Cd(CN)_4^{--}$, with halide and cyanide ions. The Cd^{++} ion concentration is so low in solutions containing high concentrations of chloride ions that H_2S will give no precipitate when added to an acid solution.

Bi^{+++}. Bismuth is a metalloid which shows oxidation states of +3 and +5. In the higher oxidation state it is usually found as the bismuthate ion, BiO_3^-, which is a very strong oxidizing agent. In the analytical scheme it is usually encountered as the simple cation, Bi^{+++}. The chloride, bromide, nitrate, and sulfate of this cation are readily hydrolyzed to form the insoluble basic or oxy salts:

$$Bi^{+++} + Cl^- + H_2O \rightleftarrows BiOCl\ (s) + 2\ H^+.$$

If excess hydrogen ions are present, the hydrolysis reaction is reversed to give a clear solution of the salt. The white hydroxide is insoluble both in excess alkali bases and in ammonium hydroxide. The sulfide, Bi_2S_3, is dark brown and has a very small K_{sp} of approximately 10^{-72}. It is not amphoteric but is soluble in boiling dilute nitric acid and in concentrated hydrochloric acid. The Bi^{+++} ion does not form complex ions readily, the yellow BiI_4^- being the only stable one. Bismuth ion may be reduced by an alkaline solution of sodium stannite, $Na_2Sn(OH)_4$, to the black metallic bismuth.

As^{+++} or AsO_3^{---}. Arsenic is a metalloid, and from its position in Group V it might be expected to be less metallic than its congeners antimony and bismuth. The hydroxides of arsenic in both of its oxidation states, +3 and +5, are definitely acidic, H_3AsO_3 and H_3AsO_4. It is only in strongly acid solutions that there is present an appreciable amount of the cations As^{+++} and As^{+5} in equilibrium with the anions AsO_3^{---} and AsO_4^{---}. When strongly acid solutions of these anions are saturated with H_2S, the yellow sulfides As_2S_3 and As_2S_5 are precipitated. Both are insoluble in concentrated hydrochloric acid, but will dissolve in hot concentrated nitric acid. Both of the sulfides are amphoteric and dissolve readily in alkali sulfides to form thioarsenite, AsS_3^{---}, and thioarsenate, AsS_4^{---} ions, respectively. Stannous chloride will reduce arsenic compounds to metallic arsenic in concentrated hydrochloric acid solutions. The Marsh test for arsenic involves the reduction of arsenic compounds by zinc in an acid solution. The reduction product is arsine, AsH_3, which may be decomposed to form a mirror of metallic arsenic.

Sb^{+++}. Of the two oxidation states possible, +3 and +5, the antimonous ion, Sb^{+++}, is the one usually encountered. Its hydroxide is more basic than that of As^{+++}. It is slightly soluble in water but is soluble in excess strong base. Salts of Sb^{+++} such as the halides, nitrates, and sulfates, hydrolyze readily to form insoluble basic or oxy salts such as SbOCl. In a slightly acid solution, Sb_2S_3 may be precipitated with H_2S, and the orange-red sulfide is soluble in alkali sulfides, forming the thioantimonite ion, SbS_3^{---}. The sulfide is soluble in moderately concentrated hydrochloric acid. Antimony compounds may be reduced to metallic antimony by metals such as iron or zinc in moderately concentrated acid solutions, but are not reduced by stannous salts.

In the ammonium sulfide group the additional ions to be considered are Co^{++} and Ni^{++}.

Co^{++}. Soluble salts of the cobaltous ion include the chloride, bromide, iodide, nitrate, and sulfate. In dilute water solutions the Co^{++} is pink. The carbonate, chromate, cyanide, oxalate, phosphate, hydroxide, and sulfide are common slightly soluble compounds of cobalt. The black CoS, with K_{sp} of approximately 10^{-21}, is precipitated almost completely from slightly basic solutions by saturation with H_2S. The freshly precipitated sulfide is readily soluble in dilute hydrochloric acid, but after standing for a while its rate of solution in a buffered acid solution of *p*H 2 is very slow. Dilute nitric acid will dissolve CoS readily. The hydroxide of Co^{++} is blue, is slightly soluble in excess NaOH solution, and is readily soluble in excess ammonium hydroxide because of the formation of the complex ammonia ion of Co^{++}. Cobaltous ion is sometimes oxidized in the presence of a complexing agent and forms complexes such as $Co(NO_2)_6^{---}$, cobaltinitrite ion, or $Co(NH_3)_6^{+++}$, where the cobaltic ion is the central ion. All cobalt salts when melted with borax in an oxidizing flame form a blue bead on cooling.

Ni^{++}. The chemistry of the nickelous ion is very similar to that of Co^{++} in many respects. The sulfide is black, has a K_{sp} of approximately 10^{-21}, and is precipitated completely by H_2S only in slightly basic solutions. Like ZnS and CoS, NiS is dissolved slowly by a dilute acid solution. The hydroxide is not amphoteric, but dissolves in excess ammonium hydroxide because of the formation of the complex ion $Ni(NH_3)_6^{++}$. A very specific reagent for the detection of Ni^{++} is the organic substance dimethylglyoxime, which forms a red precipitate with nickel in a solution alkaline with NH_4OH.

In the alkaline earth group the strontium ion, Sr^{++}, was omitted. A study of the solubility table in Experiment 43 will reveal that, in general, salts of this ion have solubilities between those of the Ca^{++} and Ba^{++} ions. Note that the carbonates have about the same solubility. The chromate of Ba^{++} is much less soluble than that of Ca^{++} or Sr^{++}. After removal of most of the Ba^{++} as chromate, the Sr^{++} may be selectively precipitated as the sulfate without affecting the Ca^{++}. Strontium salts impart a bright red color to the flame.

Optional Exercises on the Qualitative Analysis of Cd^{++}, Bi^{+++}, Sb^{+++}, AsO_3^{---}, Ni^{++}, Co^{++}, and Sr^{++}

After careful consideration of the discussion of the properties of the additional cations, outline, on a separate report sheet, the chemistry and the analytical scheme for each of the groups specified, and include the cations listed above. As far as possible, use the same reagents specified in the group analyses. When solutions or precipitates are obtained which contain only one or possibly two ions, select an appropriate reagent to make a positive identification for each ion.

1. *The Hydrogen Sulfide Group—Cu^{++}, Cd^{++}, Bi^{+++}, Pb^{++}, Hg^{++}, Sn^{++}, Sb^{+++}, AsO_3^{---}.*

(a) Write net ionic equations for each of the reactions of Cd^{++}, Bi^{+++}, Sb^{+++}, and AsO_3^{---} with the reagents given in the discussion of the properties of these ions.

(b) Expand the schematic outline of the analysis of the hydrogen sulfide group, Experiment 41, to include all the ions listed above.

(c) Carry out analyses of unknown solutions of these ions, as directed by your instructor.

2. *The Ammonium Sulfide Group—Zn^{++}, Ni^{++}, Co^{++}, Mn^{++}, Fe^{++}, Fe^{+++}, Cr^{+++}, Al^{+++}.*

(a) Write net ionic equations for each of the reactions of Co^{++} and Ni^{++} with the reagents given in the discussion of the properties of these ions.

(b) Expand the schematic outline of the analysis of the ammonium sulfide group, Experiment 42, to include all the ions listed above.

(c) Carry out analyses of unknown solutions of these ions, as directed by your instructor.

3. *The Alkaline Earth and Alkali Groups—Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+}.*

(a) Write net ionic equations for the reactions of Sr^{++} with typical reagents used in this group, and distinguish between the relative solubilities of the various salts.

(b) Expand the schematic outline of the analysis of the alkaline earth and alkali groups, Experiment 43, to include all the ions listed above.

(c) Carry out analyses of unknown solutions of these ions, as directed by your instructor.

The Analysis of General Unknown Inorganic Substances. The Solution of Solids. 44

Review of Fundamental Concepts

Previous samples which the student has analyzed for the several groups as studied in Experiments 40 to 43 all have consisted of solutions of soluble substances, and have required no other preliminary treatment than a suitable adjustment of the *p*H. If one is given, for analysis, a solid which does not dissolve in water, he must first get it into solution before applying the regular analytical procedures. Let us review briefly several principles which frequently are involved in the solution of insoluble substances.

Solvent Action by Hydrogen Ions

Dilute acids, as hydrochloric acid or nitric acid, will dissolve many metallic oxides and hydroxides, as zinc oxide and calcium hydroxide, and also the salts of weak acids, as magnesium carbonate and barium phosphate. These substances dissolve because of the formation of slightly ionized substances and the consequent displacement of the saturated solution equilibria involved. Hydrogen ion, which is a mild oxidizing agent, will dissolve many of the more active metals, as magnesium, and zinc. Dilute nitric acid is not so satisfactory for the solution of some metals, however, as aluminum, iron, and tin.

Solvent Action by Oxidizing Agents

The most commonly used oxidizing agent is *nitric acid.* When dilute, it usually is reduced to nitric oxide (NO), but sometimes to nitrous oxide (N_2O), nitrogen, or even ammonia. When concentrated, the reduction product is generally nitrogen dioxide (NO_2). It is an effective solvent for most sulfides (see p. 299) and for most of the metals. Nitric acid reacts with tin, or alloys containing tin, but leaves the tin as an insoluble hydrated oxide, called beta-stannic acid. This latter substance is difficult to dissolve either in concentrated hydrochloric acid or in strong sodium hydroxide solution, in spite of its amphoteric character. With the very noble metals, as gold or platinum, nitric acid fails to react.

The *free halogens,* as chlorine water or bromine water, may be used to oxidize the insoluble mercurous chloride (Hg_2Cl_2) to a higher oxidation state to form soluble mercuric chloride ($HgCl_2$).

Solvent Action by Reducing Agents

In a few cases, reducing agents may be used to transform a substance into a soluble form. Thus manganese dioxide, which is unaffected by nitric acid, is readily attacked by concentrated hydrochloric acid or by hydrogen peroxide, which reduces it to manganous ion. (Remember this when you want to remove the brown manganese dioxide stain from a vessel which has been used with potassium permanganate.)

Silver can be recovered from scrap silver chloride residues by first mixing such residues with 12 *F* hydrochloric acid, which favors the formation of silver chloride complex ion ($AgCl_2^-$), and then reducing this with metallic zinc. The metallic silver then can be separated and dissolved with nitric acid.

Solvent Action by Complex Ions

The great stability of many complex ions can be utilized to effect solution in a number of cases. The easiest way to dissolve silver chloride is to treat it with ammonium hydroxide solution, forming the stable *ammonia complex ion,* $Ag(NH_3)_2^+$.

Concentrated hydrochloric acid, in a number of cases, owes its effectiveness in part to the formation of a *complex chloride ion.* Tin may be dissolved in warm hydrochloric acid, partially due to the displacement of the equilibrium by the stannous chloride complex ion, $SnCl_4^{--}$, which is formed. (If a little oxidizing agent is present also, the stannic chloride ion, $SnCl_6^{--}$, will be formed, and promote the solvent action still more.) Likewise, a hematite ore (Fe_2O_3), which strangely is difficultly soluble in dilute nitric acid, dissolves readily in hydrochloric acid because of the forma-

tion of the ferric chloride complex, $FeCl_4^-$.

Oxalate ion ($C_2O_4^{--}$) is often used to control the solubility of substances in qualitative and quantitative separations. Oxalic acid is effective in removing rust stains and ink spots formed by the iron-tannin inks, because it renders ferric compounds soluble by reducing them and forming the complex ion, $Fe(C_2O_4)_2^{--}$.

Aqua regia, the frequently used mixture of nitric and hydrochloric acids, owes its effectiveness to a combination of the oxidizing action of nitric acid, and the complex ion forming action of the chloride ion. Mercuric sulfide, gold, and platinum are attacked readily by it. (See also p. 299.)

Cyanide ion (CN^-), while not used very much in elementary qualitative analysis because of its poisonous character, forms very stable complexes with a number of the metal ions. Coupled with the oxidizing action of the air itself, it is very effective in the commercial extraction of gold and silver from their ores. The equation is

$$4\,Ag + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Ag(CN)_2^- + 4\,OH^-.$$

Solvent Action by Metathesis

While insoluble salts of weak acids are generally easily dissolved by adding dilute nitric acid, insoluble salts of strong acids, as barium sulfate, present a more difficult problem. Since most metallic carbonates are insoluble, it is possible, by boiling the insoluble salt with a strong sodium carbonate solution, to obtain at least a partial replacement of the anion of the insoluble salt by carbonate ion in many instances. This type of action is called a *metathesis*. The resulting carbonate salt then can be dissolved by dilute acid.

The extent of the metathesis will depend on the relative solubility products of the original insoluble salt and of the corresponding metal carbonate. For example, if an excess of barium sulfate solid is boiled with 50 ml of 1 *F* Na_2CO_3 solution, we can calculate the amount of barium sulfate which will dissolve, as follows.[1] The reaction is

$$CO_3^{--} + BaSO_4 \rightleftarrows BaCO_3 + SO_4^{--},$$

for which the equilibrium constant expression is

$$K = \frac{(SO_4^{--})}{(CO_3^{--})}.$$

Both solid $BaSO_4$ and solid $BaCO_3$ will be present in the equilibrium mixture, so we can obtain this ratio, of (SO_4^{--}) to (CO_3^{--}), by calculating the ratio of their solubility products,[2]

$$\frac{(Ba^{++})\,(SO_4^{--})}{(Ba^{++})\,(CO_3^{--})} = \frac{1 \times 10^{-10}}{5 \times 10^{-9}} = 0.02.$$

If the concentration of SO_4^{--} formed by the reaction above is x, the concentration of CO_3^{--} remaining at equilibrium from a 1 *F* Na_2CO_3 solution will be 1 − x, so that

$$\frac{(SO_4^{--})}{(CO_3^{--})} = \frac{x}{1-x} = 0.02, \text{ or } x = \text{about } 0.02\ M\ SO_4^{--}.$$

In a volume of 50 ml, this amounts to 0.001 formula weight or about 0.23 gram of $BaSO_4$ dissolved. Using 100 ml of 2 *F* Na_2CO_3, 0.9 gram of $BaSO_4$ would dissolve. Thus, even though barium carbonate is slightly more soluble than barium sulfate, it is possible to metathesize the latter, and then after filtration, dissolve the product in acid.

Solvent Action by Fusion Processes

Where more powerful treatment is needed to effect solution, the chemist resorts to a fusion, dissolving the substance to be analyzed in a suitable molten flux. The most widely used alkaline flux is sodium carbonate. This is able to disintegrate the silicate compounds which are present in most rocks, minerals, and ores, and which resist the other methods previously discussed. They undergo a fusion metathesis, so that on cooling and adding water, sodium silicate which is soluble, and the insoluble metal carbonate or oxide, are formed. For example, if the mineral, talc, is powdered, fused with sodium carbonate, then cooled and water added, we may write as a typical equation,

$$Mg_3Si_4O_{10}(OH)_2 + 4\,Na_2CO_3 \longrightarrow 3\,MgCO_3 + 8\,Na^+ + 4\,SiO_3^{--} + H_2O + CO_2$$

The addition of acid to this mixture will dissolve the magnesium carbonate and precipitate silicic acid,

$$MgCO_3 + 2\,H^+ \longrightarrow Mg^{++} + H_2O + CO_2,$$
$$SiO_3^{--} + 2\,H^+ \longrightarrow H_2SiO_3.$$

With an acid flux, as potassium bisulfate $KHSO_4$ or better, the pyrosulfate $K_2S_2O_7$, substances of a basic character, such as a hematite ore, Fe_2O_3, often

[1] Such calculations are only approximate, since the activity of the ions may be considerably affected at such high concentrations. See also page 279 on the concept of activity.

[2] See also the discussion of fractional crystallization, Example 5 page 281.

containing silica also, would be attacked.

If oxidizable substances are present in the solid to be fused, the addition of an oxidizing agent, as sodium peroxide (Na_2O_2), or potassium nitrate (KNO_3), is an aid to solution.

Experimental Procedure

Chemicals: All reagents for Experiments 40 to 43. If the solution of solids is to be considered: Br_2, KNO_3, $K_2S_2O_7$ or $KHSO_4$ (fused), Na_2CO_3 solid, 1 *F* Na_2CO_3, Na_2O_2, $Na_2B_4O_7$, Zn (mossy).

Special supplies: For fusion only, nickel crucible, Fisher or Meker burner, and flower pot shield.

1. Typical Solution Reactions.

Instead of performing a series of prescribed experiments on the solution of insoluble substances, the student is invited to try out, on his own initiative, such procedures as are suggested to him by the questions in the application of principles section of the report sheet.

2. General Unknown Analyses.

The student will obtain a general unknown solution containing any of the ions of the limited scheme as outlined in Experiments 40–43. Follow the procedures in these experiments, step by step. Start with a single 4-ml sample, and use the filtrate from each group precipitant for the next succeeding group procedure. Report the analysis as you have done previously, as suggested in the report sheet.

Analyze *additional unknowns* as the instructor directs, and as the remaining time of the laboratory course permits. These may be additional unknown solutions, or unknown solid samples. The latter may be metal alloys, or nonmetallic mixtures, ores, minerals, etc., dissolved according to the directions in paragraph 4, following. (They should not include metals not provided for in the scheme of this manual, as these might interfere in the analysis, unless removed.) In the case of nonmetallic solids, the student may also analyze for the negative ions as outlined in Experiment 39, correlating these with the solubility of the substance. For example, if the solid is soluble in nitric acid and silver ion is found, it is not necessary to test for chloride ion. Also do not test such a solution for nitrate ion, which should be tested for in the original water extract of the solid, since all nitrates are soluble.

3. Preliminary Examination of a Solid.

A preliminary examination sometimes gives valuable clues as to the nature of a solid. It is wise to verify these through the subsequent analysis of the solution before reporting them, however. Note whether the sample appears homogenous, or is made up of several substances. Observe any characteristic crystalline form, colors, or odors. Flame tests may be made, using a nichrome wire. Borax bead tests may be made. For these, touch the heated end of a platinum wire (the "lead" of a mechanical pencil is a satisfactory substitute) to some borax, and reheat to form the colorless bead. Then touch to a fragment of the unknown, and again fuse it. Consult one of the chemistry handbooks for details as to the coloration of the bead with various metals, and also as to the flame colorations.

Organic matter, if present, interferes with many qualitative tests. It probably will not be present in samples given for elementary analyses. It may be tested for by heating a bit of the solid in a closed glass tube, or 10-cm test tube. Charring indicates organic matter. A drop of concentrated H_2SO_4 is sometimes added before warming, to give a more sensitive test. Some organic substances do not char by heat alone. If found, organic matter may be removed by oxidation with H_2SO_4 and HNO_3. Consult a general qualitative text for details.

4. The Solution of a Solid Unknown.

(a) *The Sample is a Metal or Alloy.* Most metals are attacked by warm 6 *F* HNO_3. Some, as Fe, and the Al and Mg light alloys, dissolve more readily in warm 12 *F* HCl. Sometimes a drop or two of liquid Br_2 (obtain from the instructor) added to the HCl assists the solution. In a few instances, aqua regia may be necessary. Try a very small bit of your unknown to determine the best solvent to use, then dissolve about 0.2 to 0.5 g of the metal, warming it in 3-8 ml of the acid chosen. (Use less if concentrated.) If necessary, add more acid, but avoid a large excess. When the metal is completely disintegrated, evaporate just to dryness, add several drops of acid, then 10 ml of H_2O. If a precipitate forms by hydrolysis, add a little more acid to dissolve it. If solution is complete, add H_2O to make about 20 ml volume for each 0.1 g of unknown metal alloy taken, then use about 5 ml of

this for the analytical procedure.

A white residue remaining after solution in aqua regia, which dissolves in NH_4OH or hot water, may be tested for Pb^{++} and Ag^+ by the Group 1 procedure, and the filtrate tested beginning with Group 2.

If a white residue remains from the HNO_3 treatment, which cannot be dissolved, it may be hydrated SnO_2. Separate this by centrifuge from the solution, and treat it with 1 ml of 6 *F* NaOH and 2 ml of 2 *F* NaHS, warm and agitate it for 10 minutes. Dilute with 3 ml of H_2O and just acidify with 6 *F* HNO_3. Centrifuge the precipitated sulfides and discard the filtrate. Dissolve the residue by warming it with 2 ml of 12 *F* HCl,[1] evaporate the solution to 1 ml and combine with the main filtrate.

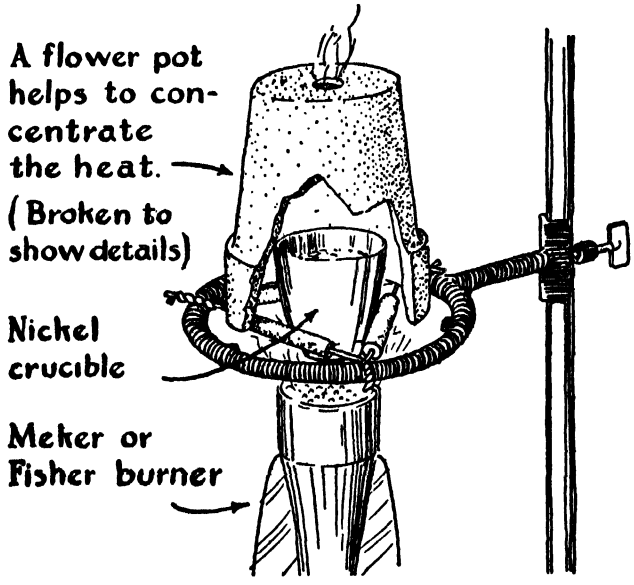


FIG. 44-1. The disintegration and solution of a silicate by fusion with sodium carbonate.

(b) *The Sample is a Non-Metallic Solid.* Try its solubility in water, and note the effect of this solution on litmus. If insoluble, make preliminary tests using a very small amount of the solid with 2-ml portions of various solvents, to determine the best one to use. Try them in this order: 6 *F* HNO_3, 16 *F* HNO_3, 12 *F* HCl, and aqua regia (i. e. add ⅓ its volume of 16 *F* HNO_3 to the 12 *F* HCl trial). Dissolve about 0.5 g of the solid mixture[2] with 2-5 ml of the reagent chosen (use less if concentrated). Warm and add more reagent if needed, but avoid a large excess. Finally, evaporate almost to dryness to remove excess acid, and dilute with water to give a total volume of about 10 ml for each 0.1 g of sample taken. Use about 5 ml of this for the analytical procedure.

If a residue still remains undissolved from the treatment with acid by the above procedures,[3] it may be subjected to a *sodium carbonate fusion.* Dry the residue by warming, place it in a small nickel crucible, and mix with 3-4 times its bulk of anhydrous Na_2CO_3, and an equal amount of K_2CO_3.[4] Heat with a Fisher burner at its maximum temperature, until all is molten. (See Fig. 44-1.) If undissolved solid remains, add a very small amount of $NaNO_3$ (or Na_2O_2), and reheat. Cool, and place the crucible on its side in a small beaker. Add 15-20 ml of distilled water, and boil gently to disintegrate the mass. (The crucible may be left soaking for some time, or over night.) Decant, filter or centrifuge the mixture. To the residue, add 2 ml of 6 *F* HNO_3 to dissolve it, warming if needed.

Likewise, the solution from the carbonate melt is made just acid with 6 *F* HNO_3, evaporated just to dryness to dehydrate any silicic acid, several drops of HNO_3 added, then 5 ml of H_2O to dissolve it. This would contain any negative ions from the insoluble substance, which could be tested for here, if desired. This solution probably would not contain metal ions, unless present as part of the negative ion, such as CrO_4^{--}. It may be tested separately, or combined with the fusion residue which was dissolved in HNO_3. This, in turn, may be analyzed separately or combined with the main filtrate from the acid treatment. This latter should first be tested for Na^+ and K^+, since they have been added by the fusion. A sodium carbonate fusion in a nickel crucible will probably add traces of this element, which will precipitate along with the zinc sulfide in our scheme. It should not interfere with these tests.

[1] Part of this solution may be tested now for tin, by following the procedure as given for Sol. 24, "Test for Tin," page 302.

[2] If the sample is quite non-homogenous, a larger amount may be advisable to secure a representative sample.

[3] Substances which may remain undissolved by the previous acid treatment include: sulfates of lead, barium, and calcium, halides of silver, some ignited sulfates or oxides or native ores of iron, chromium and tin, and most silicates.

[4] A mixture of two salts, such as this, melts at a lower temperature than either one singly.

REPORT: Exp. 44

Analysis of a General Unknown—Solution of Solids

*Name*_____

*Date*_____

*Section*_____

*Locker Number*_____

1. Application of Principles

What reagent (s) and procedures would you choose to bring about the solution of each of the following substances or mixtures? Indicate by number the type(s) of solvent action: (1) H^+ to neutralize or form a weak acid, (2) H^+ to oxidize, (3) Oxidation in general, (4) Reduction, (5) Complex ion formation, (6) Metathesis, (7) Fusion. Write equations for any important reactions in each case.

Substance	*Reagent(s) and Procedures*	*Type(s)*	*Equations*
Dolomite rock, $CaCO_3$ and $MgCO_3$			
Brass, an alloy of Cu and Zn			
Stainless steel, Fe and Cr			
Apatite, a $Ca_3(PO_4)_2$ mineral			
Gypsum, $CaSO_4 \cdot 2H_2O$			
Pyrolusite ore, MnO_2			
Magnal alloy, Al and Mg			
Calomel, Hg_2Cl_2			
Wollastonite, $CaSiO_3$			
Chromite ore, $Fe(CrO_2)_2$	Fuse with sodium peroxide.		
Gold metal, Au			

2. Problems

Would metathesis be a satisfactory method of bringing about the solution of each of the following substances? Calculate the weight of salt which could be dissolved by boiling an excess of the solid with 50 ml of 3 *F* Na_2CO_3 solution, in each case.

(a) $PbSO_4$

_____g $PbSO_4$

(b) AgCl (You will have to square the solubility product of AgCl in this case. Why?)

_____g AgCl

3. Analysis of General Unknown Substances

Summary:

Type and Sample No._____ Ions found_____

Type and Sample No._____ Ions found_____

Type and Sample No._____ Ions found_____

(For type indicate as solution, alloy, or non-metallic solid)

For each unknown, on a separate sheet, describe any preliminary tests performed, the method of solution if a solid, and make a chart of each step of the analysis, showing sample, reagent, observations, and conclusions, as in previous experiments.

Appendix I

The Measurement of Physical Quantities

A. The Use of Dimensions

The measurement of any physical quantity represents two factors, the number itself, and the unit, or units, in which the measurement is made. These units are known as the *dimensions* of the measurement. For example, a piece of silver is measured and the dimensions reported as 3.00 wide and 5.00 long. This gives little information—even the shape is uncertain, for we do not know that both quantities are expressed in the same units. But if the measurement is reported as 3.00 cm wide by 5.00 cm long, adequate information is given to describe both the size and the shape.

In the solution of all problems dealing with physical quantities, the units must be given. These may be subjected to the usual mathematical operations of multiplication and division, the same as any other quantity. Thus, the surface area of one side of the above piece of silver is obtained by multiplying the units, as well as the numbers,

$3.00\ \text{cm} \times 5.00\ \text{cm} = 15.0\ \text{cm}^2$, or square centimeters.

Furthermore, if the thickness is given as 2.00 mm and we wish to compute the volume, the dimensions first must be converted to the same units, i.e. 2.00 mm = 0.200 cm. The volume is then calculated by multiplying both the numbers and the units,

$15.0\ \text{cm}^2 \times 0.200\ \text{cm} = 3.00\ \text{cm}^3$, or cubic centimeters.

Again, if the weight of this piece of silver is found to be 31.5 grams, we may calculate the density of silver in accordance with the defining equation for density

$$D = \frac{M}{V} = \frac{31.5\ \text{g}}{3.00\ \text{cm}^3} = 10.5\ \frac{\text{g}}{\text{cm}^3}.$$

The units, or dimensions, of density are g/cm^3, read grams per cubic centimeter. Since these are unlike dimensions (weight and volume), they cannot be reduced further, and are left simply with the indicated division.

Units frequently may be cancelled in processes of division: *Example 1.* Compare the relative weights of equal volumes of the heaviest metal, osmium (density 22.48 g/cm^3), and of the lightest metal, lithium (density 0.53 g/cm^3).

$$\frac{\text{Density of osmium}}{\text{Density of lithium}} = \frac{22.48\ \text{g/cm}^3}{0.53\ \text{g/cm}^3} = 42.$$

The units cancel out, and the result, 42, a ratio of two densities, is a pure number, without dimensions.

Example 2. If the density of silver is 10.5 g/cm^3, what will a block of silver weigh whose measurements are 4.00 cm, 5.00 cm, and 10.0 cm?

The volume is: 4.00 cm × 5.00 cm × 10.0 cm = 200 cm^3. From the formula for density, D = M/V, we have, by transposing,

$$M = D \times V = 10.5\ \frac{\text{g}}{\text{cm}^3} \times 200\ \text{cm}^3 = 2100\ \text{g}.$$

By cancelling the cm^3 in both numerator and denominator, the dimension is given correctly in grams.

Students who have trouble in deciding whether to multiply or to divide in the solution of a given problem, will be helped by a consideration of dimensions. This is illustrated by the following

Example: The density of gasoline is 7.0 pounds per gallon ($7.0\ \frac{\text{lb}}{\text{gal}}$). How many gallons would it take to weigh 100 pounds?

If we multiply, the dimensions would be, $\text{lb} \times \frac{\text{lb}}{\text{gal}} = \frac{\text{lb}^2}{\text{gal}}$, which is obviously incorrect.

If we divide, the dimensions would be, $\text{lb} \div \frac{\text{lb}}{\text{gal}} = \text{lb} \times \frac{\text{gal}}{\text{lb}} = \text{gal}$. Since volume is required, this is obviously the correct procedure. Therefore,

$$100\ \text{lb} \div 7.0\ \frac{\text{lb}}{\text{gal}} = 100\ \text{lb} \times \frac{\text{gal}}{7.0\ \text{lb}} = 14.3\ \text{gallons of gasoline.}$$

B. Significant Figures

When the scientist records or publishes experimental data, he indicates the degree of certainty of each item of data by expressing the numerical value to the proper number of figures which are justifiable, or significant, according to the accuracy of the equipment, method, and observation.

Definition: The number of *significant figures* in

a quantity is the number of trustworthy figures in it, the last "trustworthy" figure, however, being somewhat doubtful. Thus, in writing the value 492 ml, we mean that the quantity is definitely known to the nearest 10 ml, but not necessarily to the nearest 1 ml. If we wish to give a more precise meaning to the last significant figure, we may write the value as 492 ± 2 ml, or 492 ± 4 ml, depending on whether the true value is known to lie between 490 and 494 ml, or between 488 and 496 ml. In general, the last significant figure in a value is to be regarded as somewhat uncertain. The number of significant figures in 0.49 is two, in 6.96 is three, in 20.5 is three, in 491736 is six, and so on.

When a zero is part of a number, it is a significant figure if it occurs between any two digits other than zero, or to the right of the number beyond the decimal point. It is not a significant figure if it occurs on either side of the number merely as a means of fixing the decimal point. For example, the zero in 205.1 is significant, likewise in 2.50; but the zeros in 0.025 or in 22,400 are not significant figures. If we measure a length as 5.2 meters, we might likewise write this using different units as 520 centimeters, 5200 millimeters, or even as 0.0052 kilometers. We have not changed the accuracy of the expression by the units we use. In each case, the values are expressed to two significant figures—to the nearest 10 centimeters in this measurement.

Zeros to the right of a number, which are needed to fix the decimal point, in general merely represent unknown digits. Because of the ambiguity as to the number of significant figures in such cases, scientists commonly resort to a notation using exponential powers of ten. Suppose a student measures the volume of thirty-two grams of oxygen as 22,400 ml. If the reliability of the measurement justifies only two significant figures, we write it 2.2×10^4 ml; if three significant figures, 2.24×10^4 ml; or if five significant figures, 2.2400×10^4 ml. Unless there is some particular reason to do otherwise, one digit is usually retained to the left of the decimal point.

While a rigorous treatment of the number of figures which are significant when one performs various mathematical operations is a rather complicated problem, the following approximate rules will suffice for our purposes.

In addition and subtraction no more figures should be used than can be trusted in the quantity having the fewest trustworthy figures.

Examples:

401.1	cm		307.4	g
9763.			−6.193	
+1.504				
10165.605 = 10166 cm.			301.2	g.

In the addition, the sum should be expressed only to the nearest centimeter, since 9763 is expressed only to the nearest centimeter; also in the subtraction the difference should be expressed only to the nearest tenth of a gram. In the actual operation of adding or subtracting, do not bother to add or subtract columns which obviously cannot affect the final result. In rounding off a value to the desired number of significant figures, increase the last figure retained by one if the first discarded figure is 5 or greater.

In a subtraction, the number of significant figures is not necessarily the same in the answer as in the values subtracted.

Example:

29.744 g (wt. of dish + silver)
29.232 (wt. of dish)
0.512 g (wt. of silver).

Note that five significant figures in the weighings are needed to obtain a weight of silver which is certain to three significant figures.

In multiplication and division, the same number of significant figures should be retained in each of the factors. It is often advantageous, however, to carry one, but never more than one, extra figure in the factor where such a figure is available. The product or quotient should be expressed to the same number of significant figures that are contained in the factor having the least number of significant figures, except in certain cases where this would give a lower percent of certainty than in the factors involved, in which case one is justified in carrying one additional figure.

Examples:

(1) *Multiplication:* What is the weight in grams of 2.75 gram atoms of silver, whose atomic weight is 107.88?

$$2.75 \text{ g at} \times 108 \frac{\text{grams}}{\text{g at}} = 297.00 \text{ g} = 297 \text{ g (answer).}$$

The atomic weight of silver is rounded off to 108, since 2.75 has three significant figures, and since 108 differs from 107.88 by only about 1 part in 1000. The answer is known to only three figures, hence it is incorrect to write it as 297.00 g.

(2) *Division:* How many moles in a liter of

glycerine (weight 1255 grams), if the molecular weight of glycerine is given as 92?

$$\text{No. moles} = 1255\ \text{g} \div 92\ \frac{\text{g}}{\text{mole}} = 13.6\ \text{moles}.$$

Since the molecular weight of glycerine was expressed to two significant figures, one might expect to express the answer as 14 moles. To do so, however, would express the answer to an accuracy of only 1 part in 14, while the molecular weight was expressed to an accuracy of 1 part in 92, hence one should carry three significant figures, 13.6 moles, as the answer.

Resume: The proper use of significant figures involves nothing more than the use of good common sense in mathematical computations. One of the main purposes of stressing the subject in this manual is to eliminate the tendency of students to carry out their calculations to numerous decimal points, blissfully ignorant of the fact that excessive places are utterly meaningless.

C. Experimental Errors

Since it is impossible, in practice, to make an absolutely exact measurement, the scientist measures as closely as his method, equipment, and powers of observation permit. In recording his measurements, he expresses the data to the appropriate number of significant figures to indicate their respective degrees of certainty. Errors of method are those inherent in the method, irrespective of the equipment or observational powers employed. This is the most difficult type of error to detect. Errors of equipment are those which are inherent in the construction and calibration of the equipment. Errors of observation are those inherent in the average experimenter's powers of perception, and should, of course, be distinguished from blunders.

In the following chart, each value under "Precision of Measurement" represents the sum of the average observational error and the error involved in the particular type of apparatus, as used in this course. For example: If the bottom of the meniscus of a liquid contained in a 50-ml graduated cylinder is somewhere between the 45.0 ml and the 46.0 ml graduations, you should read this to the nearest estimated 0.1 ml, as 45.7 ml. You would recognize, however, that this reading is uncertain by ± 0.2 ml. This uncertainty could be recorded in the reading as 45.7 ± 0.2 ml. The structure of the apparatus, the properties of the liquid, and the physical abilities of the eye prevent any more precise estimation of the volume. This chart should be of value in locating sources of principal errors in your experiments, and in indicating the degree of certainty of your data.

Instrument	*Precision of Measurement*
Mercury barometer	0.5 mm
Analytical, or pulp, balance	0.001 g
Triple-beam balance	0.02 g
Platform balance	0.5 g
50-ml burette	0.02 ml
100-ml gas-measuring tube	0.05 ml
10-ml graduated pipette	0.05 ml
500-ml graduated cylinder	2 ml
50-ml graduated cylinder	0.2 ml
10-ml graduated cylinder	0.1 ml
110°C thermometer	0.2°C

In the experimental work performed in this course, the inaccuracy of the results, including errors of method, equipment, and observation, should not exceed 3 to 5 percent of the accepted values, and in most cases will be more accurate. If the deviation of the experimental results from the true value exceeds 5 percent, a blunder usually is indicated. The inaccuracy of a result usually is expressed as *percent error* and is obtained by dividing the difference between the accepted value and the experimental value by the accepted value, and multiplying the quotient by 100. Thus, if the experimental result for the molal volume of oxygen were 22.1 liters, and the accepted value were 22.4 liters, the percent error of the result would be:

$$\%\ \text{error} = \frac{\text{Accepted value} - \text{Experimental value}}{\text{Accepted value}} \times 100$$

$$= \frac{22.4 - 22.1}{22.4} \times 100 = 1\%$$

The percent error is always expressed as a positive number, whether the experimental value is larger or smaller than the accepted value.

It is to be noted that the percent error is a measure of the accuracy of the result, not of the precision of the measurements. *Precision* is a measure of how closely measurements which are re-

peated check with one another, while *accuracy* is a measure of how closely the final result checks with the true or accepted value. You should strive toward both precision and accuracy, as the former leads to the latter, and accuracy is the aim of the competent experimenter.

It is often useful to calculate the *percent of uncertainty* of a measurement, which provides a measure of the certainty of the measurement, exclusive of any errors of method. This is calculated by dividing the uncertainty of the measurement by the measured value and multiplying the quotient by 100. Thus, if a piece of metal is weighed on the analytical balance and its weight recorded as 2.397 grams, since the uncertainty of the measurement is 0.001 g (see preceding table), the percent of uncertainty is:

$$\% \text{ uncertainty} = \pm \frac{0.001}{2.4} \times 100 = \pm 0.04\%.$$

This means that the experimental value is known to lie within the range of 0.04% greater and 0.04% less than the true value. To calculate the percent of uncertainty of a final result when several measurements are involved, the sum of the percent uncertainties of the several measurements is taken.

Drill Problems

(You may refer to the answers to some of these problems, on P. 341, *after* solving them on your own initiative.)

1. Carry out the operations on the data given in each of the following cases to calculate the quantity called for. Show your method, including the dimensions of measurement. (These units will tell you which mathematical operation to perform.)

(a) Velocity = 50 mi/hr, time = 0.5 hr, distance = ?
(b) Velocity = 186,000 mi/sec, distance = 93,000,000 mi, time = ?
(c) Time = 9.3 sec, distance = 100 yd, velocity = ?
(d) Density Al = 2.70 g/cm^3, weight = 2700 g, volume = ? If this were shaped as a cube, length of one edge = ?
(e) Weight Hg = 272 g, volume = 20 cm^3, density = ?
(f) Weight apples = 240 lb, amount in each box = 40 lb/box, number of boxes = ?
(g) Weight H_2O = 180 g, molecular weight = 18 g/mole, number of moles = ?

2. How many significant figures in each of the following numbers.

(a) 3005
(b) 3500
(c) 0.035
(d) 0.350
(e) 3.050
(f) 3.0005

3. Carry out the following operations, recording the answer correctly in accordance with the rules of significant figures:

(a) Subtract 5.1 from 28.347
(b) Subtract 5.10 from 28.347
(c) Multiply 0.020 by 1.111
(d) Divide 36.02 by $(3.0)^2$

4. A beaker of water is weighed as 1200 grams. How would you write this number so as to avoid ambiguity, if the weight is known to the nearest (a) ten grams, (b) one hundred grams, (c) gram, (c) tenth of a gram.

5. The length of a table is measured as 2 meters, 3 centimeters, and 4 millimeters. Express this length as (a) meters, (b) centimeters, (c) millimeters, (d) kilometers. How many significant figures in each case?

6. A series of beakers are weighed as follows: 125.2 g, 90.3 g, 56.2 g, and 20.237 g. How should you record the sum of these weights so as to avoid any incorrect conclusions as to the precision of measurement.

7. Three determinations of the percent of chlorine in sodium chloride were: 60.1%, 60.5%, and 60.3%, averaging 60.3%. The accepted value, based on the atomic weights (Na 22.997, Cl 35.457), is 60.658% Cl. What is the percentage error in the analysis, and to how many significant figures should it be expressed?

8. What is the percent of uncertainty in measuring 50 ml of water in (a) a 50-ml graduated cylinder, (b) a 500-ml graduated cylinder? (Note: Assume the precision of measurement given in the table in Appendix I, Sec. C.)

Table I—Logarithms

Natl. Nos.	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

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TABLE II

The Metric System of Units

Fundamental Units	*Conversion Factors*
Weight: 1 kilogram (kg) = 1000 grams (g) 1 gram = 1000 milligrams (mg)	Weight: 1 pound = 454 grams 1 kilogram = 2.20 pounds
Length: 1 meter (m) = 100 centimeters (cm) 1 centimeter = 10 millimeters (mm)	Length: 1 inch = 2.54 centimeters 1 meter = 39.4 inches 1 kilometer = 0.62 miles
Volume: 1 liter (l) = 1000 milliliters (ml) 1000 milliliters = 1000.028 cubic centimeters (cm^3)	Volume: 1 quart = 946 milliliters 1 liter = 1.06 quarts

TABLE III

Various Units and Conversion Factors

Length:
1 Angstrom unit (Å) = 10^{-8} centimeter
1 micron = 10^{-3} millimeter

Volume:
1 cubic foot = 28.3 liters
= 7.48 gallons
1 ounce (US liquid) = 29.6 milliliters

Mass:
1 gram = 15.4 grains
1 ounce (avoirdupois) = 28.3 grams
1 ounce (apothecary, troy) = 31.1 grams

Pressure:
1 atmosphere (atm) = pressure of a mercury column 760 mm or 29.92 inches high
= 14.696 lb per sq in
= 1.0133 bars (dynes per cm^2)
= 1033.3 grams per cm^2

Temperature:
Absolute zero (0°K) = −273.18°C
Conversion formulas: $°K = °C + 273$

$$°F = \frac{9}{5}°C + 32$$

$$°C = \frac{5}{9}(°F - 32)$$

Electrical:
1 ampere (unit of current) = a flow of one coulomb per second.
1 volt (unit of potential) = the potential difference necessary to cause a current of one ampere through a resistance of one ohm.
1 Faraday (electrochemical) = 96,500 coulombs, the quantity of electricity which will deposit one gram equivalent of a substance at an electrode.

Miscellaneous:
Avogadro's number = 0.6023×10^{24} molecules per mole
The gas constant (R) in the perfect gas law equation (PV = nRT) = 82.0 ml atm per degree per mole
= 1.9868 calories per degree per mole
= 8.3145 joules per degree per mole
1 calorie (cal) = the energy required to raise one gram of water one °C (more precisely, from 14.5° to 15.5°C)
1 British thermal unit (BTU) = the energy required to raise one pound of water one °F (more precisely, from 39° to 40°F)
1 British thermal unit = 252 calories.

TABLE IV

The Vapor Pressure of Water at Different Temperatures

Temperature (°C)	*Vapor Pressure* (*mm of mercury*)	*Temperature* (°C)	*Vapor Pressure* (*mm of mercury*)	*Temperature* (°C)	*Vapor Pressure* (*mm of mercury*)
−10 (ice)	1.0	22	19.8	45	71.9
− 5 "	3.0	23	21.1	50	92.5
0	4.6	24	22.4	60	149.4
5	6.5	25	23.8	70	233.7
10	9.2	26	25.2	80	355.1
15	12.8	27	26.7	90	525.8
16	13.6	28	28.3	100	760.0
17	14.5	29	30.0	110	1074.6
18	15.5	30	31.8	150	3570.5
19	16.5	35	42.2	200	11659.2
20	17.5	40	55.3	300	64432.8
21	18.6				

TABLE V

Temperature Corrections for Barometer Readings

Subtract the corrections to allow for differences in the expansion of mercury and of the brass scale on the barometer, at various temperatures.

Temperature (° C)	*Barometer Reading* (*mm*)						
	640	*660*	*680*	*700*	*720*	*740*	*760*
16	1.7	1.7	1.8	1.8	1.9	1.9	2.0
18	1.9	1.9	2.0	2.1	2.1	2.2	2.2
20	2.1	2.2	2.2	2.3	2.3	2.4	2.5
22	2.3	2.4	2.4	2.5	2.6	2.7	2.7
24	2.5	2.6	2.7	2.7	2.8	2.9	3.0
26	2.7	2.8	2.9	3.0	3.0	3.1	3.2
28	2.9	3.0	3.1	3.2	3.3	3.4	3.5
30	3.1	3.2	3.3	3.4	3.5	3.6	3.7

TABLE VI

Concentration of Desk Acid and Base Solutions

Reagent	*Formula*	*Formality*	*Density*	*Percent Solute*
Acetic acid, glacial	$HC_2H_3O_2$	17 *F*	1.05 g/ml	99.5%
Acetic acid, dil		6	1.04	34
Hydrochloric acid, conc	HCl	12	1.18	36
Hydrochloric acid, dil		6	1.10	20
Nitric acid, conc	HNO_3	16	1.42	72
Nitric acid, dil		6	1.19	32
Sulfuric acid, conc	H_2SO_4	18	1.84	96
Sulfuric acid, dil		3	1.18	25
Ammonium hydroxide, conc	NH_4OH	15	0.90	58
Ammonium hydroxide, dil		6	0.96	23
Sodium hydroxide, dil	NaOH	6	1.22	20

TABLE VII

THE VOLATILITY OF ACIDS FROM WATER SOLUTION

	B. P.
Volatile acids:	
Carbonic acid	very volatile
Hydrogen sulfide	very volatile
Sulfurous acid	very volatile
Hydrochloric acid 20%	110°C
Acetic acid	118
Nitric acid 68%	120.5
Hydrobromic acid 47%	126
Hydroiodic acid 57%	127
Practically non-volatile:	
Phosphoric acid	$-H_2O$ 213
Sulfuric acid	330

Note: Where percent composition is given, this is the composition of the constant boiling mixture.

TABLE VIII

REPLACEMENT (OR ACTIVITY) SERIES OF SOME METALS

Very active with H_2O or acids.	K, Ba, Ca, Na	Oxides reduced by electrolysis, but not by H_2 or CO.
Active with acids, or with steam when metal is hot.	Mg, Al, Mn, Zn, Cr, Fe	Oxides reduced by C or Al (hot), but not by H_2 or CO.
Less reactive with acids.	Cd, Ni, Sn, Pb, H	Oxides reduced by heating with H_2 or CO.
Active only with stronger oxidizing acids, as HNO_3, H_2SO_4. No H_2 formed.	Cu, Sb, Bi, Hg, Ag	Oxides reduced to metal (decomposed), by heat alone.
Active only with aqua regia.	Au, Pt	

TABLE IX

THE SOLUBILITY OF SOME COMMON GASES, AT 20°C

	Gas	*Solubility l/100 l H_2O*	
Very soluble—thousands of volumes of gas in 100 volumes of water	SO_2	3,937	*Henry's Law*—The solubility of a gas is proportional to the partial pressure of the gas above the solvent. This law does not hold for very soluble gases at high concentration.
	HCl	47,500	
	NH_3	70,000	
Fairly soluble—hundreds of volumes of gas in 100 volumes of water	CO_2	88	
	Cl_2	230	
	H_2S	258	
Slightly soluble—one to four volumes of gas in 100 volumes of water	N_2	1.5	
	H_2	1.8	
	CO	2.3	
	O_2	3.1	

TABLE X—GENERAL SOLUBILITY RULES FOR COMMON SALTS AND BASES

NO_3^-	All *nitrates* are soluble.
$C_2H_3O_2^-$ . . .	All *acetates* are soluble, ($AgC_2H_3O_2$ only moderately).
Cl^-	All *chlorides* are soluble, except AgCl, Hg_2Cl_2, and $PbCl_2$. ($PbCl_2$ is slightly soluble in cold water, moderately soluble in hot water.)
SO_4^{--}	All *sulfates* are soluble, except $BaSO_4$ and $PbSO_4$. ($CaSO_4$, Hg_2SO_4, and Ag_2SO_4 are slightly soluble; the corresponding bisulfates are more soluble.)
CO_3^{--}, and PO_4^{---}	All *carbonates* and *phosphates* are insoluble, except those of Na^+, K^+, and NH_4^+. (Many acid phosphates are soluble, as $Mg(H_2PO_4)_2$, and $Ca(H_2PO_4)_2$.)
OH^-	All *hydroxides* are insoluble, except NaOH, KOH, NH_4OH, and $Ba(OH)_2$. ($Ca(OH)_2$ is slightly soluble.)
S^{--}	All *sulfides* are insoluble, except those of Na^+, K^+, and NH_4^+, and those of the alkaline earths: Mg^{++}, Ca^{++}, and Ba^{++}. (Sulfides of Al^{+++} and Cr^{+++} hydrolyze and precipitate the corresponding hydroxides.)
Na^+, K^+, NH_4^+ .	All salts of *sodium*, *potassium*, and *ammonium* are soluble, except several uncommon ones, as $Na_4Sb_2O_7$, $K_2NaCo(NO_2)_6$, $(NH_4)_2NaCo(NO_2)_6$, K_2PtCl_6, $(NH_4)_2PtCl_6$.
Ag^+	All *silver* salts are insoluble, except $AgNO_3$ and $AgClO_4$. ($AgC_2H_3O_2$ and Ag_2SO_4 are only moderately soluble.)

TABLE XI

THE RELATIVE CONCENTRATION OF IONS IN 0.1 *F* SOLUTIONS OF ELECTROLYTES

Classification	*Acids*	*Bases*	*Salts*
Strong electrolytes	HCl HBr HI HNO_3 H_2SO_4	$NaOH$ KOH $Ba(OH)_2$	Almost all soluble salts
Moderately weak electrolytes	$H_2C_2O_4$ H_2SO_3 H_3PO_4 HNO_2	$Ca(OH)_2$ (b)	
Weak electrolytes	$HC_2H_3O_2$ H_2CO_3 (a) H_2S H_3BO_3 HCN	NH_4OH $Mg(OH)_2$ (b) Insoluble hydroxides of the heavy metals: as $Al(OH)_3$ and $Fe(OH)_3$	Salts of certain metals, as $HgCl_2$ and $Pb(C_2H_3O_2)_2$, are poorly ionized, or form complex ions with excess of the negative ion.

(a) A saturated solution of CO_2 at 20° C is about 0.04 *F*.

(b) Many metallic hydroxides, although they may be highly ionized, are too insoluble to give a high concentration of ions. The solubility of $Ca(OH)_2$ at 20° C is about 0.02 *F*, and of $Mg(OH)_2$ is about 0.0002 *F*.

TABLE XII

THE COLOR CHANGES AND *p*H INTERVALS OF SOME IMPORTANT INDICATORS

Name of Indicator	*pH Interval*	*Color Change*	*Solvent*
Methyl violet	0.2 — 3.0	Yellow, blue, violet	Water
Thymol blue	1.2 — 2.8	Red to yellow	Water (+NaOH)
Benzopurpurin 4B	1.2 — 4.0	Violet to red	20% alcohol
Methyl orange	3.1 — 4.4	Red to orange yellow	Water
Bromphenol blue	3.0 — 4.6	Yellow to blue violet	Water (+NaOH)
Congo red	3.0 — 5.0	Blue to red	70% alcohol
Bromcresol green	3.8 — 5.4	Yellow to blue	Water (+NaOH)
Methyl red	4.4 — 6.2	Red to yellow	Water (+NaOH)
Chlorphenol red	4.8 — 6.8	Yellow to red	Water (+NaOH)
Bromcresol purple	5.2 — 6.8	Yellow to purple	Water (+NaOH)
Litmus	4.5 — 8.3	Red to blue	Water
Bromthymol blue	6.0 — 7.6	Yellow to blue	Water (+NaOH)
Phenol red	6.8 — 8.2	Yellow to red	Water (+NaOH)
Thymol blue	8.0 — 9.6	Yellow to blue	Water (+NaOH)
Phenolphthalein	8.3 — 10.0	Colorless to red	70% alcohol
Thymolphthalein	9.3 — 10.5	Yellow to blue	70% alcohol
Alizarin yellow R	10.0 — 12.0	Yellow to red	95% alcohol
Indigo carmine	11.4 — 13.0	Blue to yellow	50% alcohol
Trinitrobenzene	12.0 — 14.0	Colorless to orange	70% alcohol

TABLE XIII

Oxidation-Reduction Potentials[1]

Substances at unit activity (effective concentration) and at 25°C.

Couple	Volts	Couple	Volts
Li — Li^+	+3.045	As — $HAsO_2$ (H^+)	−0.2475
K — K^+	+2.925	Bi — BiO^+ (H^+)	−0.32
Cs — Cs^+	+2.92	Cu — Cu^{++}	−0.337
Ba — Ba^{++}	+2.90	H_2O — O_2 (OH^-)	−0.401
Sr — Sr^{++}	+2.89	$Mn(OH)_3$ — MnO_2 (NH_4^+)	−0.50
Ca — Ca^{++}	+2.87	I^- — I_2	−0.5355
Na — Na^+	+2.714	MnO_2 — MnO_4^- (OH^-)	−0.60
Mg — Mg^{++}	+2.37	H_2O_2 — O_2 (H^+)	−0.67
Al — Al^{+++}	+1.66	F^{++} — Fe^{+++}	−0.771
Mn — Mn^{++}	+1.18	Hg — Hg_2^{++}	−0.789
SO_3^{--} — SO_4^{--} (OH^-)	+0.93	Ag — Ag^+	−0.7991
H_2 — H_2O (OH^-)	+0.828	H_2O — O_2 $(10^{-7}$ M $H^+)$	−0.815
Zn — Zn^{++}	+0.763	Hg — Hg^{++}	−0.854
Cr — Cr^{+++}	+0.74	H_2O — HO_2^- (OH^-)	−0.88
$H_2C_2O_4$ — CO_2 (H^+)	+0.49	Cl^- — ClO^- (OH^-)	−0.89
S^{--} — S (OH^-)	+0.48	Hg_2^{++} — Hg^{++}	−0.92
Fe — Fe^{++}	+0.44	NO — NO_3^- (H^+)	−0.96
H_2 — H_2O $(10^{-7}$ M $H^+)$	+0.414	Br^- — Br_2	−1.0652
Cr^{++} — Cr^{+++}	+0.41	H_2O — O_2 (H^+)	−1.229
Cd — Cd^{++}	+0.403	Mn^{++} — MnO_2 (H^+)	−1.23
Pb — $PbSO_4$	+0.356	Cr^{+++} — $Cr_2O_7^{--}$ (H^+)	−1.33
Co — Co^{++}	+0.277	Cl^- — Cl_2	−1.3595
Ni — Ni^{++}	+0.250	Pb — PbO_2 (H^+)	−1.455
Sn — Sn^{++}	+0.136	Cl_2 — ClO_3^- (H^+)	−1.47
$Cr(OH)_3$ — CrO_4^{--} (OH^-)	+0.13	Cl^- — $HClO$ (H^+)	−1.49
Pb — Pb^{++}	+0.126	Au — Au^{+++}	−1.50
HO_2^- — O_2 (OH^-)	+0.076	Mn^{++} — MnO_4^- (H^+)	−1.51
H_2 — H^+	0.000	BiO^+ — Bi_2O_4 (H^+)	−1.6
H_2S — S (H^+)	−0.141	$PbSO_4$ — PbO_2 (H^+)	−1.685
Sn^{++} — Sn^{++++}	−0.15	MnO_2 — MnO_4^- (H^+)	−1.695
H_2SO_3 — SO_4^{--} (H^+)	−0.17	H_2O — H_2O_2 (H^+)	−1.77
Sb — SbO^+ (H^+)	−0.212	F^- — F_2	−2.87
Ag — $AgCl$	−0.2222	HF — F_2 (H^+)	−3.06

The potentials listed are those which the several "half-cells" would give when connected with a H_2 — H^+ half-cell, in which all ions present are at an effective concentration of 1 M. It is necessary to use this effective concentration, or 'activity," rather than the ordinary molarity, since dissolved substances do not behave as "perfect solutions" in concentrations as great as 1 M.

Since, in many cases, the H^+ or OH^- enters into the reaction for the cell, changes in the pH will affect the potentials. It is, therefore, necessary to specify whether the data given are for 1 M H^+ of 1 M OH^-. Cases in which this is not given are not greatly affected by this factor, since the H^+ or OH^- plays no part in the half-reaction.

[1] Values in this chart are taken from the data given in Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall, Inc., 1952.

TABLE XIV

Equilibrium Constants (at 25° C)

Water	$H_2O = H^+ + OH^-$	10^{-14}
Weak Acids:		
Acetic	$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$	1.8×10^{-5}
Boric	$H_3BO_3 = H^+ + H_2BO_3^-$	5.8×10^{-10}
Carbonic	$H_2CO_3 = H^+ + HCO_3^-$	$K_1 = 4.5 \times 10^{-7}$
	$HCO_3^- = H^+ + CO_3^{--}$	$K_2 = 6 \times 10^{-11}$
Chromic	$H_2CrO_4 = H^+ + HCrO_4^-$	$K_1 = 5.9 \times 10^{-2}$
	$HCrO_4^- = H^+ + CrO_4^{--}$	$K_2 = 6 \times 10^{-7}$
Formic	$HCHO_2 = H^+ + CHO_2^-$	2×10^{-4}
Hydrocyanic	$HCN = H^+ + CN^-$	4×10^{-10}
Hydrofluoric	$HF = H^+ + F^-$	7.2×10^{-4}
Hydrogen peroxide	$H_2O_2 = H^+ + HO_2^-$	2.4×10^{-12}
Hydrogen sulfide	$H_2S = H^+ + HS^-$	$K_1 = 1.1 \times 10^{-7}$
	$HS^- = H^+ + S^{--}$	$K_2 = 1.0 \times 10^{-15}$
Nitrous	$HNO_2 = H^+ + NO_2^-$	4.5×10^{-4}
Oxalic	$H_2C_2O_4 = H^+ + HC_2O_4^-$	$K_1 = 5.9 \times 10^{-2}$
	$HC_2O_4^- = H^+ + C_2O_4^{--}$	$K_2 = 6.4 \times 10^{-5}$
Phosphoric	$H_3PO_4 = H^+ + H_2PO_4^-$	$K_1 = 7.5 \times 10^{-3}$
	$H_2PO_4^- = H^+ + HPO_4^{--}$	$K_2 = 2 \times 10^{-7}$
	$HPO_4^{--} = H^+ + PO_4^{---}$	$K_3 = 1 \times 10^{-12}$
Phosphorous	$H_3PO_3 = H^+ + H_2PO_3^-$	$K_1 = 1.6 \times 10^{-2}$
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{--}$	$K_2 = 1.2 \times 10^{-2}$
Sulfurous	$H_2SO_3 = H^+ + HSO_3^-$	$K_1 = 1.2 \times 10^{-2}$
	$HSO_3^- = H^+ + SO_3^{--}$	$K_2 = 1 \times 10^{-7}$
Weak Bases:		
Ammonium hydroxide	$NH_4OH = NH_4^+ + OH^-$	1.8×10^{-5}
Complex Ions and Amphoteric Hydroxides:		
Cupric ammonia	$Cu(NH_3)_4^{++} = Cu^{++} + 4\ NH_3$	5×10^{-14}
Silver ammonia	$Ag(NH_3)_2^+ = Ag^+ + 2\ NH_3$	6×10^{-8}
Zinc ammonia	$Zn(NH_3)_4^{++} = Zn^{++} + 4\ NH_3$	3×10^{-10}
Mercuric chloride	$HgCl_4^{--} = HgCl_2 + 2\ Cl^-$	1×10^{-2}
Silver chloride	$AgCl_2^- = Ag^+ + 2\ Cl^-$	1×10^{-5}
Aluminum hydroxide	$Al(OH)_4^- = Al(OH)_3 + OH^-$	2.5×10^{-2}
Chromic hydroxide	$Cr(OH)_4^- = Cr(OH)_3 + OH^-$	10^2
Lead hydroxide	$Pb(OH)_3^- = Pb(OH)_2 + OH^-$	50
Stannous hydroxide	$Sn(OH)_3^- = Sn(OH)_2 + OH^-$	2×10^3
Zinc hydroxide	$Zn(OH)_4^{--} = Zn(OH)_2 + 2\ OH^-$	10

TABLE XV

Solubility Products (18° to 25° C)[1]

Acetates:	
AgAc	2×10^{-3}
Halides:	
AgCl	1.6×10^{-10}
AgBr	4×10^{-13}
AgI	1×10^{-16}
Hg_2Cl_2	1×10^{-18}
$PbCl_2$	1.7×10^{-5}
PbI_2	9×10^{-9}
Carbonates:	
Ag_2CO_3	8×10^{-12}
$BaCO_3$	5×10^{-9}
$CaCO_3$	4.8×10^{-9}
$CuCO_3$	1×10^{-10}
$FeCO_3$	2×10^{-11}
$MgCO_3$	1×10^{-5}
$MnCO_3$	9×10^{-11}
$PbCO_3$	1×10^{-13}
$SrCO_3$	1×10^{-9}
Chromates:	
Ag_2CrO_4	1×10^{-12}
$BaCrO_4$	2×10^{-10}
$PbCrO_4$	2×10^{-14}
$SrCrO_4$	3.6×10^{-5}
Hydroxides:	
$Al(OH)_3$	1×10^{-33}
$Ca(OH)_2$	8×10^{-6}
$Cr(OH)_3$	1×10^{-30}
$Cu(OH)_2$	6×10^{-20}
$Fe(OH)_2$	1×10^{-15}
Hydroxides, continued:	
$Fe(OH)_3$	1×10^{-38}
$Mg(OH)_2$	6×10^{-12}
$Mn(OH)_2$	1×10^{-14}
$Pb(OH)_2$	1×10^{-16}
$Sn(OH)_2$	1×10^{-26}
$Zn(OH)_2$	1×10^{-17}
Oxalates:	
CaC_2O_4	2×10^{-9}
MgC_2O_4	9×10^{-5}
BaC_2O_4	1×10^{-7}
Sulfates:	
Ag_2SO_4	1.2×10^{-5}
$BaSO_4$	1×10^{-10}
$CaSO_4 \cdot 2H_2O$	2.4×10^{-5}
Hg_2SO_4	6×10^{-7}
$PbSO_4$	2×10^{-8}
$SrSO_4$	2.8×10^{-7}
Sulfides:	
Ag_2S	10^{-51}
CdS	10^{-28}
CoS	10^{-21}
CuS	10^{-40}
FeS	10^{-22}
HgS	10^{-54}
MnS (flesh colored)	10^{-16}
NiS	10^{-21}
PbS	10^{-28}
SnS	10^{-28}
ZnS (β)	10^{-24}

[1] See Study Assignment *E* for a brief discussion of the limitations which one should place on the interpretation of calculations based on solubility products. In the case of exceedingly insoluble substances, the values of the constants are not very precisely known.

TABLE XVI

Table of Ionic Valences

Positive Ions		*Negative Ions*	
Name	*Formula*	*Name*	*Formula*
Hydrogen	H^+	Acetate	$C_2H_3O_2^-$
Ammonium	NH_4^+	Bromide	Br^-
Lithium	Li^+	Chloride	Cl^-
Potassium	K^+	Hypochlorite	ClO^-
Silver	Ag^+	Chlorite	ClO_2^-
Sodium	Na^+	Chlorate	ClO_3^-
Cuprous	Cu^+	Perchlorate	ClO_4^-
Cupric	Cu^{++}	Fluoride	F^-
Mercurous	Hg_2^{++}	Iodide	I^-
Mercuric	Hg^{++}	Hydroxide	OH^-
Barium	Ba^{++}	Nitrate	NO_3^-
Cadmium	Cd^{++}	Nitrite	NO_2^-
Calcium	Ca^{++}	Carbonate	CO_3^{--}
Lead	Pb^{++}	Bicarbonate	HCO_3^-
Magnesium	Mg^{++}	Chromate	CrO_4^{--}
Strontium	Sr^{++}	Dichromate	$Cr_2O_7^{--}$
Zinc	Zn^{++}	Oxalate	$C_2O_4^{--}$
Cobaltous	Co^{++}	Binoxalate	$HC_2O_4^-$
Cobaltic	Co^{+++}	Sulfate	SO_4^{--}
Nickelous	Ni^{++}	Bisulfate	HSO_4^-
Nickelic	Ni^{+++}	Sulfite	SO_3^{--}
Manganous	Mn^{++}	Bisulfite	HSO_3^-
Manganic	Mn^{+++}	Sulfide	S^{--}
Iron, ferrous	Fe^{++}	Bisulfide	HS^-
ferric	Fe^{+++}	Thiosulfate	$S_2O_3^{--}$
Tin, stannous	Sn^{++}	Borate	BO_3^{---}
stannic	Sn^{++++}	Phosphate	PO_4^{---}
Aluminum	Al^{+++}	Metaphosphate	PO_3^-
Bismuth	Bi^{+++}	Phosphite	PO_3^{---}
Chromic	Cr^{+++}	Ferricyanide	$Fe(CN)_6^{---}$
		Ferrocyanide	$Fe(CN)_6^{----}$

Answers to Drill Problems

Study Assignment A, Page 11:

1. (*a*) 10^3, (*c*) 5.5×10^3, (*e*) 10^{-3}, (*g*) 3×10^{-12}, (*i*) 2.006×10^6
2. (*a*) 4.26×10^4, (*c*) 3.75×10^{-5}, (*e*) 4.65×10^{-1}, (*g*) 3.0103×10^4
3. (*a*) 10^6, (*c*) 4.3×10^4, (*e*) 10^3, (*g*) 10, (*i*) 6.3×10^6, (*k*) 4×10^3, (*m*) 1.4×10^4
4. (*b*) $KE = \frac{1}{2} mv^2$, (*e*) $V_t - V_o = V_o(t - t_o)/273$
5. (*b*) 2×10^5 cm/sec
6. (*a*) 2.1668, (*c*) 7.5660 − 10, or $\bar{3}.5660$, (*e*) 23.7798
7. (*a*) 304.0, (*c*) 3.583×10^4 (*e*) 0.0005508
8. (*a*) 231 ml
9. (*a*) 0.42, (*c*) 30.43, (*e*) 58.40, (*g*) 9.0×10^5
10. (*a*) 1.6, or −7.6, (*c*) $\pm 4.1 \times 10^{-3}$

Appendix I, Page 332:

1. (*b*) 500 sec or 8.3 min, (*d*) 1000 cm^3, 10 cm, (*f*) 6.0 boxes
2. (*b*) 2, (*d*) 3, (*f*) 5
3. (*a*) 23.2, (*c*) 0.022
5. (*b*) 203.4 cm, (*d*) 0.002034 km. Four significant figures, regardless of the unit used.
7. 0.6%