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Author Maynard, J.L., and Taylor.

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The authors will be grateful for suggestions leading to the improvement of the book.

J. L. MAYNARD
December 1943. T. I. TAYLOR

Introduction

The Scientific Method. The present age is one in which science and scientific discoveries have played a predominant role in the intellectual, social, and economic life of man. It may truly be described as a scientific age.

Present scientific knowledge is an outgrowth of the application of the scientific method which has as its basis experimentation, observation, and the measurement of things. The scientific method may be outlined briefly as follows:

1. *Experimentation, Observation, and the Measurement of Things.* These are the first requirements of the scientific method.
2. *Classification.* Similarities and dissimilarities are noted and classified.
3. *Generalization.* By inductive reasoning the properties or behavior of a group or class are stated. This statement serves as an hypothesis, and, after further evidence, the hypothesis may become a theory—a general principle offered to account for the generalized observations, which are the laws.
4. *Deduction.* Deduction is the logical process of extending and determining the implications of the hypothesis. It leads to the prediction of new facts and to a greater understanding of those already determined.
5. *Verification.* Verification is the process of checking the hypothesis by comparing the implications and predictions with further observations, experiments, and measurements of things.

All fields of science employ the scientific method, either directly or indirectly. A *science* is, then, an organized body of knowledge arrived at through the application of the scientific method.

CLASSIFICATION OF SOME OF THE SCIENCES

- Abstract sciences
  - Logic
  - Mathematics
- Natural sciences
  - a. Physical sciences
    - Physics
    - Chemistry
    - Astronomy
    - Geology
    - Etc.
  - b. Biological sciences
    - Botany
    - Zoology
    - Physiology
    - Bacteriology
    - Paleontology
    - Etc.

Chemistry is one of these sciences. It deals with the preparation, properties, composition, and use of substances; the changes which substances undergo; the energy relations involved in physical and chemical changes; and the laws and theories describing and inter-

Laboratory Rules

1. **The performance of unassigned experiments is forbidden.**
2. Cleanliness, neatness, good technique, efficiency, integrity, and correct attitude are important, and they all contribute toward the laboratory grade. If chemicals are spilled, clean the desk at once. Damage to the desk resulting from neglect of the student is charged to his account.
3. Loud talking, unnecessary noise and visiting are not tolerated.
4. All laboratory work is to be done independently unless otherwise directed. Do not hesitate to ask the laboratory instructor for advice. Use the textbook for reference unless otherwise directed by the instructor.
5. Report accidents to the laboratory instructor immediately. *Be careful!* Follow directions closely and observe all of the precautions indicated in the experiments.
6. Before leaving the laboratory make certain that the top of the desk is clean and that the gas and water are turned off. At the close of each laboratory period wash all glassware and porcelainware that have been used during the period; apparatus must be clean and dry at the beginning of each period.
7. Do not dispose of solid waste materials in the sinks unless specifically directed to do so. Use the waste receptacles provided for this purpose.

Writing Up the Experiments

Enter all data on the Report Sheets found at the end of each experiment. Make an entry on the report sheet for each superscript number placed in the directions for carrying out the experiments.

Note: It will be necessary to use pencil instead of pen in making entries on the report sheets because of limitations on the use, and uncertainties in the procuring, of suitable paper.

Experiment I

THE GAS BURNER

Discussion. Many operations in the chemical laboratory must be carried out at temperatures far above those prevailing in the laboratory. For example, in order to bend a piece of glass tubing it must be heated to its softening point (above 400° C or 752° F); normally, water must be heated to a temperature of 100° C or 212° F before it boils; lastly, a great variety of chemical reactions must be carried out at elevated temperatures.

A Bunsen burner, or some modification of this type, designed to burn natural or artificial gas (or some mixture of these) is used as a source of heat in the chemical laboratory. Each burner is essentially a device arranged to produce a mixture of air and the gas which is to be burned; the flame is produced at the top of the mixing tube. An ordinary domestic gas range is equipped with a number of modified Bunsen burners.

In this experiment a study is made of the construction of the gas burner, the structure of its flame, and the relative temperatures produced in different regions of the flame.

Apparatus and Materials: A 7-cm. ($2\frac{3}{4}$ in.) length of each of the following kinds of wire: Nichrome, iron, aluminum, copper, and lead; sodium chloride (common salt); Meker-type burner and blast lamp as laboratory exhibits.

(A) The Component Parts of a Burner. Unscrew the upright mixing tube of a Bunsen (Fig. 2) or a Tirril type (Fig. 3) burner. Identify the materials of which this tube and the remaining parts of the burner are made.[1] Make the identification on the basis of the color of the metallic parts. If a black coating obscures the true color of the metal, a small part of the surface must be freed from the coating by means of a file.

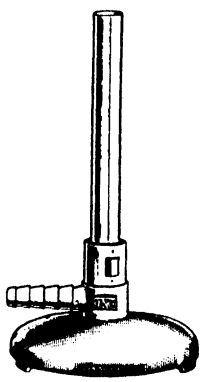


FIG. 2. Bunsen burner

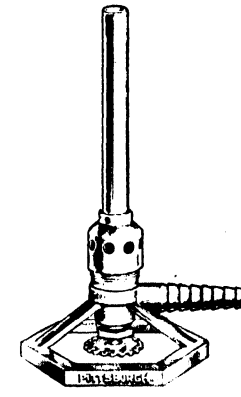


FIG. 3. Tirril burner

Note the position and diameter of the gas jet in relation to the mixing tube.[2] Turn in the adjustment screw at the base of the Tirril burner as far as it will go. What effect does this operation have on the gas jet?[3] Remove the screw from the burner and observe the shape of the tip. This part of the burner acts as a valve to control the supply of gas; it is called a *needle valve*. Make a drawing to suggest the shape of the inside of the jet and the position of the valve when it is in the *closed* position.[4] Bunsen burners are not equipped with this means of regulating the flow of gas.

Force a piece of rubber tubing onto the horizontal gas inlet tube of the burner, and then connect the other end of the tubing with the gas supply on the laboratory bench. (Do not replace the upright tube.) Why is the inlet tube corrugated?[5] Now turn on the gas and light the burner. If a Tirril burner is used, the supply of gas is always regulated by the needle valve on the burner; the cock on the laboratory bench is opened to give the maximum flow of gas. Note the color of the flame. Tiny particles of carbon formed in the interior of the flame become incandescent as they pass outward from this region. The

glow of the particles is largely responsible for the color of the flame. Most of the carbon particles burn when they come in contact with the air at the periphery of the flame. Hold a porcelain evaporating dish in the yellow part of the flame. Note the deposition of soot (carbon). What has to be done to soot or coal (another form of carbon) before it will burn in air? [6] Why does the soot on the porcelain dish fail to burn? [7]

(B) Normal Operation of a Burner. Turn off the gas, and then replace the upright tube on the burner. Close the air holes at the base of the mixer tube of the Bunsen burner by turning the collar at the base of the tube; shut off the supply of air from the Tirril burner by screwing down the upright tube as far as it will go. Turn on the gas and light the burner. Operation of the burner in this way produces a *luminous* flame. As in part (A) the gas is burning in air without being mixed with air previous to combustion.

Now open the air holes. Describe the change in the character of the flame.[1] This is the *nonluminous* type of flame. The supply of air is now great enough to burn up particles of carbon as soon as they are formed, that is, before they have an opportunity to become incandescent. If too much air is admitted to the flame it burns with a rustling sound and shows a tendency to go out. Open the air holes wide enough to bring about this condition, and then shut off the supply of gas. Open the needle valve to allow a slow stream of gas to pass into the burner. Hold a lighted match over the top of the tube. What happens? [2] The flame is said to be *striking back* if it travels down the tube and burns below at the jet. Continued combustion at this point not only results in the escape of carbon monoxide (*a dangerous poison!*), but it also heats the burner tube to such an extent that anyone touching the tube may suffer severe burns.

Entrance of air through the air holes is demonstrated in the following manner. Obtain from the reagent shelf as much sodium chloride (common salt) as will cover the bottom of a small porcelain crucible (Fig. 1). Transfer the salt from the crucible to a mortar and grind the substance as fine as possible with the pestle (Fig. 1) provided for that purpose. Pick up a very small portion of the powdered salt between the thumb and forefinger, and drop the powder into the *nonluminous* flame. What change is observed in the character of the flame? [3] Take another small amount of salt, bring it close to and just above the air holes, and allow the salt to fall past the air holes. Explain what occurs.[4]

(C) Structure of a Burner Flame. Study the nonluminous flame carefully, and then make a sectional drawing to show its structure.[1] Adjust the flame to a height of about 10 cm. (approx. 4 in.). Thrust the head of a match quickly into the center of the innermost cone just above the top of the burner tube. What information does the result give regarding the temperature of this portion of the flame? [2] Hold a 7-cm. length (about $2\frac{3}{4}$ in.) of Nichrome wire longitudinally in the same region of the flame. How does the appearance of the wire substantiate the preceding observation? [3] The lowest blue cone is a mixture of gas and air but the mixture is *not burning*. Surrounding this cone is an almost invisible one in which one stage of combustion is occurring. The light-blue outermost cone is the region in which complete combustion is taking place. Thrust the Nichrome wire into various parts of the flame, and note the relative degrees of brightness shown by the wire. Use these observations as a basis for indicating on the drawing the relatively hot and the relatively cold regions of the flame. Designate the zone of highest temperature. Objects to be heated are placed in the latter region. Retain the wire for use in later experiments.

(D) Relative Temperatures of Luminous and Nonluminous Flames. The complete combustion of a definite quantity of a given gas yields the same amount of heat regardless of whether the gas is burned in a luminous or a nonluminous flame. However, the *temperature* of the nonluminous flame is considerably higher than that of the luminous flame. The reason for this difference is deduced from the results of the following experiment.

Produce a luminous flame about 20 cm. (8 in.) in height. Now open the air holes. What change is observed in the height of the flame? [1] Has a change been made in the rate

of flow of the gas? [2] What can be said about the relative amounts of space in which equal quantities of gas are being burned in a luminous and in a nonluminous flame? [3] By use of the above data give an explanation of the difference in temperature observed for the two types of flame.[4]

(E) Approximate Temperature of the Nonluminous Flame. An approximation of the temperature of the hottest region of the nonluminous flame is made by determining which of a number of metals can be melted within 2 minutes when held in the flame. The melting point of each metal is given both in degrees Centigrade (°C) and in degrees Fahrenheit (°F). Use a 7-cm. ($2\frac{3}{4}$ in.) length of wire of each of the metals in the order in which they are placed in the following list:

Metal	M.P. °C	M.P. °F
Lead	327	620
Aluminum	659	1218
Copper	1083	1981
Iron	1535	2795

Tabulate the results of the foregoing tests.[1] Within what range does the temperature of the flame lie? [2] Refer to the textbook for the melting points of the following metals and list each in one of two classes depending upon whether it is fusible or infusible at the temperature of the burner flame: [3] cadmium, calcium, chromium, iridium, magnesium, molybdenum, platinum, silver, tin, tungsten.

(F) Other Types of Burners. A simple *Bunsen* burner (Fig. 2) is suitable for general laboratory purposes, but the *Tirril* type (Fig. 3) is more widely used because of the higher temperature of its flame and because of the close regulation of air and gas possible with this burner. Although the temperature of the bare flame is well above 1000° C, the maximum temperature obtainable inside a porcelain crucible heated in the flame is considerably lower than 1000° C. Why? [1]

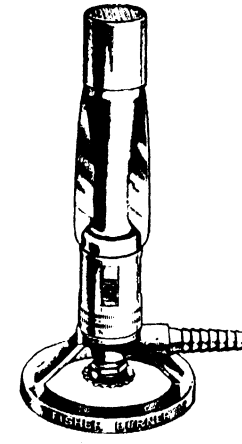


Fig. 4. Meker-type burner

The *Meker-type* burner (Fig. 4) is so constructed as to give a relatively short and very hot flame. Note the diameter of the top of the mixing tube of a Meker burner as compared with that of the Tirril burner (about 3 cm. as compared with 1 cm.). A Meker burner produces a temperature of about 1200° C inside a covered platinum crucible. From the lists of metals given in part (E), select those that could not be melted in a crucible heated by a Meker burner.[2]

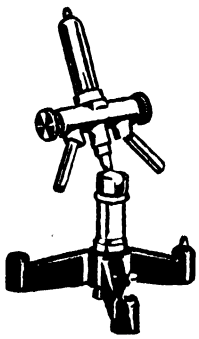


Fig. 5. Blast lamp

Blast lamps (Fig. 5) require a supply of compressed air for their operation. Although temperatures obtainable in a crucible by use of a blast lamp are not much higher than those given by a Meker burner, the thin pencil of flame produced by the blast lamp is invaluable for heating small areas. This type of flame is essential for the working and blowing of glass. Much higher temperatures are obtainable with a blast lamp if oxygen is used in place of air. Oxygen and nitrogen together make up 99 per cent of the volume of the air. Nitrogen is more plentiful than oxygen in this mixture, inasmuch as there are 3.7 volumes of nitrogen to 1 volume of oxygen. The latter alone is essential for combustions taking place in air; nitrogen does not enter into the process of combustion. On the basis of this information suggest a reason for the fact that the temperature of the oxygen-gas flame is higher than that of the air-gas flame.[3]

Name (last name first) _____ Desk No. _____ Date _____

Experiment I

THE GAS BURNER

(A) The Component Parts of a Burner

1.

2.

3.

4.

5.

6.

7.

(B) Normal Operation of a Burner

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment I (Cont'd)

(C) Structure of a Burner Flame

1.

2.

3.

(D) Relative Temperatures of Luminous and Nonluminous Flames

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment I (Cont'd)

(E) Approximate Temperature of the Nonluminous Flame

1.

2.

3.

(F) Other Types of Burners

1.

2.

3.

Experiment II

GLASS WORKING AND THE CONSTRUCTION OF A WASH BOTTLE

Discussion. Many experiments in chemistry require the use of glass apparatus. It is important, therefore, to know the characteristics of the glassware used. It is also necessary to be able to carry out some of the elementary procedures in glass working.

The glassware used in the laboratory is generally constructed of two types of glass: (1) Glass apparatus which may be safely heated over a flame is preferably made of a low-expansion borosilicate glass such as "Pyrex." This includes beakers, flasks, certain test tubes, etc. Apparatus made of this kind of glass is recognized by the green Pyrex label. Pyrex glassware does not crack readily because excessive strains are not produced during heating. This is due to its low coefficient of thermal expansion. It is also rather resistant to mechanical shock. (Other heat-resisting brands are available.) (2) Certain pieces of glassware commonly used in the laboratory are made of a soft lime-soda glass which varies in composition and properties. This type of glass softens and melts at a lower temperature than does Pyrex glass. It expands to a greater extent when heated and, if the glass is thick or irregular, its uneven expansion causes it to crack. The same generalization also applies to rapid cooling. For the above reasons great care must be used when heating or cooling soft-glass apparatus. Graduated cylinders, funnels, bottles, and watch glasses *must not be heated directly* over a flame. Uniform, thin-walled, soft-glass test tubes may be heated over a flame, but this must be done slowly and evenly.

Glass tubing used in the laboratory is generally made of soft glass. This type is chosen because it is inexpensive and can be readily softened in the flame of a Bunsen or Tirril burner. The softened glass can be bent, drawn, or blown into any desired shape. It is necessary to use a blast lamp or oxygen torch when working Pyrex glass tubing.

Apparatus and Materials: Five feet of 6-mm. soft-glass tubing; 15-in. of soft-glass rod; $1\frac{1}{2}$ to 2-in. piece of rubber tubing ($\frac{1}{4}$ in. in diameter); No. 5 two-holed rubber stopper to fit a 500-ml. Florence flask; 2-in. piece of platinum or Nichrome wire (B. & S. gauge No. 26); triangular file. Cork borers and a cork to fit the 500-ml. Florence flask are needed if rubber stoppers are not available.

(A) Cutting Glass Tubing. In order to cut a piece of glass tubing or a piece of glass rod, place it on the desk top and make a single scratch across the tube with the edge of a triangular file. It is not necessary to saw with the file. A single firm push forward is generally sufficient. Hold the tube with the thumbs on the side opposite the scratch as shown in Fig. 6. Push outward with the thumbs and at the same time pull in the opposite direction with the hands. The tube should break evenly at the scratch. If it does not break easily, scratch the tube again, otherwise it may break in the hands. Practice by cutting two or three pieces 15 cm. (6 in.) long for use in part (C). Suggest a reason why a file mark makes a glass tube break more easily.[1]

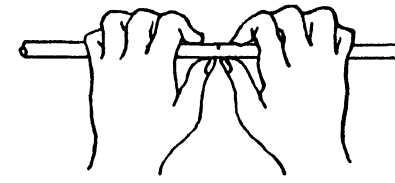


FIG. 6. Breaking glass tubing after a cut has been made with a file

To cut large glass tubing, make a file mark completely around the glass tube. Touch the scratch with a piece of rod heated to redness. If the tube does not crack immediately,

place a drop of water on the scratch. This procedure is also used to cut small glass tubing near one end where it is impossible to hold the glass tube.

(B) Removing Jagged Edges. Fire-Polishing. Jagged edges resulting from uneven cutting or from accidental breaking of glass tubes may be removed by striking them with the flat surface of a wire gauze held at an angle of 45 degrees to the tube.

All newly cut glass tubes have minute sharp points and edges. These must be melted smooth (fire-polished) so that they will not cut the hands. This process also facilitates the insertion of glass tubes in rubber tubing and through the holes in rubber stoppers. The ends of glass tubes can be fire-polished by holding the tubing almost vertically with the rough edge above the inside blue cone of a nonluminous flame. Rotate the tube and heat it until the glass just begins to flow. This occurs shortly after the flame becomes bright yellow in color. If the glass is held in the flame too long, the end of the tube narrows and finally closes completely. Do not allow this to happen. Cut two 7- to 8-in. glass rods and fire-polish the ends. These will be used as stirring rods in later experiments. Heat the end of a piece of glass tubing and immerse it in cold water. What happens? Explain.[1]

Do not place hot glass tubing on the desk top. Place it on a piece of asbestos or a wire gauze. Glass remains hot for a considerable length of time because of its rather high heat capacity and its low heat conductivity. Students are sometimes burned by picking up glass tubing before it has cooled. *Call the instructor immediately in case of burns or other accidents.*

(C) Bending Glass Tubing. When bending glass tubing, it is necessary to heat the glass uniformly over a length equal to the radius of the bend desired. This is done by using a flame spreader, sometimes called a wing top or fish tail (Fig. 1).

Turn out the flame, place the flame spreader on the top of the burner, and then light the burner. The width of the flame should be from 5 to 8 cm. Hold the tube lengthwise

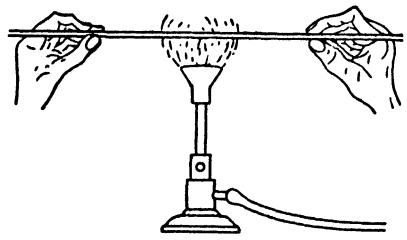


FIG. 7. Heating glass tubing

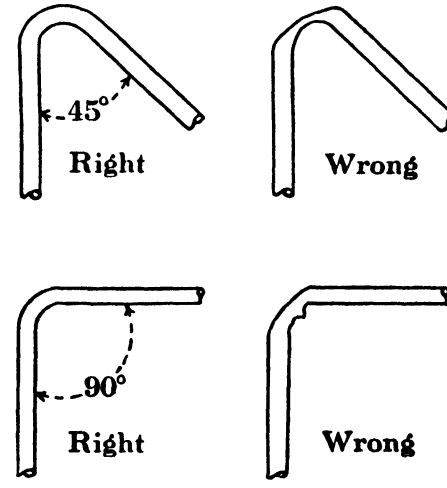


FIG. 8. Correct and incorrect bends

in the flame (as shown in Fig. 7) and rotate it continually to insure uniform heating. Continue heating it until the glass softens and begins to sag. Remove the softened tube from the flame and immediately bend the glass to the desired angle. Hold the tube in this position for a few seconds until it hardens. Fire-polish the ends and place the tube on a piece of asbestos or wire gauze to cool. If the tube was not heated uniformly enough or hot enough, the bend may be wrinkled, flattened, or crooked as shown in Fig. 8. If any one of these conditions is the case, try again to secure a proper bend.

Bend each of the two 15-cm. (6-in.) glass tubes prepared in part (A) into a right-angle bend as shown in Fig. 8. Cut two more pieces of the same length, and make one 60-degree

bend and one 120-degree bend (Fig. 9). While the hot tubes are being bent, hold them over the diagram to secure the proper angle. Keep these bent tubes for use in later experiments. The bends as well as the other glass pieces made in the experiment must be approved by the instructor and checked by him in the proper place on the report sheet.[1]

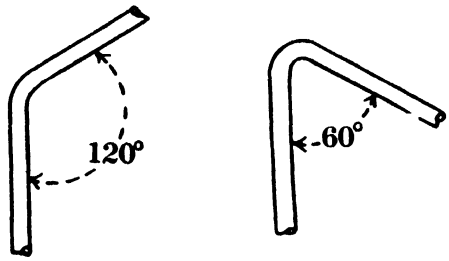


FIG. 9. Glass bends

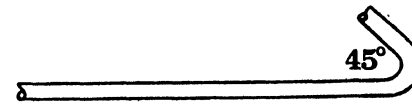


FIG. 10. Delivery tube

Make a 45-degree bend near one end of a 40-cm. (16-in.) length of glass tubing (Fig. 10). Cut off the short end approximately 1 in. from the bottom of the bend and then fire-polish both ends of the tube. This will be used for a delivery tube in later experiments.

(D) Drawing Out Glass Tubing for Nozzles and Melting-Point Tubes. Glass jets or nozzles (similar to medicine droppers) are made by drawing out glass tubing after it has been heated to softness.

Remove the flame spreader, light the burner, and open the air holes until a hot non-luminous flame is obtained. Heat a 10-cm. (4-in.) piece of 6-mm. glass tubing until it softens and begins to collapse. Rotate the tube continually without twisting or bending it out of shape. Remove the tube from the flame and pull it slowly and carefully in a straight

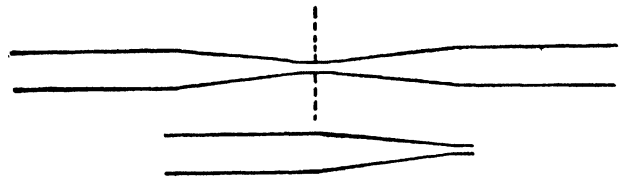


FIG. 11. Steps in making a nozzle

line until its center is reduced to the desired diameter—about 1 mm. When the glass is cool, cut the tube at its center (Fig. 11). Fire-polish both ends, but do not allow the small end to melt until it is completely closed. Use one nozzle for the wash bottle and save the other for use in a later experiment.

Prepare from 8 to 10 capillary melting-point tubes from 6-in. soft-glass test tubes or from 10-mm. thin-walled soft-glass tubing. Turn on the gas as far as possible and open the air holes to obtain the highest possible temperature. (If a Meker burner or a blast lamp is available, either may be used to advantage.) Rotate a soft-glass tube in the flame until it is *very soft.* Both ends must be rotated at the same rate to prevent the tube from twisting at the center. Remove it from the flame and immediately pull it out as rapidly

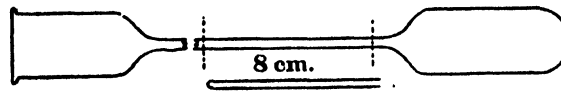


FIG. 12. Preparation of melting-point tubes

and as far as is possible. The capillary tube produced should be 1 to 2 mm. in diameter, that is, slightly smaller than the diameter of a safety match (Fig. 12). Cut the capillary tube into sections 7 to 8 cm. ($2\frac{1}{2}$ to 3 in.) long. Seal one end (preferably the smaller end) by

carefully melting it in the outermost edge of the flame. If a sufficient number of melting-point tubes is not obtained, repeat the procedure on another soft-glass tube. Request the laboratory instructor to check the tubes.[1] Store them in a corked test tube for use in a later experiment on the determination of melting points.

(E) Making Small Glass Test Tubes. Heat a piece of glass tubing 15 to 20 cm. (6 to 8 in.) long near the center of the tube until it is very soft and has partially collapsed. Remove the tube from the flame and draw it out very rapidly. The result is that the tube has a sharp taper (Fig. 13). Cut off the tail well up to where the taper begins to enlarge.

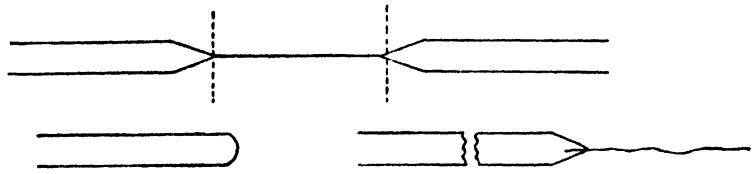


FIG. 13. Small glass test tube; sealing a wire in glass

Heat the end until the opening closes and the entire end is red-hot. Remove the tube from the flame. Now blow into the open end. What would happen if this were done too vigorously? [1] Continue heating and blowing until the glass is of an even thickness and a well-rounded end is obtained. Cut off the open end so as to make a test tube 4.5 cm. ($1\frac{3}{4}$ in.) long. Keep it for use in a later experiment.

Small test tubes of Pyrex glass may be made in the same way by using a blast lamp or an oxygen torch for heating.

(F) Sealing Platinum or Nichrome Wire in Glass. Heat a glass tube and draw it out rapidly in the manner described in part (E). Cut off the tube near the taper so that a small opening remains (Fig. 13). Insert the wire (1 to 2 in. long) and melt the glass around it. To prevent the wire from falling to one side rotate the tube constantly. As an alternative method the open end of a tube may be melted in the flame until a small opening remains. Insert the wire and melt the glass around it as described above.

Platinum wire is generally more satisfactory than Nichrome or Chromel wire because it is more resistant to chemical action, and can be sealed more tightly into soft glass. If the Nichrome wire is small (B. & S. gauge No. 26), it can be sealed into the glass sufficiently well and may be used satisfactorily for experiments in general chemistry. Suggest a reason why Nichrome wire cannot be sealed into soft glass as tightly as platinum wire.[1] (**Hint:** Consider the differences in thermal expansion of the metals and the glass.)

(G) Inserting Glass Tubes in Stoppers. Glass tubes must be fire-polished and cooled before they are pushed through the holes in rubber stoppers. Wet both the glass tube and the stopper with water or glycerine. Hold the tube *near the end to be inserted, preferably with a towel.* Push it through the hole with a careful screwlike motion. Try to insert a dry glass tube in a dry rubber stopper. Do not insert it far. Remove the glass tube and wet it with water or glycerine. Insert it again. Explain the difference.[1]

DANGER! Do not push the glass tube too vigorously or grasp it where the tube is bent. Always hold the tube near the stopper, otherwise the glass may break. Failure to observe these precautions may result in severe cuts. Care should also be used when removing glass tubes from stoppers. If the glass tube cannot be removed easily, try to work it loose by forcing the small end of a file between the rubber and the glass tube. Allow water to drip into the opening, then carefully twist the file so that the latter precesses around the glass tube. It is always safer to hold the glass tube with a towel. If the tube does not loosen easily, the rubber stopper should be cut away with a knife.

(H) Boring Holes in Corks. (This part may be omitted if two-holed rubber stoppers are available for the construction of a wash bottle.) If a cork is used to stopper the wash

bottle described in the next section, two parallel holes must be bored through the cork. The holes are bored with cork borers, which are thin brass tubes sharpened at one end. A brass rod is inserted through the holes at the other end in order to facilitate the twisting of the borer. The borer must be sharp enough to cut the hole smoothly. It is sharpened with a regular sharpener obtained from the stockroom. If this is not available run the blade of a knife inside the borer to scrape off the metal that has been bent over during previous use. Choose a borer slightly smaller than the glass tube which is to be used. Soften the cork by rolling it in a cork softener or between a block of wood and the desk top. Hold the borer perpendicular to the surface and, with a twisting motion, bore about halfway through the cork. Remove the borer and judge as nearly as possible where the hole should come through the other end. Bore through from this end until the holes meet. This procedure gives holes with smooth edges at both ends, and thus insures a tight joint. A rat-tail file is used to remove the loose cork from the hole and, if necessary, to make the hole larger. The brass rod furnished with the set is used to push the cork out of the borer. If the holes are too large, bore holes in a new cork. Never wrap paper around glass tubes to make them fit holes that are too large. Study the construction of the wash bottle (Fig. 14) and explain how the usual method of closing the short tube and blowing a few bubbles of air through the long tube into the wash bottle will determine whether the joints are airtight.[1]

If holes are to be bored in a rubber stopper, the borer must be well lubricated with water or glycerine. Choose a borer the same size as or slightly larger than the glass tube.

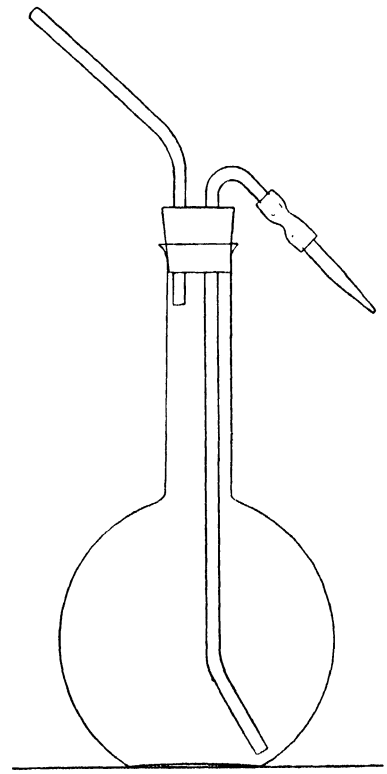


FIG. 14. A wash bottle

(I) Construction of a Wash Bottle. Construct a wash bottle from a 500- or 1000-ml. Florence flask as shown in Fig. 14. Bend the glass tubes by heating them with a flame spreader as explained in part (C). Determine the correct angle by holding the tubes over the diagram while they are being bent. The lower bend should not be a sharp one, other-

wise it may be difficult to push the tube through the rubber stopper. If the bend is too sharp, the tube may be pushed through the stopper before the top bend is made. Determine the location of the top bend by holding the tube beside the flask. Attach the nozzle prepared in part (D) to the long tube by means of a short piece of rubber tubing, 2 to 3 cm. (1 to 1½ in.) long. The end of the tube at the top bend should be cut long enough to allow the nozzle to be directed with the first two fingers. The short tube should extend only slightly below the rubber stopper. Submit the wash bottle to the instructor for his approval.[1]

(J) Use of the Wash Bottle. Wash out the flask thoroughly with tap water and rinse it with a little distilled water. Fill the flask about two thirds full of distilled water and keep it on the desk for rinsing washed glassware, washing precipitates, and making up solutions.

After glassware has been washed in tap water, it should be rinsed with distilled water. Why is this advisable? [1] To use the wash bottle, hold it in one hand and blow into the short tube so as to force the distilled water out through the nozzle. Use the first two fingers to direct the stream over the inner surface of the glassware. The wash bottle is used in a similar way to wash precipitates that have been collected on a filter paper. The stream of water is directed below the upper edges of the filter paper until the funnel is about half full. This procedure is described more fully later. In the same way, distilled water is transferred to a graduated cylinder to make up or to dilute solutions. Why are solutions diluted or made up with distilled water? [2] What would happen after blowing into the short tube if the latter extended below the surface of the water? [3]

Larger amounts of distilled water for rinsing glassware or for making large volumes of solutions are obtained by turning the wash bottle upside down. The water will run out of the short tube. Try it. What happens in the long tube? [4] Why is it necessary that the long tube reach near the bottom? Consider both methods of using the wash bottle.[5] Notice the direction of the lower bend. Explain.[6]

(K) Questions on Glass and Glass Working

1. Explain why a graduated cylinder or a bottle should not be heated over a flame.

2. What might happen if a soft-glass test tube were heated with a flame above the level of a liquid in the tube? Explain.

3. Tell how to determine whether a piece of glass apparatus is made of soft glass or hard glass (Pyrex). Give two ways.

4. What is meant by fire-polishing? Why should all glass tubes be fire-polished?

5. Why is a flame spreader used when soft-glass tubing is to be bent? If it is not used, what type of bend might result?

6. Why does glass stay hot longer than a piece of metal of the same size? If one end of a piece of metal is held in a flame, the other end becomes hot in a short time. Explain why this does not happen so readily with glass.

Name (last name first) _____ Desk No. _____ Date _____

Experiment II

GLASS WORKING AND THE CONSTRUCTION OF A WASH BOTTLE

(A) Cutting Glass Tubing

1.

(B) Removing Jagged Edges. Fire-polishing

1.

(C) Bending Glass Tubing

1.

(D) Drawing Out Glass Tubing for Nozzles and Melting-Point Tubes

1.

(E) Making Small Glass Test Tubes

1.

(F) Sealing Platinum or Nichrome Wire in

1.

(G) Inserting Glass Tubes in Stoppers

1.

(H) Boring Holes in Corks

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment II (Cont'd)

(I) Construction of a Wash Bottle

1.

(J) Use of the Wash Bottle

1.

2.

3.

4.

5.

6.

(K) Questions on Glass and Glass Working

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment II (Cont'd)

(K) Cont'd

4.

5.

6.

Experiment III

BALANCES AND WEIGHING

Discussion. Experimental work with known quantities of material involves the determination of the weights of various materials and objects. Approximate weights (to the nearest gram or 0.1 g.) suffice in many instances while other cases demand a more precise value (to the nearest milligram or even 0.1 mg.). These weights are obtained by the use of various types of balances and scales, some of which are described in the following sections.

Apparatus and Materials: Trip balance; horn-pan balance; analytical or small beam balance; set of appropriate weights; numbered objects of unknown weight (crucibles, crucible covers, or watch glasses).

(A) Trip Balances. Several varieties of this type of balance are used in the laboratory for weighings which need be accurate only to the nearest 0.1 g. If the object to be weighed is made of glass, metal, wood, or porcelain it is placed directly on the platform of the balance. Liquids, solid chemicals, or powdered materials of any kind are not placed in direct contact with the platform or pan of the balance but are always weighed in a container, such as a watch glass, a porcelain crucible, a beaker, or a flask. Materials that are dry, or that do not take up moisture from the air, may be weighed on a piece of filter paper.

1. Weighing on a Three-Beam Trip Balance (Fig. 15). (Only a portion of the class should be assigned to this part of the experiment; the remainder of the class should proceed with parts (B) and (C)).

Push the three weights, W_1, W_2, and W_3, over to the extreme left of the beams upon which they ride. The front beam weighs from 0 to 10 g. in 0.1-g. divisions, the rear beam weighs from 0 to 100 g. in 10-g. divisions, while the center beam weighs from 0 to 500 g. in 100-g. divisions. Tap the platform (A) and note the action of the pointer (P). The latter should not come to rest until it has completed at least two swings above and below the middle point of the scale (Sc). In addition, the pointer should swing an equal number of divisions on each side of the center of the scale. Ask the laboratory instructor to adjust the balance if one or both of the preceding conditions are not fulfilled. The adjustment screw (AS) is used to bring about the proper condition.

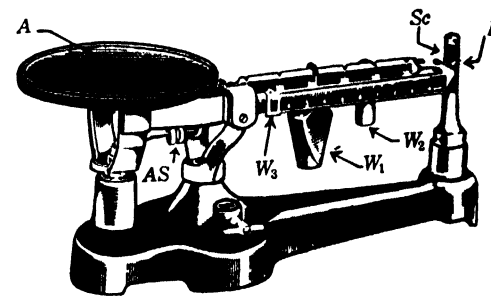


FIG. 15. Three-beam trip balance (single platform)

Place a 7-cm. porcelain evaporating dish (Fig. 1) on the platform of the balance. Move the weight on the central beam to the first division to the right. If this causes the pointer to remain permanently at the bottom of the scale, the weight is too heavy, and should be returned to the extreme left of the beam. Now try the weight on the rear beam. Adjust its position until the weight of the dish is as nearly balanced as is possible, and then complete the procedure by using the weight on the front beam. The dish is properly counterbalanced when the pointer swings an equal number of divisions above and below the middle of the scale. Record the weight of the dish.[1] Return each weight to the left end of its beam, and remove the dish from the platform. Now pour sand into the dish until it is

about half full. Determine the weight of the dish and its contents.[2] What is the weight of the sand alone? [3] This procedure is called *weighing by difference;* it is used to determine the weights of substances that must not be placed directly on the platform of a balance.

2. Weighing Out a Stated Quantity of Material. Most experiments must be carried out with known weights of the materials involved. In this instance it is desired to weigh out 24.5 g. of sand. Determine the weight of the largest of the evaporating dishes furnished in the desk set.[4] Now set the beam weights so that the total weight they represent is 24.5 g. greater than that of the dish alone.

Obtain sand in a small beaker. Incline the beaker and tap it gently so that the sand flows a little at a time into the evaporating dish on the balance. Tap the platform after each addition of sand and note the swings of the pointer. Continue the addition of small portions of sand until the correct amount has been obtained. If too much sand is added, it should be removed with a steel spatula until the combined weight of the dish and the sand is slightly less than the desired weight. Now add sand in very small amounts until the correct weight is reached. Do not neglect to cause the pointer to swing after each addition of sand! *After the weighing has been completed, return all sand to the container from which it was originally obtained. Do not dispose of it in the sink!*

3. Weighing on a Single-Beam Trip Balance (Fig. 16). This part of the experiment is not to be performed if weighings have been carried out on a three-beam balance. If the

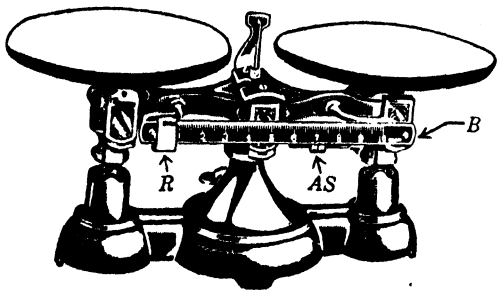


FIG. 16. Single-beam trip balance (two platforms)

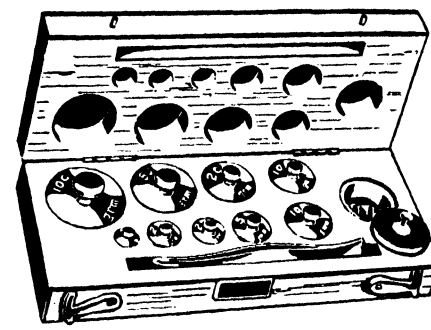


FIG. 17. Laboratory weights

laboratory is not equipped with the latter type of balance the following experiment is to be performed.

Laboratories are not generally equipped with enough single-beam trip balances to accommodate a large number of students. Thus only part of the class should be assigned to perform this part of the experiment; the remainder of the class may be assigned to other sections of Exp. III.

A set of loose weights is required for the single-beam trip balance whenever an object weighing more than 10 g. is to be weighed. The extra weights are necessary because the rider (*R*) on the beam (*B*) weighs only from 0 to 10 g. (in 0.1-g. divisions). A set of weights suitable for general laboratory use is shown in Fig. 17.

Tap one of the platforms of the balance and note the action of the pointer. The latter should not come to rest until at least two swings have been made to the left and to the right of the middle of the pointer scale. Furthermore, the pointer should swing an equal number of divisions on each side of the center of the scale. Request the laboratory instructor to adjust the balance if one or both of the preceding conditions are not fulfilled. An adjustment screw (*AS*) is used to bring about the desired condition.

Place the object to be weighed on the left-hand platform of the balance. Select a weight which is presumably too heavy, remove it from the weight box by means of a forceps,

and place the weight on the right-hand platform. (*Never handle weights with the fingers; always use forceps!*) If the pointer swings further to the right than to the left of the center-point of the scale, the weight selected is too heavy. In this event remove the weight, replace it in the box, and try the effect of the next smaller weight. If this is not heavy enough add the next smaller weight or weights until, *as a maximum*, the total of the weights on the platform is 10 g. less than the last-used *single* weight that was found to be too heavy. Now complete the weighing by moving the rider to the right until the pointer swings an equal number of divisions on each side of the middle of the pointer scale. Count the weights on the platform and add to this total the weight indicated by the rider. Record the total *at once*, and then return the weights to their proper places in the weight box. *Always remove the weights in the order of decreasing size*, and make a second count of the total as the weights are being removed from the platform. This check serves to correct any mistake that might have been made in the first counting.

The following example is given as an illustration of the procedure for weighing. Each student is to follow through the procedure with the 150-ml. beaker furnished as part of the desk equipment. After a check of the adjustment of the balance shows that the pointer swings an equal number of divisions on each side of the center of the scale, a 150-ml. beaker is placed on the left-hand platform of the balance. A trial with the 100-g. weight shows it to be too heavy; the 50-g. weight is also found to be too heavy. The 20-g. weight and two 10-g. weights are added, and the swing of the pointer shows that a total of 40 g. is too light. Thus the weight of the beaker is fixed somewhere between 40 and 50 g. The rider is now moved to the right until, at a reading of 6.4, the pointer swings an equal number of divisions on either side of the middle of the scale. Addition of the weights used (20 + 10 + 10) and the amount indicated by the rider (6.4) gives a total of 46.4 g. as the weight (to the nearest 0.1 g.) of the beaker. Record the weight of the beaker actually used during this experiment.[5]

4. Weighing Out a Stated Quantity of Material on a Single-Beam Trip Balance. Carry out this operation on the single-beam trip balance in the manner described on page 20 for a three-beam balance.

5. Use of a Counterbalance. Difficulty arises in weighing out a stated quantity of material in the event that the combined weight of a container and its contents exceeds the total mass of the available weights. The sum of the weights in the set shown in Fig. 17 is 200 g.; this plus the 10-g. capacity of the rider on the balance limits the capacity of this combination of weights and balance to 210 g. Suppose it is desired to weigh out 200 g. of material in a container whose weight is 50 g. There are two ways in which this may be accomplished with the 210-g. combination:

a. Make two separate weighings with smaller portions (about 100 g. each) of material and thus avoid exceeding the capacity of the system, or

b. Use a counterbalance for the container.

Method (**b**) is recommended because it is more convenient. Select a beaker whose weight is somewhat less than that of the container that is being used. Place the beaker on the right-hand platform of the balance and add sand until the weight exactly counterbalances the weight of the container on the left-hand platform. Now add weights to a total of 200 g. and proceed by the method used to weigh out a stated quantity of material (p. 20). Thus, since no weights from the box are used in weighing the container, all the weights plus the rider may be used to weigh materials. The weight of the container is, of course, unknown, and in many experiments it need not be determined; if necessary, the container may be weighed separately.

(B) Beam Balances and Their Use. 1. Horn-Pan Balances. These have a lacquered brass beam, a pointer, and two horn pans suspended from the beam by braided cords as

shown in Fig. 18. This balance is not of a rugged construction, and it lacks stability because it is merely suspended by the hook (*H*) during use. Under the best conditions the balance can be used to determine the weights of relatively light objects to the nearest 0.01 g. (10 mg.).

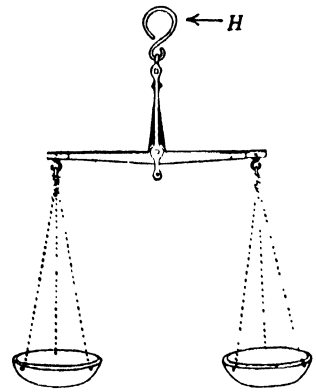


FIG. 18. Horn-pan balance

2. The Barber or Mohr-Type Beam Balance. This type of balance (hereinafter referred to as a *beam balance*) is suitable for general laboratory purposes, and may be used to determine weights to the nearest 0.01 or 0.005 g. A higher degree of accuracy may be obtained by an experienced operator working on a balance in perfect condition. The parts of the balance come packed in a flat wooden box and must be assembled before the balance is ready for use. A laboratory instructor will demonstrate the proper method of setting up the balance.

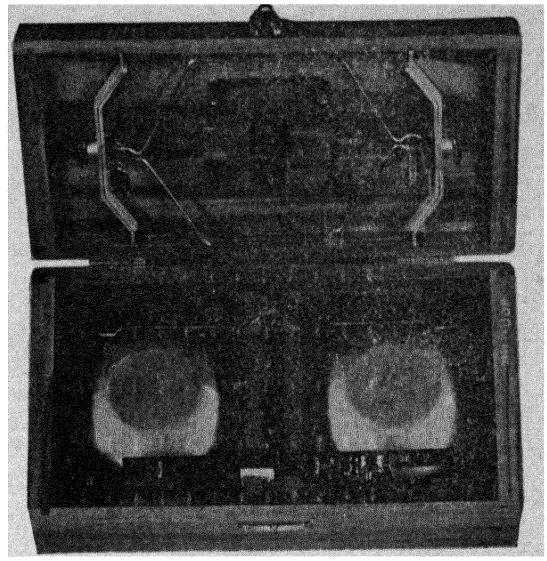
Obtain a beam balance from the stockroom. The construction of this balance is similar to that of the *analytical balance*. Study the section on the construction of an analytical balance (p. 24) in connection with Fig. 21. Now make a schematic freehand drawing of the beam balance, and mark the following parts: column, pointer, pointer scale, beam, central knife-edge, terminal knife-edges, stirrups, and pans.[1]

3. Weighing on the Beam Balance. Weighing on the beam balance is carried out in much the same manner that this operation is performed on the analytical balance. Determine the weight of a porcelain crucible and its cover (Fig. 1) or of an object of unknown weight obtained from the stockroom,* according to the directions given in part (F) of this experiment.[2] Remember that there is no rider on the beam balance. Thus, final adjustments that are made by the rider on the analytical balance are made by *fractional weights* (those less than 1 g.) when the beam balance is used. Allowance must also be made for other differences in the details of the construction of the two types of balances. Part of this problem involves a test of the student's ability to apply the directions given in part (F) to the procedure of weighing on the beam balance.

(C) The Analytical Balance. 1. The Principle of Weighing. All balances used in the laboratory are essentially levers of the first class. A lever of this class is one in which the fulcrum lies between the points of application of the forces. Analytical balances (those on which precise weighings are made) are of the equal-arm type, *i.e.*, the arms of the lever are of equal length. Objects to be weighed on these balances are placed on the left-hand pan. Thus, assume an object of *mass* (*M*) is placed on this pan of a balance (Fig. 19). The weight of the object is obtained by adding bodies of known mass (*weights*) to the right-

* Each object should be numbered and its weight should be kept on a record in the stockroom. Use crucibles, crucible covers, or watch glasses. The object should be returned to the stockroom after the weight has been determined.

hand pan of the balance until the pointer (P) is returned to the position it occupied before M was placed on the balance. At this point the balance is said to be in a position of

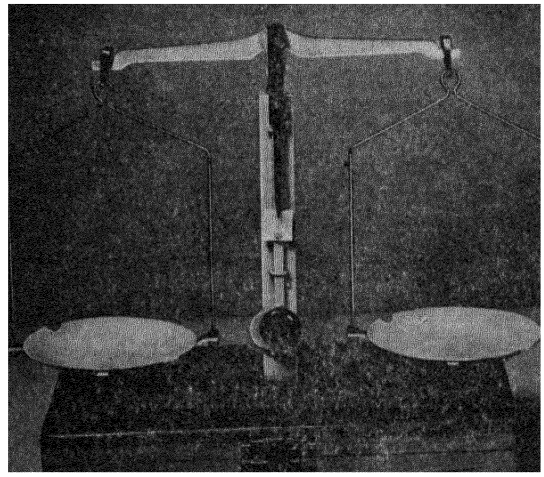


Beam balance packed in its case

equilibrium. If F and F_1 are the forces acting on the left- and right-hand sides of the lever (*beam*) at the points indicated in Fig. 19, and l and l_1 are the distances as shown, then

$$Fl = F_1 l_1$$

Since $l = l_1$ in the equal-arm balance, then $F = F_1$ at equilibrium. F and F_1 are forces representing the attraction of the earth (gravity) for the bodies on the two balance pans.



Beam balance set up for use

The *measure* of F is therefore the force exerted by gravity on M, and is, strictly speaking, the *weight* of M. An expression, $F = Mg$, in which g is the acceleration of gravity, gives the numerical value of F.

However, the chemist is not interested in the *force* with which a body is attracted to the earth, but in the *amount* of matter (mass) in a body. It is desired, therefore, to determine M. When $F = F_1$, then, since g is constant and is the same value for both, $M = M_1$, where M_1 is the mass of the weights on the right-hand pan. Thus the balance is shown to be an instrument for determining *mass*, not weight. The mass of a body is independent of its position on the surface of the earth, but, since the value of g varies from place to place, then the *weight* of a body varies in a corresponding manner. However, the mass of a body is ordinarily spoken of as its weight because the weight of a body at any one locality is proportional to its mass (g being constant at a single locality). Thus the operation of comparing an unknown mass with a known mass on an equal-arm balance is known as weighing. Weight in this case is therefore a synonym for mass and is not being used in its strictly correct sense.

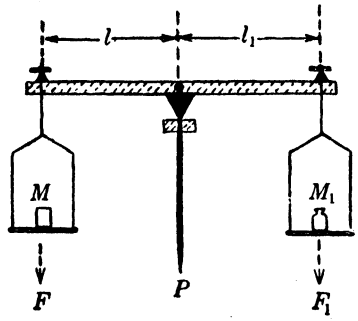


FIG. 19

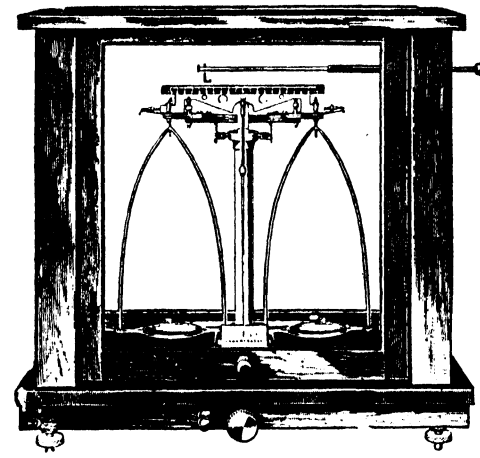


FIG. 20. The analytical balance

2. Construction of the Analytical Balance. A balance of this type (Figs. 20, 21) is essentially an equal-arm lever free to swing in a vertical plane over a central support. Two pans, one for the object to be weighed and the other for the weights, are suspended from the metal beam (B). See Fig. 21. An agate knife-edge (V) set in the center of B, rests upon an agate plate (A) set over the central column (C). Two terminal knife-edges (T_1 and T_2), mounted with edges upward, are fixed over the ends of the beam at equal distances from V. The pans (P_1 and P_2) are hung from a pair of stirrups (St_1 and St_2), supported by the terminal knife-edges (T_1 and T_2). These knife-edges make contact with the stirrups against agate plates fixed in the tops of the stirrups. A long pointer (Y) extends downward from the beam to a scale (Sc) located at the base of the central column (C).

In order to protect the knife-edges from wear and from shocks occasioned by placing objects on or removing them from the pans, a device called the *beam rest* is used to separate the knife-edges and the plates. When the crossbar (CB) of the beam rest is raised by turning the milled head (H) the studs (S_1 and S_2) engage the underside of the beam. This raises the latter slightly and thus separates the three knife-edges from their respective agate plates. The balance is kept in this position when not in use or when objects are being placed on or removed from the pans.

A *pan-arrest* mechanism operated by the push-button (PB) keeps the pans from swinging when the beam is lowered onto the knife-edges preparatory to weighing. The pan supports (PS_1 and PS_2) are lowered by pushing the button; this permits the pans to move

vertically when the beam is released. Return of the button to its original position elevates PS_1 and PS_2 so that the pans are held lightly in position.

Graduations on the beam permit weight adjustments smaller than 10 mg. to be made by moving a small wire weight called the *rider* (R) along the beam. A rider rod (RR) provided with a rider hook (RH) enables the operator to fix the position of the rider without raising the door of the balance. If the graduation over the terminal knife-edge (T_2) is 10, then the weight of the rider should be 10 mg. When the rider is placed on any graduation

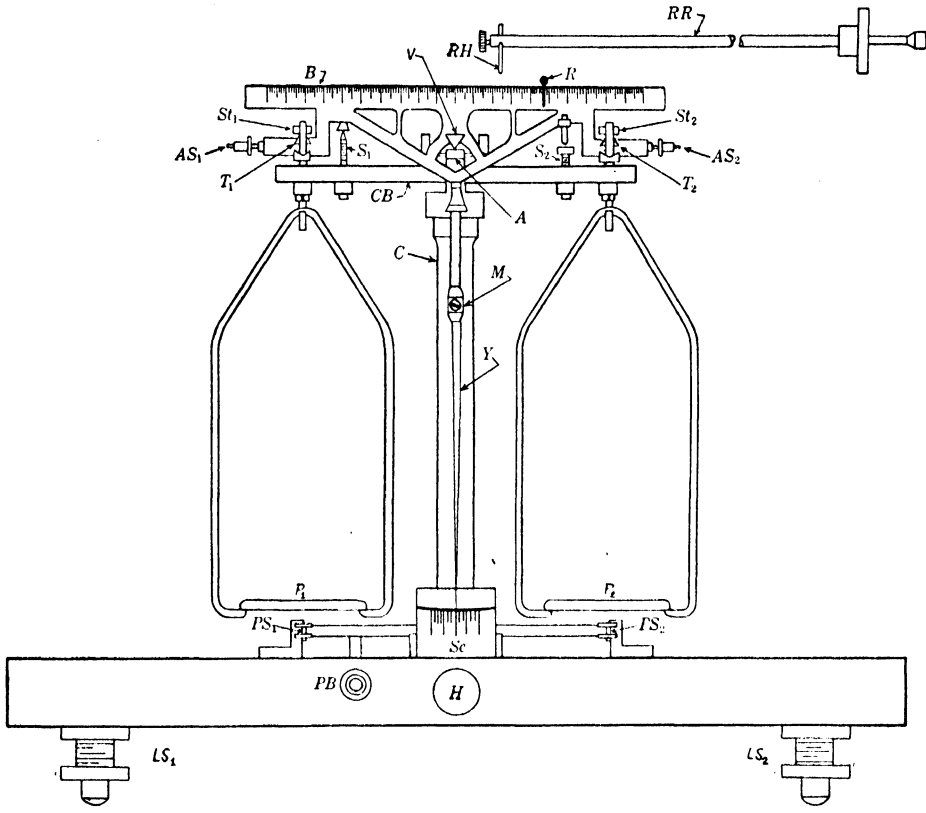


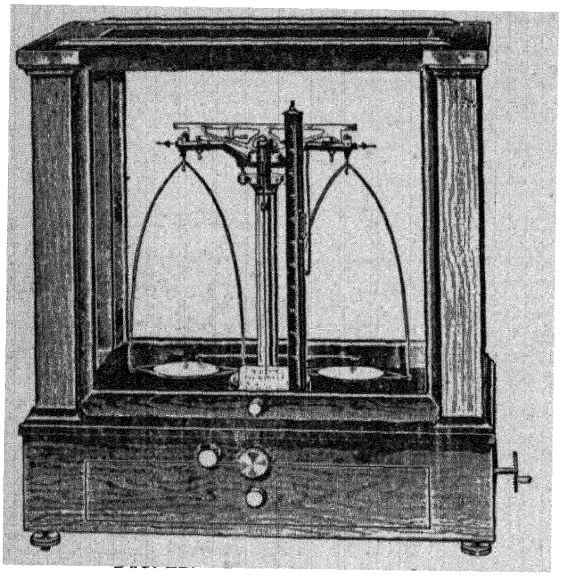
FIG. 21. The analytical balance (schematic)

on the beam, the effective weight of the rider is the same as the number of the division on the scale. The effect produced is the same as when a weight of equal mass is placed on the pan. It must be emphasized that the weight of the rider in milligrams must correspond with the number of major graduations appearing on the arm from the central to the terminal knife-edge. Each of the major divisions is usually subdivided into 10 parts to indicate tenths of milligrams.

Alteration of the sensitivity of the balance is accomplished by changing the position of the movable mass (M) attached to the pointer. Adjusting screws (AS_1 and AS_2) placed at the ends of the beam, are moved in or out to cause the beam to rest in a horizontal position when the pans are empty. A pair of leveling screws (LS_1 and LS_2) are used in conjunction with built-in spirit levels to insure the horizontal position of the instrument.

(D) The Chainomatic Balance. A fine gold chain takes the place of the rider in this type of balance (Fig. 22). Adjustments smaller than 50 or 100 mg. are made by transferring more or less of the effective weight of the chain to the beam. One end of the chain is attached to the right-hand arm of the beam, the other is fastened to a block which is moved up and

down along a graduated pillar by means of a crank. A vernier (Fig. 23) permits readings to 0.1 mg. Weighings can be made more conveniently with this arrangement than with the rider.



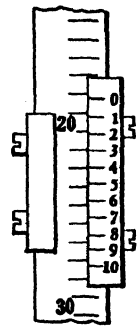


FIG. 23. Chain scale and vernier when chain is exerting 18.3 mgs. on beam

(E) Weights. Reference masses called *weights* are used in the determination of the mass of an object. The following weights are ordinarily found in a set of analytical weights:

Grams:	100, 50, 20, 10, 10, 5, 2, 1, 1, 1
Milligrams:	500, 200, 100, 100, 50, 20, 10, 10, 5, 2, 2, 1
Riders:	5 and 10 mg.

Weights smaller than 10 mg. are not ordinarily needed because the rider serves this purpose. Certain chainomatic balances do not require weights smaller than 1 g.; in others the chains make all adjustments smaller than 200, 100, or 50 mg.

Integral weights (1 to 100 g.) in the cheaper sets are made of bronze or brass protected by a coating of lacquer; weights in the more expensive sets are plated with nickel, chromium, gold, or platinum. Fractional weights (smaller than 1 g.) are usually made of platinum, nickel-silver, or aluminum.

Weights in the finest sets are kept in boxes containing a separate velvet-lined compartment for each weight, to prevent abrasion during the removal and replacement of the weights. Ivory- or bone-tipped forceps are used to handle weights; all-metal forceps or the fingers are never used. A definite order of arrangement is followed in most weight boxes (Fig. 24).

(F) Direct Weighing by the Method of Swings. Each student should be given an opportunity to use the analytical balance. Large classes must necessarily be divided into small sections because of the limited number of balances available. While one section is working at the balances, the remainder of the class can be given other experiments to perform.

The determination of the equilibrium position or zero point of an empty balance is the first step in any method of weighing on a beam balance. Lower the beam by turning the knurled screw (*H*) in a counterclockwise direction. The rider must not be on the beam unless the latter is numbered from zero at the left end; in this case the rider must be placed on the zero mark. When the beam is lowered it does not swing freely because the pan

arrests hold the pans in place. Now lower the pan supports by pushing in the pan-arrest button (*PB*) and allow the beam to swing freely. If it does not do so, or if the swings of the pointer do not carry it over at least three divisions on either side of the middle of the scale, open the balance door and waft air against a pan by waving the hand. Do not touch the pan! A swing of from three to five divisions is desirable.

Close the balance door, allow the beam to make several swings, and then note the *furthest* point reached by the pointer on each side of the center point. Each swing will be shorter than the one preceding it, and thus the furthest point is different on successive swings. Take an odd number of readings (3) of the furthest points of three successive swings on one side, and an even number (2) on the other. Record these data as shown in the example given in the next paragraph.[1] Assign positive values to swings on the right, and negative values to those on the left. Now raise the pan supports and the beam before proceeding with the calculations. Do not arrest the motion of either the pans or the beam until the pointer is on or near the zero position in the course of a swing!

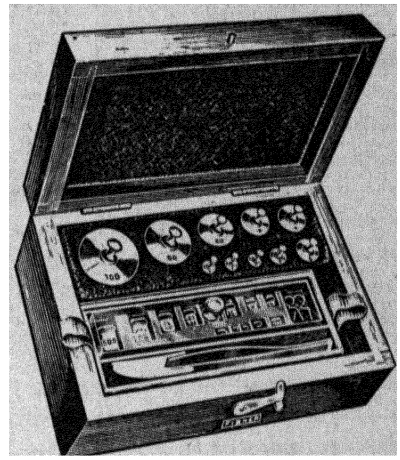


FIG. 24. Analytical weights

Proceed with the calculations by adding each set of readings separately. Now calculate the average value for each set. Obtain the mean of the two averages by adding them algebraically and dividing the sum by 2. The mean value represents the *zero point*, and the sign indicates on which side of the center point it is to be found. The zero point of a well-adjusted balance is usually found to be within one division of the zero on the scale. However, it is not necessary or advisable for the student to adjust the screws (AS_1 and AS_2) so as to bring this about. An example of a zero-point calculation is shown as follows:

Scale readings on left	Scale readings on right
(1) − 4.8	(1) +4.2
(2) − 4.6	(2) +4.0
(3) − 4.4	+8.2
−13.8	

$$\text{Average} = \frac{-13.8}{3} = -4.6 \qquad \text{Average} = \frac{+8.2}{2} = +4.1$$

$$\text{Mean} = \frac{-4.6 + 4.1}{2} = -0.25 \text{ or } -0.3$$

These calculations locate the zero point at 0.3 of a division to the left of the center line of the scale.

After the zero point has been determined and the value has been recorded, place a 5- or a 7-cm. watch glass (Fig. 1) on the left-hand pan. Select a weight estimated to be slightly *heavier* than the watch glass, remove it from the weight box with the forceps, and place it gently on the right-hand pan. If the weight is heavier than the object selected, the pointer may move to the left, despite the fact that the pan supports are in place, because these supports are depressed by an excess of from 2 to 3 g. Thus, failure of the pointer to move shows the mass of the weight is within 2 or 3 g. of that of the watch glass. In this case push in the pan-arrest button slightly and note the direction in which the

pointer swings. If the swing is to the left, gently raise both beam and pan arrests, remove the weight from the pan and replace it by the next *smaller* weight.* A swing of the pointer to the right on the first test requires the same procedure except that the weight originally selected is replaced by the next larger one in the set. In any event, add or remove weights systematically until the pointer does not move when the beam is lowered. From this point on it is unnecessary to raise and lower the beam during the systematic addition and removal of the smaller weights. Permit the beam to swing after each change of weights by lowering the pan supports. Note the behavior of the pointer each time the beam is allowed to swing. The addition of the last 10 mg. or fraction thereof is made by means of the rider (5 mg. if a 5-mg. rider is used). *When the object is exactly counterbalanced, the pointer swings an equal number of divisions to either side of the zero point.*

During the final counterbalancing process with the rider (or with the chain on a chainomatic balance) place it systematically, *i.e.*, first near the center, then one quarter of the distance from one end and so on, until the weight of the object is counterbalanced.

Record the weight of the watch glass or, if so directed by the instructor, obtain an object of unknown weight from the stockroom, record its number, and determine its weight.[2]

Certain precautions and procedures in addition to those given in the preceding section are necessary if a weight is to be determined with the highest degree of precision possible with an analytical balance.

It cannot be emphasized too frequently that chemicals, powders of any kind, or containers that are not clean and dry on the outside, must *not* be placed on the platforms or pans of any type of balance. Chemicals or powdered substances must be weighed on watch glasses or filter paper, or in crucibles or beakers. Their weights are determined by difference. Thus the use of containers of known weight (to the nearest 0.1 or 0.01 g.) saves a considerable amount of time. If weighings are made on a trip balance or on a horn-pan balance, the weights of the containers need not be redetermined each time they are used. Balanced watch glasses are obtainable.

(G) Summary of the Steps Taken in Weighing on a Beam Balance

1. Determine the zero point of the balance.

2. Arrest the beam and the pans.

3. Place the object to be weighed on the left-hand pan of the balance.

4. Select a weight estimated to be slightly greater than that of the object. Place the weight on the right-hand pan.

5. Release the beam (and pans if necessary) and note the swing of the pointer.

6. Arrest the beam and pans, remove the weight, and replace it by the next smaller or next larger weight in the set. Again note the swing of the pointer to either side of the zero point.

7. Continue the systematic removal or addition of weights until the pointer swings an equal number of divisions to either side of the zero point.

8. Arrest the beam and pans.

9. Record the weight at once in the proper place on the report sheet.

10. Confirm the total weight by checking each individual weight as it is removed from the balance.

11. Replace all weights in their proper places in the box.

12. If an analytical balance is used, close the window of the balance as soon as the object and the weights have been removed from the pans.

---

* Always raise the beam and arrest the pans *before* any weight is removed from or placed on the pan. Never make any changes in the number of weights on the pan while the beam is free to swing!

Name (last name first) _____ Desk No. _____ Date _____

Experiment III

BALANCES AND WEIGHING

(A) Trip Balances. *Weighing on a three-beam trip balance*

1.

2.

3.

Weighing out a stated quantity of material

4.

Weighing on a single-beam trip balance

5.

(B) Beam Balances and Their Use

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment III (Cont'd)

2.

(F) Direct Weighing by the Method of Swings

1. Scale readings on left

(1)

(2)

(3)

Average =

Scale readings on right

(1)

(2)

Average =

Mean =

2.

Experiment IV

DETERMINATION OF THE DENSITY OF A LIQUID; PRECISION AND ERRORS *

Discussion. The density of a substance at a given temperature is defined as its mass per unit volume:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

In the metric system the mass is expressed in grams and the volume in cubic centimeters, The absolute density is, therefore, expressed in grams per cubic centimeter. However. since the volume of a substance is usually measured in milliliters (1.000027 cc.), the density is often expressed in grams per milliliter. This is practically identical with the absolute density.

The experimental determination of the density of a liquid requires the measurement of the mass in grams of a known volume measured in milliliters. Choice of a balance to weigh the liquid depends upon the precision with which the volume is known. The volume of the liquid may be measured with a graduated cylinder, a burette, or a pipette (Figs. 25, 26, 28,

FIG. 25. Transfer pipette

FIG. 26. Measuring pipette

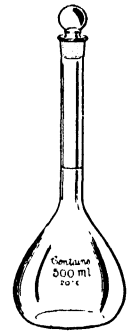


FIG. 27. Volumetric flask

FIG. 28. Geissler-type burette

FIG. 29. Mohr-type burette

29). The order of increasing precision in measuring a definite volume with each is the order listed. As pointed out in the section Precision and Errors (Appendix A) the experimentally determined density is no more precise than is the precision of the least precise measurement. In other words, both measurements should be made with about the same percentage precision.

* The section Precision and Errors, found in the Appendix, should be studied by the student before this experiment is performed.

A volume of water of about 50 ml. can be measured in a graduated cylinder to within ±0.2 ml., which is a percentage precision of (0.2 ÷ 50.0) × 100 = ±0.4%. The weight should be determined with about the same percentage precision; 50 ml. of water will weigh roughly 50 g. This weight should be determined with a precision of ±0.4% or (50 × 0.004) = ±0.2 g. The weight of an object may be measured to the nearest 0.1 g. on a laboratory trip balance. This balance is therefore the one chosen to weigh the liquid when the volume is measured by means of a graduated cylinder. It would be a waste of time and effort to weigh the liquid on a beam balance with any greater precision than ±0.1 g.

If, however, a volume is measured by means of a burette with a precision measure of ±0.02 ml. (32.22 ml. ± 0.02 ml.), the percentage precision is (0.02 ÷ 32.22) × 100 = 0.06%. The weight should be determined with about the same percentage precision (32 g. × 0.06%) = ±0.02 g. This requires a beam balance with which the weight may be determined to the nearest 10 mg. (0.01 g.). Any greater precision in weighing is not necessary because it does not increase the precision of the result. The method used to determine the precision of the result is described in the section Precision and Errors. The above examples illustrate the general principles used to select apparatus and instruments with which to make a given measurement. The method and apparatus chosen will depend upon the precision desired.

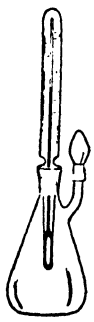


FIG. 30. A pycnometer

More precise determinations of the density of a liquid are made with a special piece of apparatus known as a pycnometer (Fig. 30). This is a glass container whose precise volume is known.

The term *specific gravity* is sometimes used interchangeably with density. The specific gravity is defined as the ratio of the weight of the substance to the weight of an equal volume of water at 3.98° or at another specified temperature. If the weights of 1 ml. of the two substances are compared, then the specific gravity is simply the ratio of the density of the substance to the density of water at definitely stated temperatures. Because the weight of 1 ml. of water at 3.98° is 1 g., the specific gravity of a substance and its density are the same when the comparison is made with water at 3.98°. However, if the comparison is made to water at any other temperature, the density of the substance is slightly less than its specific gravity. Thus, sp. gr. 25°/25° = 1.810 means that the weight of a given volume (1 ml., for example) of the substance at 25° is 1.810 times greater than the weight of the same volume (1 ml.) of water at 25°, that is,

$$\text{Sp. gr. } 25°/25° = \frac{\text{Density of the substance at } 25°}{\text{Density of water at } 25°} = 1.810$$

Solving for the density of the substance at 25°,

$$\text{Density} = (\text{Sp. gr. } 25°/25°) \times (\text{Density of water at } 25°)$$

$$\text{Density} = (1.810) \times (0.9971) = 1.795 \text{ g./ml.}$$

The specific gravity of a liquid is generally determined in the following manner. Measurements are made to determine the loss in weight incurred by a solid of known weight and volume upon its immersion in the liquid and in water at known temperatures. *The ratio of the loss of weight in the liquid to the loss of weight in water is the specific gravity at the stated temperatures.* This follows from the fact that the above procedure really measures the ratio of the weights of an equal volume of the liquid and of water. The volume is that of the solid. Weight determinations in accordance with the above procedure are facilitated by the use of a Westphal balance (Fig. 31).

A similar principle is used in making an ordinary hydrometer (Fig. 32). This instrument consists of a weighted glass float with a uniformly calibrated stem. The bottom of the hydrometer is loaded with lead shot or mercury until the instrument is partly submerged in water at a given temperature. A mark is placed at the water-line on the hydrometer stem, and further calibrations are obtained by using other liquids of known specific gravity. In liquids that are less dense than water, the hydrometer sinks to a greater depth than it does in water; in liquids denser than water it will be buoyed up with a greater force,

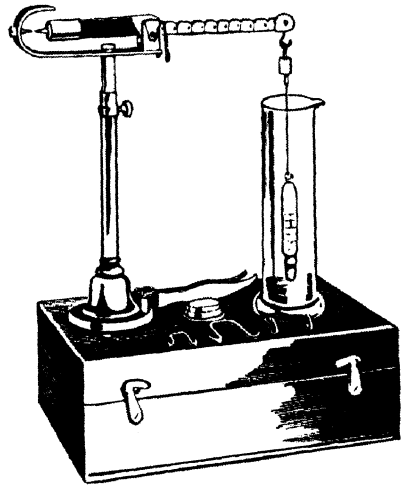


FIG. 31. Westphal specific gravity balance

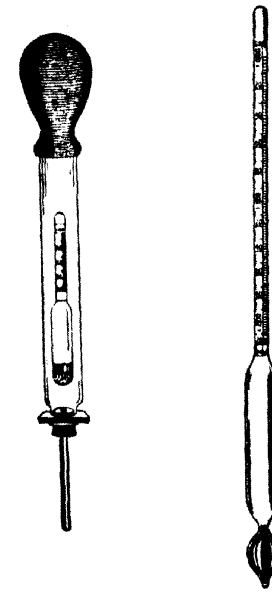


FIG. 32. Hydrometers

and therefore will not sink so far. The distance between graduations for a given change in specific gravity is proportional to the volume displacement per unit length of the stem.

Apparatus and Materials: Trip balance; concentrated (36*N*) sulfuric acid; burette; 50 ml. of a liquid of unknown density; * 10-ml. pipette; beam balance.

(A) Approximate Determination of the Density of a Liquid. Clean and dry a 100-ml. graduated cylinder. Weigh it as carefully as possible on the laboratory trip balance. Record the weight to the nearest 0.1 g. on the *report sheet*, using the form supplied there. (**Note:** If the balance is a two-plate platform balance, it may be necessary to counterbalance the dry graduate by pouring sand into a small beaker on the right-hand pan. See Exp. III. This procedure is followed when the weights furnished are not sufficiently large to weigh the graduate plus its contents.) Fill the graduate to about the 50-ml. mark and weigh the graduate plus the water. Read the volume by observing the lowest part of the meniscus (Fig. 37). Record the volume to the nearest 0.2 ml. by estimating the distance the meniscus lies between the two lines on the graduate. For example, if the meniscus lies just a little way above the 51-ml. mark, that is, about one fifth of the way to the 52-ml. mark, the volume is read 51.2 ml., etc. After reading the volume, determine the temperature of the water. Dry the graduate and repeat the measurements with about 55 or 60 ml. of water. Calculate the density of the water to the correct number of significant figures. Record the data on the form given on the report sheet.[1]

* *Liquids of unknown density.* Data for making up solutions of ammonium chloride or calcium chloride of a given density may be obtained from the *Handbook of Chemistry and Physics*, published by the Chemical Rubber Company.

Read the section Precision and Errors given in Appendix A. Calculate the average density and determine the average deviation.[1] Using the average deviation as the precision measure, calculate the percentage precision.[1] Is the precision attained greater or less than that estimated from the analysis of the method made in the section on errors? Compare the values.[2] If the precision lies outside of the estimated limits, it means that greater care must be used in reading the volumes and in making the weighings.

Look up the accepted value for the density of water at the recorded temperature. Calculate the percentage error of the result.[1] Does the accepted value of the density lie between the limits set by the precision measure?[3] If not, to what type of errors other than accidental errors might this be due?[4]

Why was it necessary to dry the graduated cylinder before beginning the determination?[5] When reading the position of the meniscus, why was it necessary to keep the graduate perpendicular to the desk top, and to keep the eye at the same height as the bottom of the meniscus?[6] Why is the temperature recorded when the density of a liquid is determined, whereas the atmospheric pressure is not?[7]

(B) Determination of the Density of Sulfuric Acid. *Danger!* Sulfuric acid is very corrosive to the skin, eyes, and clothes. If sulfuric acid or any other corrosive chemical should get on the hands or in the eyes, wash immediately with water, and notify the instructor. If acids are accidentally spilled on the desk top or on the clothes, wash with water and rub with a little sodium bicarbonate (soda) or *dilute* (4*N*) ammonium hydroxide solution. Never pour water into concentrated sulfuric acid because the heat generated may cause the solution to boil so vigorously that some of the liquid will be thrown out of its container. In this event the greatest danger is to the eyes! *Acids should always be poured slowly and carefully into water.*

Clean and dry the 100-ml. graduated cylinder. Determine the density of concentrated sulfuric acid from the reagent bottle and record the data on the form given on the report sheet.[1] Return the sulfuric acid to the acid bottle. Do not contaminate the acid.

The density or the specific gravity of the sulfuric acid in a fully charged automobile storage battery should be about 1.25. If a solution with this density contains 34 per cent sulfuric acid by weight, calculate the number of grams of sulfuric acid in 100 ml. of solution.[2] Draw a sketch of a hydrometer and indicate on its stem the relative positions of the following values:[3]

	Specific Gravity
Water	1.00
Sulfuric acid in a discharged battery	1.05
Sulfuric acid in a charged battery	1.25
Concentrated sulfuric acid (use value determined above)	

Use of Reagent Bottles. 1. Pouring Liquids from Bottles. Liquid reagent bottles may have coin-shaped (Fig. 33) or flat-head stoppers (Fig. 34). The stopper is removed from the first type by taking the top of the stopper between the second and third fingers at the back of the right hand as illustrated in Fig. 33. The receiving vessel, such as a graduate, test tube, or beaker, is held in the left hand while the liquid is being poured. This procedure cannot be used to remove a stopper with a flat head. To remove the latter type of stopper, grasp it with the *left* hand between the last two fingers and the palm of the hand. Hold the graduate, test tube, or beaker with the thumb and first two fingers of this same hand. Pour the liquid from the bottle with the right hand (Fig. 34). Never lay down the stopper because it may become contaminated and make the contents of the bottle unfit for use. The rim on the neck of the bottle should touch the inside edge of the receiving vessel to prevent the liquid from running back on the side of the bottle. If too much liquid has been poured from the bottle, it should not be returned inasmuch as there is danger of contaminating the rest of the liquid in the bottle. For similar reasons, never dip a stirring

rod, platinum wire, pipette, medicine dropper, or other apparatus into a reagent bottle. Always pour the liquid into a graduated cylinder, small beaker, or test tube, and then dip into this. Reagent bottles from the side-shelf *must not be taken to the desk.* The chemicals are listed in alphabetical order with a number on each bottle corresponding to its position

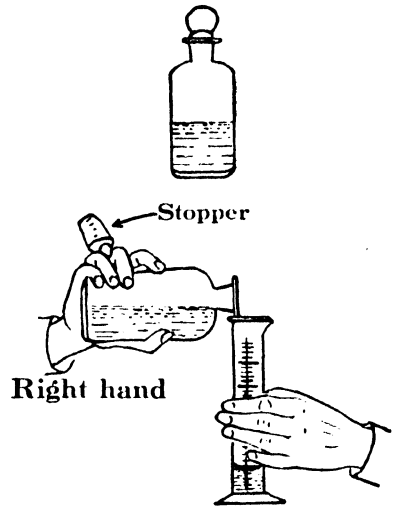


FIG. 33. Pouring a liquid from a bottle

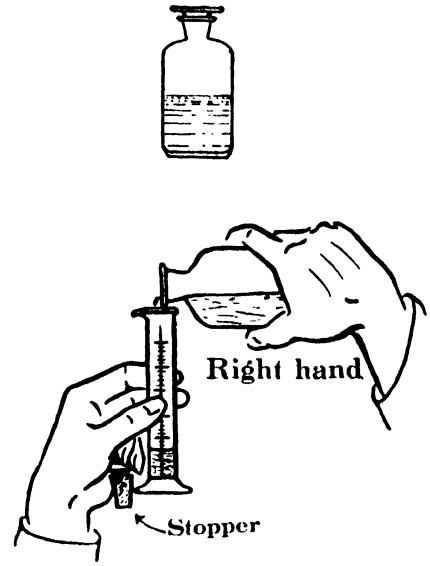


FIG. 34. Pouring a liquid from a bottle

on the side-shelf. Replace each bottle in its proper position. Since chemicals are expensive, never take more from the bottles than is necessary. Liquids that are to be disposed of are always poured into the sink and washed down with water.

All solids are, in general, disposed of in waste jars. Filter papers, burned matches, broken glassware and many solid chemicals are deposited in these jars. Exceptions are such solids as sodium peroxide, sulfur, and phosphorus, which are apt to cause fires, and should be disposed of in special bottles provided by the stockroom.

2. Removing Solids from Bottles. Figure 35 indicates the method to be used in removing solids from bottles fitted with hollow glass stoppers. The bottle is tilted in such a manner that the solid fills the hollow part of the stopper. As the stopper is removed, the bottle is tilted back in order not to spill the solid. If the solid is to be weighed on the laboratory trip balance, a watch glass or small beaker should be used as explained in Exp. III. Dry and noncorrosive solids may be weighed on pieces of paper. If the balance has two platforms, two pieces of paper of equal weight may be placed, one on each platform. Weights equivalent to the amount of material desired are then added to the right-hand pan, first by means of the beam rider, then, if necessary, by weights from the weight box. The solid is transferred from the stopper to the paper or to the watch glass on the left-hand platform by carefully rotating and tilting the stopper. If too much solid is obtained, do not return it to the bottle but remove a small amount from the paper or the watch glass by means of a spatula. Dispose of the solid in the waste jar.

FIG. 35. Removing a solid from a bottle

Special solutions or solids not found on the side-shelf are obtained from the stockroom in *small beakers* or on *watch glasses.*

Figure 36 illustrates a method by which a solid is placed on the bottom of a test tube in such a way that no particles adhere to the sides of the tube. A narrow strip of paper is folded lengthwise down the center and the solid is placed in the fold. The paper with the solid on it is carefully slipped into a test tube held in a horizontal position. The test tube is then tilted, and the solid falls down the fold to the bottom of the tube.

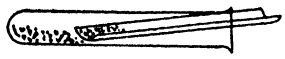


FIG. 36. Placing a solid in the bottom of a test tube

(C) More Accurate Determination of the Density of a Liquid. Use of a Burette. A more accurate determination of the density of a liquid requires a balance of greater sensitivity than the trip balance, and a more precise means of measuring the volume than is possible with a graduated cylinder. Greater care must also be used in eliminating such sources of error as evaporation, changes in temperature, and uncleanliness of apparatus.

Place a clean, stoppered 50-ml. Erlenmeyer flask on the left-hand pan of the small beam balance or the analytical balance. Place an unstoppered flask of the same size on the right-hand pan and add sand until the stoppered flask is counterbalanced. Keep the flask containing the sand just as it is for use when the liquid added to the other flask is weighed.

Clean a Geissler or Mohr burette (Figs. 28–29). If drops of water cling to the inside of the burette, the surface is greasy and the burette must be cleaned very thoroughly. Use a long-handled burette brush (from the stockroom) with cleaning powder or soap and water.* Rinse the burette well with tap water and then twice with 5-ml. portions of distilled water. Allow the burette to drain completely each time, before the next portion is added.

Fasten the burette to the ring stand by means of a burette clamp. Turn the burette until the handle of its stopcock or the knobs of the pinchcock are on the right-hand side; the graduations on the burette now face toward the front of the desk. Operate the stopcock or pinch clamp with the thumb and first finger of the left hand by placing the thumb in front of the burette and the fingers behind it. Fill the burette with distilled water from the wash bottle. The water should remain in the wash bottle long enough to have the same temperature as that of the laboratory. Fill the tip of the Geissler-type burette by opening the stopcock wide for a fraction of a second. Remove the air from the rubber connection and the glass tip of a Mohr burette by turning the tip upward and allowing a small amount of water to flow out.

Now allow water to drain from the burette until the lower part of the meniscus is at the zero mark or slightly below it. Read and record [2] the position of the meniscus to the nearest 0.02 ml. as described below. Keep the eye level with the meniscus at the time the reading is made (Fig. 37). If the graduations extend one half the distance around the burette, the eye will be on the same level when the front and back portions of the graduations coincide. The bottom of the meniscus may be seen more plainly by using a piece of paper which has a wide black stripe drawn across the center with a pencil (Fig. 38). When the paper thus prepared is held behind the burette just below the meniscus, a reflection from the meniscus facilitates the reading of its position.

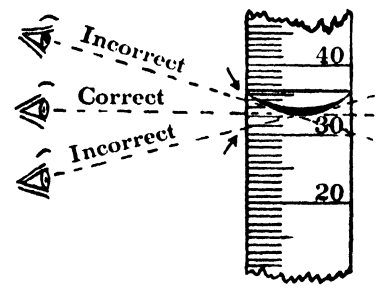


FIG. 37. Reading the meniscus

* Burettes and pipettes may also be cleaned by allowing "cleaning mixture" to stand in them for one half to one hour. Cleaning mixture is made by adding 7 g. of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) to each 100 ml. of concentrated sulfuric acid. Because cleaning mixture is so corrosive to the clothes and skin, the use of soap is recommended.

If the graduations do not extend at least half way around the burette, a narrow strip of paper with straight edges may be used for the same purpose. Hold the strip of paper around the burette with the ends of the paper squarely together (Fig. 39). Move the eye up and down until the back edge of the paper is just hidden by the front edge.

Draw off from 20 to 25 ml. of water into the weighed and stoppered flask. Wait 30 sec. before taking the final reading. Why? [1] Read the bottom level of the meniscus to the nearest 0.02 ml. by estimating the fraction of the distance the meniscus lies between the two marks. For example, if the bottom of the meniscus is almost but not quite one half the distance between the 24.40- and the 24.50-ml. mark, the reading is taken as 24.44 ml. Record the reading on the report sheet.[2] Replace the stopper in the flask and weigh the

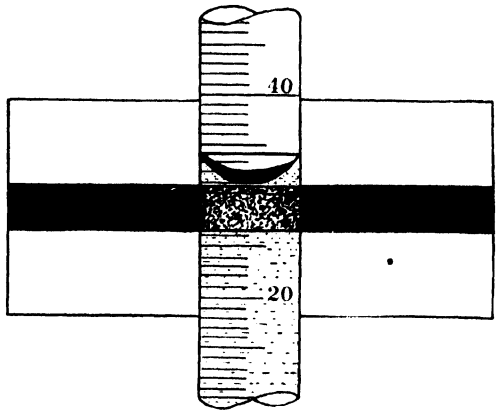


FIG. 38. Making the meniscus visible

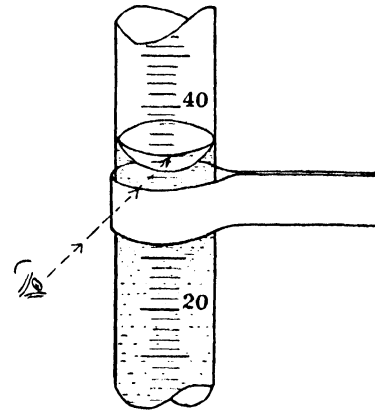


FIG. 39. An aid in reading a meniscus

water to the nearest 0.01 g. (10 mg.) with the counterbalancing flask being placed on the right-hand pan. Measure the temperature of the water and calculate the density of water at this temperature from the data obtained. Use the correct number of significant figures. Repeat the determination using a different volume of water. Record the data on the form given on the report sheet.[2]

Calculate the average density and the average deviation of the two measurements.[2] Calculate the percentage precision and the percentage error.[2] Is the precision attained greater or less than that estimated in the section in Appendix A which deals with precision and errors? [3] If the accepted value does not lie within the limits set by the precision measure, suggest certain sources of error which might account for this discrepancy.[4] Compare the precision attained in part (A) with that attained in this section.[5]

(D) Determination of the Density of an Unknown Liquid. Obtain 50 ml. of an unknown liquid and record its number.[1] Determine its density in the manner described for water in part (C). Before filling the burette, rinse it with two 3-ml. portions of the solution. It is not necessary that the initial reading of the burette be zero. Record the data on the form given on the report sheet.[2] The laboratory instructor will check the accuracy of the result when the report sheets are handed in.

(E) Calibration of a Pipette from the Known Density of a Liquid. Use of a Pipette. Clean and dry the 50-ml. flask and make certain that the flask containing the sand exactly counterbalances it. Clean a 10-ml. pipette. If drops of water cling to the inside surface when water runs out of the pipette, it is greasy and must be cleaned. The pipette can be cleaned by sucking a hot soap solution into it, and then shaking the pipette while the solu-

tion runs out.* Rinse the pipette with tap water and then with distilled water. Fill the pipette with distilled water by applying gentle suction with the mouth until the water rises above the mark on the stem. Quickly close the upper end of the tube with the first finger (not the thumb!), in order to hold the water in place. By slightly raising the finger and twisting the pipette a little with the thumb and the other fingers, allow the water to flow out slowly until the bottom of the meniscus is in exact coincidence with the mark. Now stop the flow of water and touch the tip of the pipette to the edge of the vessel from which the distilled water was taken. This action will remove a drop adhering to the tip. Deliver the water into the 50-ml. flask while holding the tip of the pipette near the side of the flask in order to prevent splashing. As soon as the water ceases to flow out freely, complete the transfer by touching the tip of the pipette to the water. Allow the pipette to drain for 15 sec. (count slowly). Allow the tip to remain in contact with the water during the drainage period. The water remaining in the tip should *not* be blown or shaken out. Fill the pipette once more and in the same manner transfer the water to the 50-ml. flask. Weigh the flask and the water with the counterbalance in position on the left-hand pan of the balance. Measure the temperature of the water and look up the density of water at this temperature. Calculate the volume of water delivered by the pipette.[1] Return the apparatus as soon as the experiment has been completed.

How could this *calibrated* pipette be used to determine the density of another liquid? [2]

* Cleaning mixture may be used but it is not recommended because of the danger of spilling it on clothing or of sucking it into the mouth. If it is used, a safety trap should be inserted between the pipette and the mouth. Dilute sodium hydroxide solution may be used if difficulty is experienced in cleaning the pipette with soap solution. (Caution!)

Name (last name first) _____ Desk No. _____ Date _____

Experiment IV

DETERMINATION OF THE DENSITY OF A LIQUID

(A) Approximate Determination of the Density of a Liquid

1.

	Trial 1	Trial 2
Weight of graduate + water	g.	g.
Weight of graduate	_____g.	_____g.
Weight of water	g.	g.
Volume of water	ml.	ml.
Temperature	°C.	°C.
Density	g./ml.	g./ml.
Average density		
Deviations		
Average deviation		
Percentage precision		
Accepted density at above temperature		
Percentage error		

2.

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IV (Cont'd)

(A) Cont'd

7.

(B) Determination of the Density of Sulfuric Acid

1.

Weight of graduate + sulfuric acid . . . . . _____

Weight of graduate . . . . . _____

Weight of sulfuric acid . . . . . _____

Volume of sulfuric acid . . . . . _____

Calculated density at room temperature . . . . . _____

Accepted density 1.84

Percentage error . . . . . _____

2.

3.

(C) More Accurate Determination of the Density of a Liquid

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IV (Cont'd)

(C) Cont'd

2.

	Trial 1	Trial 2
Final reading of the burette		
Initial reading of the burette	_____	_____
Volume of water		
Weight of the water		
Temperature		
Density		
Average Density		
Deviations		
Average deviation		
Percentage precision		
Accepted density at the above temperature		
Percentage error		

3.

4.

5.

(D) Determination of the Density of an Unknown Liquid

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IV (Cont'd)

(D) Cont'd

2.

	Trial 1	Trial 2
Final reading of the burette		
Initial reading of the burette	———	———
Volume of unknown liquid		
Weight of the unknown liquid		
Temperature		
Density		
Average density		
Deviations		
Average deviation		
Percentage precision		

(E) Calibration of a Pipette

1.

	Trial 1	Trial 2
Weight of water in the 50-ml. flask		
Temperature of water		
Density of water		
Volume of water		
Volume of pipette		
Average		

2.

Experiment V

DETERMINATION OF THE DENSITY OF A SOLID

Discussion. The measurement of the density of a solid requires a knowledge of the volume and the weight of the solid material. If the solid is of a regular geometric shape and is devoid of air spaces, its volume may be calculated from the measurement of its dimensions. However, most solids are irregular, and their volume must be obtained by one of the following indirect methods. (1) The volume of a solid is equal to the increase in the volume of a liquid resulting from the immersion of the solid in the liquid. Air must not be trapped in void spaces, and the solid must not dissolve in or react chemically with the liquid. (2) When a solid is suspended in a liquid, it is buoyed up by a force equal to the weight of the liquid displaced. Therefore, the volume of a solid may be calculated from the loss in weight incurred when the solid is suspended in a liquid of known density. The volume of the solid is equal to the loss in weight divided by the known density of the liquid.

Apparatus and Materials: Forty grams of dry sand; from 20 to 30 g. of a solid of unknown density; * beam balance; 20 cm. of fine copper wire; solid piece of metal weighing from 10 to 20 g.; * metal bridge to fit over the pan of the beam balance.*

(A) Determination of the Density of a Solid. Weigh out approximately 40.0 g. of dry sand to the nearest 0.1 g. Fill the 100-ml. graduate to about the 50-ml. mark and read the volume as accurately as possible to the nearest 0.2 ml. Carefully pour the sand into the water in such a way that no air bubbles are carried down and trapped in the sand. Read the final position of the meniscus. The increase in volume is taken as the volume of the sand. Calculate the density of the sand.[1]

Note: Since the increase in volume is determined from the difference between two readings on a 100-ml. graduate, the uncertainty in the volume may be as much as ± 0.4 ml. (± 0.2 ml. for each reading). If the increase in volume were 20.0 ml. $\pm$ 0.4 ml., the percentage precision would be about 2 per cent. The weight of the sand is taken as the difference between the weight of the paper or container and the combined weight of the container and the sand. Since each weighing is made to the nearest 0.1 g., the uncertainty in the weight is taken as 40.0 g. $\pm$ 0.2 g. or a percentage precision of 0.5 per cent. Thus it can be seen that the precision in weighing the 40.0 g. of sand on the trip balance is greater than the precision in measuring the 20 ml. by difference in a 100-ml. graduate. The uncertainty in the density is therefore due almost entirely to the uncertainty in reading the volume. It is not necessary, therefore, to weigh the sand more precisely than to the nearest 0.1 g. This confirms the generalization that the result of a determination is no more reliable than the least precise measurement. The above analysis of the method suggests that careful reading of the volume is necessary to obtain the best result.

What error would have resulted if the sand had been wet? [2] Why is it impossible to obtain the volume of the sand by pouring it into a dry graduate? [3] Explain why the density

---

* *Solid unknowns.* The following solids in almost any form—wires, pellets, rods, strips, broken pieces, etc.—will serve as unknowns: ferrous sulfide, marble chips, iron nails, aluminum, copper, lead, zinc, broken glass, etc.

Solid metal pieces for part (C). These may be obtained by cutting pieces 5 cm. long from $\frac{3}{8}$-in. rods of iron, copper, or other metals. Iron bolts of about the same size may also be used.

Metal bridges for part (C). These may be made by cutting strips of thin galvanized iron from $1\frac{1}{2}$ to 2 in. wide and bending them to the proper shape (Fig. 40).

of salt or sugar cannot be determined by this method when water is used as the liquid.[4] Suggest a suitable liquid.[5]

Knowing the density of water, how could it be determined whether the graduations on the 100-ml. graduate are correct? [6]

(B) Density of an Unknown Solid. Record the number of a 20- to 30-g. sample of an unknown solid.[1] Determine its density by the same procedure described for sand.[2]

(C) Determination of the Density of a Solid by Loss in Weight. Obtain from the stockroom a solid piece of metal weighing from 20 to 30 g. Weigh it to the nearest 0.01 g. on the beam balance or on the analytical balance. Place a metal bridge over the left pan of the balance (Fig. 40) in such a way that it does not touch the stirrups or the pan. Bend a fine copper wire 20 cm. long over the hook at the top of the stirrups. If there is no hook, bend the wire over the stirrups where they come together. Fold up the bottom end of the wire until it is 1 to 2 cm. above the bridge. Fill a 150-ml. beaker two thirds full of water and place it on the bridge so that the folded end of the wire is immersed. Weigh the copper wire in this position.[1] Remove the wire from the stirrups and tie the bottom end of the wire around the metal. The distance of the metal from the top of the wire should be such that the metal will be completely immersed, but will not touch the bottom of the beaker when suspended from the top of the stirrups. The unused portion of the wire should be folded around the metal. Hang the metal from the stirrups into the water, and weigh the metal plus the wire.[1] Subtract the weight of the partly immersed wire from the weight of the metal plus the wire. The difference is the weight of the metal while it is immersed in water. Measure the temperature of the water and look up its density at that temperature. Calculate the volume of the metal from its loss in weight when suspended in the water.[1] (See **Discussion**). Calculate the density of the metal from this volume and from the weight of the metal.[1]

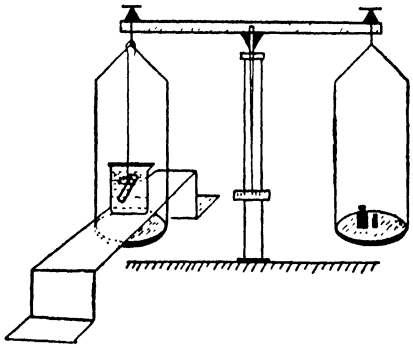


FIG. 40. Density by loss of weight

To what type of solids is the above method limited? [2] What must be known about the liquid? [3] If the solid were lighter than the liquid used, how would the density be determined? [4] Explain how the apparatus described above could be used to determine the specific gravity of a liquid.[5] (See **Discussion** in Exp. IV.)

Pycnometers of the type shown in Fig. 30 are generally used for determining the density of a liquid. These pycnometers may also be used to determine the volume and density of a solid. The data taken in the determination of the density of a particular solid were as follows:

Weight of the empty pycnometer	15.125 g.
Weight of the pycnometer + water	35.480 g.
Weight of the pycnometer + solid	30.525 g.
Weight of the pycnometer + solid + water to fill	43.975 g.
Temperature of the water	25°
Density of water at 25°	0.9971 g./ml.

Calculate the density of the solid.[6] (**Hint:** Determine how much less water the pycnometer has in it after the solid is present. The volume of this weight of water is the volume of the solid. Summarize the calculations on the report sheet.[6])

Calculate the density of a solid if it is 25.0 cm. long, 5.2 cm. wide, 2.3 cm. thick, and weighs 750.0 g.[7] Calculate the density of a metal sphere if it is 2.4 cm. in diameter and weighs 50.0 g.[8] (Volume of a sphere $= \frac{4}{3}\pi r^3$, $\pi = 3.142$).

Name (last name first) _____ Desk No. _____ Date _____

Experiment V

DETERMINATION OF THE DENSITY OF A SOLID

(A) Determination of the Density of a Solid

1.

Weight of container + sand . . . . . .

Weight of container . . . . . _____

Weight of sand . . . . . .

Final reading of the graduate . . . . . .

Initial reading of the graduate . . . . . _____

Volume of sand . . . . . .

Density of sand . . . . . .

2.

3.

4.

5.

6.

(B) Density of an Unknown Solid

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment V (Cont'd)

(B) Cont'd

2.

Weight of container + solid . . . . . .

Weight of container . . . . . _____

Weight of solid . . . . . .

Final reading on the graduate . . . . . .

Initial reading on the graduate . . . . . _____

Volume of solid . . . . . .

Density of solid . . . . . .

(C) Determination of the Density of a Solid by Loss in Weight

1.

Weight of the metal . . . . . .

Weight of the metal while immersed . . . . . _____

Loss in weight . . . . . .

Weight of metal plus wire while immersed. . . . . .

Weight of the wire . . . . . _____

Weight of the metal while immersed . . . . . .

Temperature of water . . . . . .

Density of water . . . . . .

Volume of the metal . . . . . .

Density of the metal . . . . . .

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment V (Cont'd)

(C) Cont'd

4.

5.

6.

7.

8.

Experiment VI

DETERMINATION OF THE BOILING POINT AND THE MELTING POINT. THE TRANSITION TEMPERATURE OF A HYDRATE

Discussion. The Boiling Point. As the temperature of a liquid is raised there is an increase in the number of its molecules leaving the surface in a unit time. Finally, bubbles of vapor form within the body of the liquid, and the rapid escape of these bubbles causes a violent agitation of the surface of the liquid. The liquid is now said to be boiling, and the *temperature* at which this occurs is called the boiling point. Boiling is therefore distinguished from evaporation in that, when a liquid boils, the process is attended by the formation of bubbles of vapor within the liquid itself; evaporation is confined wholly to the *surface* of the liquid.

Factors Affecting the Boiling Point. The temperature at which a liquid boils is dependent, not only upon the nature of the liquid itself, but also upon the pressure prevailing at the time the boiling point is determined. An increase in the atmospheric pressure causes a rise in the boiling point of a liquid; a decrease results in a lowering of the boiling point.

Each individual substance capable of existing in the liquid state has its own definite boiling point. Consequently, this property is used to identify or characterize a substance in the same way that density and other physical properties are employed.

Inasmuch as the boiling point of a substance is affected by changes in pressure, it has been found necessary to set up a *standard pressure* at which all boiling points can be compared. A pressure of 760 mm. has been selected as the standard. Thus, if the boiling point of water is given as 100°, the measurement is understood to have been made at a pressure of 760 mm. Nevertheless, it is quite true to say that the boiling temperature of water is 70° at a pressure of 233.8 mm.; it is also correct to say that carbon tetrachloride boils at a temperature of 70°, but in this case the pressure is 620 mm. Boiling temperatures should not therefore be used to distinguish one substance from another unless the values used have been determined at the same pressure. Unless otherwise stated, a boiling-point value is understood to be the temperature at which a substance boils under a pressure of 760 mm.

Transition Temperature. The physical state and the physical properties of a substance may be changed by an increase or a decrease in temperature. A solid may be changed to a liquid and then into a gas, each with its own set of physical properties. The temperatures at which these transformations take place under specified conditions are referred to, in general, as *transition temperatures.* These particular transition temperatures are the melting point and the boiling point respectively.

A substance in a high state of purity, that is, free from other substances, melts sharply; an impure sample of the same material may melt over a considerable range of temperature. If the transition of the solid to the liquid occurs within 1 degree or less, the solid is relatively pure; impurities not only cause melting to occur over a wider range of temperature, but also *lower* the melting point. Thus, an impure substance melts, or at least begins to melt, at a temperature lower than the melting point of the pure material.

Few completely pure substances melt at exactly the same temperature. The melting point is thus seen to be a specific physical property and, as such, is used to describe and to

identify a substance. In contrast with the boiling point, the temperature of a melting solid may be considered, for all practical purposes, to be independent of pressure. However, a melting point cannot be used to characterize all substances because some of them decompose before the melting point is reached; others change directly from the solid state into the gaseous condition without passing through an intermediate liquid stage. This change is called *sublimation.*

The melting-point determination is inferior only in accuracy to the method used to determine the freezing point of a liquid. Nevertheless, melting points are reliable when a correct procedure is used to determine them, and when a mercury thermometer of known accuracy is used to measure the temperatures. Conversely, if a melting-point determination is made on a pure substance of *known* melting point, the correctness of the thermometer scale can be determined by noting the position of the mercury thread when the substance melts. If the position of the thread does not coincide with the known melting point, a correction must be applied to readings made with this thermometer.

Certain substances may show different physical properties in the *same* physical state. Thus, solids, for example sulfur, may change from one crystalline form to another at definite transition temperatures; hydrates lose water of crystallization as the temperature is raised. Glauber's salt, sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), changes from the hydrated form to the anhydrous form (Na_2SO_4) at 32.38°. This change is accompanied by the absorption of heat.

Several methods are used to determine transition temperatures. One of the most common is the "thermometric method." The procedure followed is similar to that used in the determination of the melting point of fairly large amounts of materials. A test tube containing a quantity of the material is heated at a constant rate. The temperature of the solid increases uniformly until the transition temperature is reached. The transformation then takes place with the heat being absorbed as fast as it is supplied. Consequently the temperature remains constant until the transformation is complete; the temperature then rises rapidly.

A similar behavior is shown in the reverse process, namely, slow cooling of the substance from a higher temperature to a lower one. When the temperature falls to the transition point, the high-temperature form (anhydrous Na_2SO_4) begins to change to the low-temperature form. Heat is liberated in the process. This heat maintains the temperature at a constant value until the transformation is complete.

The thermal effects noted at the transition temperature are shown graphically on the time-temperature curves constructed in this experiment.

Apparatus and Materials: Capillary tubes as prepared in Exp. II; 40-cm. length of 8-mm. glass tubing; steel spatula; small triangular file; watch; thermometer (250°); 45 cm. No. 12 (B. & S. gauge) copper wire; 0.1 g. naphthalene; 0.3 g. unknown substance; * 20 g. of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$).

(A) Determination of the Boiling Point. 1. Carbon Tetrachloride. Fit a clean *dry* 500-ml. Florence flask with a two-holed rubber stopper. Insert a thermometer in one of the holes, and adjust its position so that the bulb is from 2 to 3 cm. above the bottom of the flask when the stopper is firmly seated in the neck of the flask. It will be necessary to change the position of the thermometer if the location of the meniscus at the boiling point is hidden by the stopper.

Fire-polish both ends of a 40-cm. length of 8-mm. glass tubing, and insert it in the rubber stopper (use glycerol) until the end of the tubing extends just below the bottom of the stopper. Measure out 15 ml. of carbon tetrachloride into the flask, and then set up the apparatus as shown in Fig. 41.

* The stockroom should be prepared to hand out an unknown selected from the list on page 52.

Heat the flask with a short (3.5 cm.) nonluminous flame until the liquid boils gently. (**CAUTION!** *Do not boil the liquid so vigorously that a part of it is ejected from the top of the condenser tube.*) Read the thermometer as soon as the liquid is boiling steadily enough to cause a rapid succession of drops of the condensate to fall back into the flask. The temperature should now remain at a constant value. Record the temperature (to the nearest 0.2°) and the barometric pressure.[1] A student unacquainted with the method of reading the mercury barometer must receive instruction in this procedure from the laboratory instructor.

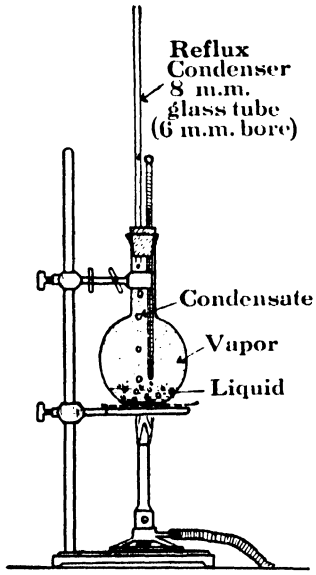


FIG. 41. Determination of the boiling point

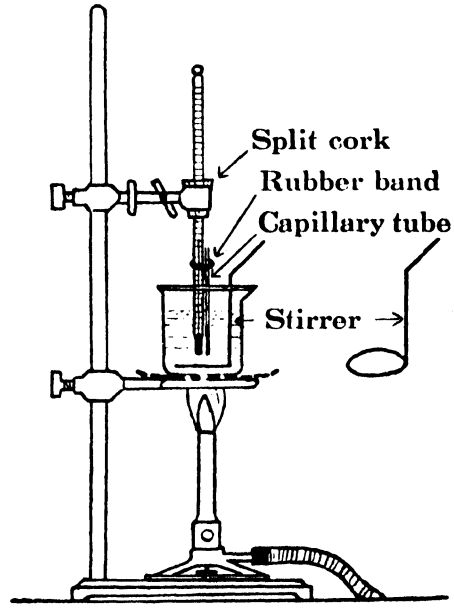


FIG. 42. Melting-point apparatus

(B) Determination of the Melting Point of a Known Substance. A melting-point determination is usually made on small samples packed into thin-walled capillary tubes such as were prepared in Exp. II. These tubes should be from 70 to 80 mm. in length.

Crush about 0.1 g. of naphthalene crystals on a watch glass with the steel spatula, and then scrape the powder into a small pile. (Because of the flexibility of the steel blade it is necessary to place the forefinger on top of the blade directly above the crystals while the latter are being crushed.) Now introduce part of the naphthalene into the tube by pushing the powder against the spatula with the open end of the tube. The latter should then be held in a vertical position, and rubbed gently with a triangular file. What is accomplished by this operation? [1] Pack the naphthalene in the capillary by allowing the latter to fall through a long vertical tube (the 40-cm. length of 8-mm. tubing used in part (A) as a condenser) onto a wooden surface. Continue the introduction of naphthalene until a compact column of solid which is not more than 2 to 3 mm. in height is obtained. Prepare a second tube in the same way.

Attach one of the filled tubes to a thermometer with a small rubber band or a narrow section cut from a piece of the rubber tubing (8-mm. tubing) used on the gas burner. The position of the capillary must be adjusted so that the column of naphthalene is exactly opposite the center of the thermometer bulb. What is the reason for this particular location? [2]

Bend 45 cm. of heavy copper wire (No. 12, B. & S. gauge) into the shape of the stirrer shown in Fig. 42. The diameter of the loop is to be slightly less than that of a 150-ml.

beaker. Place the properly bent wire and 100 ml. of water in the beaker, and set up the apparatus as shown in the figure. The thermometer with its attached melting-point tube is held by a split cork (size No. 10) whose halves are firmly pressed into contact with the thermometer by means of a burette clamp. Prepare the cork by boring a hole through it with a cork borer whose diameter is slightly less than that of the thermometer. Then use a knife to split the cork from top to bottom along its diameter.

1. Approximate Melting Point. When the melting point of a substance is not known, a considerable amount of time is saved by making a rapid, approximate determination, and then a slow, careful one.

Heat the beaker strongly with a nonluminous flame, and stir the water thoroughly and continually by quickly raising and lowering the copper stirrer. Do not bring the stirrer above the surface of the water! If this is done, the downward movement of the stirrer will splash hot water out of the beaker. Explain why it is necessary to use water or another liquid in this procedure, and tell why the thermometer and its capillary should not be held above an open flame.[3] Observe and record the approximate temperature at which the naphthalene melts.[4]

2. More Exact Melting Point. Remove the capillary from the water bath and allow the temperature of the water to fall to at least 15° below the approximate melting point. Now attach the second capillary containing naphthalene to the thermometer and place it in the bath. In this determination it is essential that the heating during the last 15° rise be slow and constant; a rise of 2° per minute is recommended. As before, the bath must be stirred continually throughout the procedure. Watch the sample and the temperature carefully, and note the temperature at which the naphthalene begins to melt and that at which it becomes entirely liquid. Record these values as the melting-point range.[5] Compare this with the accepted value of 80.2°. A difference of more than 2° may result from any one or a combination of such factors as too rapid heating, inadequate stirring, impurities present in the sample, or errors inherent in the thermometer.

What is the upper limit of the range of temperature obtainable with this melting-point apparatus? Why?[6] Concentrated sulfuric acid (b.p. 330°) with a practical upper limit of 200° is the most frequently used bath in this type of melting-point apparatus; glycerol and cottonseed oil are also used for temperatures above 100°. Special apparatus is required for temperatures above 250°.

(C) Tentative Identification of an Unknown Substance. Obtain a 0.3-g. sample of a substance whose identity is to be determined. Note the odor of the substance. Prepare two melting-point tubes containing this compound. Make an approximate and then a more exact determination of the melting point. Record the latter value.[1] Identify the substance tentatively as one of the following compounds:[2]

Substance and Formula	Melting Point
Acetamide, CH_3CONH_2	82°
Borax, $Na_2B_4O_7 \cdot 10H_2O$	75°
p-Dichlorobenzene, $C_6H_4Cl_2$	53°
Diphenyl, $C_6H_5 \cdot C_6H_5$	69–70°
Palmitic acid, $C_{15}H_{31}COOH$	64°
Potassium aluminum sulfate, $KAl(SO_4)_2 \cdot 12H_2O$	92°
Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$	45–50°
Stearic acid, $C_{17}H_{35}COOH$	69–70°
Thymol, $(CH_3)(C_3H_7)C_6H_3OH$	51.5°
Triphenylmethane, $HC(C_6H_5)_3$	92.5°

It is seen that the melting points of certain of the substances in the above list lie fairly close together; those of potassium aluminum sulfate and triphenylmethane are within 0.5° of one another, while those of diphenyl and stearic acid are exactly the same. Errors

in identification due to the close proximity or to the coincidence of melting points are avoided by carrying out an operation known as the *mixed melting-point* determination. If this determination is not to be made, the following differences in properties are made use of in those cases of doubtful identity:

Thymol (51.5°) and *p-dichlorobenzene* (53°) have pronounced odors that are quite unlike. Compare the odor of the unknown with those of 0.1 g. samples of thymol and p-dichlorobenzene obtained from the stockroom.

Potassium aluminum sulfate (92°) is soluble (dissolves) in water; *triphenylmethane* (92.5°) is insoluble in water. Try the solubility of the unknown in water.

Stearic acid feels waxy when rubbed between the fingers; crystals of diphenyl are gritty.

(D) Positive Identification by Mixed Melting Point. The following experimental facts form the basis for this determination. When a substance A is mixed with a little of substance B, the mixture melts below the melting point of A; when B is mixed with a little of A, the mixture melts at a temperature below the melting point of B. If A and B are different substances melting at the *same* temperature, then *all mixtures* of A and B melt below the common melting point. If A and B are identical, the melting point of the *mixture* is the same as that of either A or B.

Suppose an unknown substance A is found to melt at 100°. A table of melting points shows that compounds B, C, and D also melt at or very near this same temperature. A comparison of the properties of A with those of B, C, and D makes it seem possible that A might be identical with any one of these three. However, when the melting points of the mixtures AB, AC, and AD are determined, it is found that A depresses the melting points of B and C, but not that of D. With which of the known substances is A identical? [1]

Secure from the stockroom 0.1-g. samples of the two compounds whose melting points are identical with or closest to the melting point of the unknown. Mix a small amount of the unknown with an equal or slightly smaller amount of each of the known substances obtained from the stockroom. Determine the melting point of each mixture. Record each value together with the names of the components of the respective mixtures.[2, 3] Interpret the results in accordance with the discussion in the two preceding paragraphs, and then state the conclusion reached with regard to the identity of the unknown substance.[4]

(E) Determination of the Transition Temperature of Sodium Sulfate Decahydrate (Glauber's Salt). The constant application of heat to a solid causes its temperature to rise until the melting point is reached. Heat that is supplied at this point goes into the conversion of the solid to a liquid, and the temperature remains constant until complete liquefaction has taken place. A further supply of heat serves to raise the temperature of the liquid. Conversely, when a liquid is allowed to cool, its temperature falls until the freezing point is reached. The temperature remains constant during crystallization because this process takes place with the evolution of heat. After this stage, the temperature again falls.

Add about 20 g. of sodium sulfate decahydrate to a large test tube. Place the test tube with its contents in a 400-ml. beaker approximately two thirds full of water that has been warmed to a temperature of about 26 to 28°. Set the beaker on a wire gauze which has been placed on a ring clamped to the ring stand (Fig. 43). Close the air holes on the burner and turn down the gas until the flame is not more than from 1 to 2 cm. high. Now heat the water with this small flame.

Place a thermometer in the test tube and stir the crystals continually. Record the time and temperature at the end of each minute until the temperature reaches 38 to 40°.[1] This requires about 20 min. The rise in temperature of the water in the beaker should not exceed a rate of 0.3 to 0.5° per min. The slower the rate of heating, and the more thorough the stirring, the more accurately can the transition temperature be measured. When the transition temperature is approached, the solid becomes mushy or even fluid, and the

temperature remains nearly constant for several minutes. As soon as the transformation is complete, the temperature rises rather rapidly. Continue the readings until the temperature rises to 40°. These data are to be plotted and a curve is to be drawn on graph paper in the manner described in the section dealing with the use of graph paper.

Remove the tube from the beaker and allow it to cool in the air. During the period of cooling, the contents of the tube must be stirred continually with the thermometer. Record the time and the temperature at 1-min. intervals.[2] When the temperature has fallen to 33°, scrape into the liquid some of the crystals that cling to the upper part of the test tube. These crystals aid in starting the formation of crystals in the solution. Continue the readings for 3 or 4 min. until the temperature remains constant. Then immerse

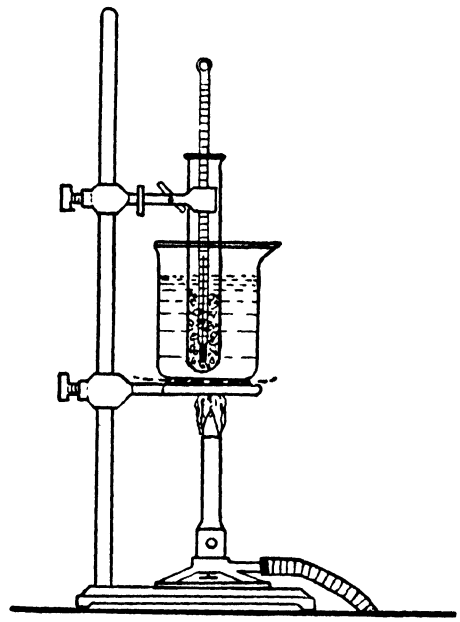


FIG. 43. Determination of the transition temperature

the bottom of the test tube in water at a temperature of 25°. This speeds up the transformation and shortens the time required to complete the experiment. Continue to stir and to take readings until the liquid becomes mostly solid at a temperature of 25 to 26°.

Use of Graph Paper. The two sets of data taken above may be represented graphically on rectangular coordinate graph paper as illustrated in Fig. 44. Plot the time readings as abscissae (horizontal axis) along the longer side of the sheet of graph paper, and the temperature as ordinates (vertical axis). Label the two axes as illustrated in Fig. 44. Let 1 cm. on the temperature axis be equivalent to 1° and 1 cm. on the time axis be equivalent to 1 min., or to 2 min. if there is not a sufficient number of divisions on the graph paper. Begin at the origin (point of intersection of the two axes) with 27 or 28° on the temperature axis and label each centimeter line consecutively until the line for 40° is reached. Label each line on the time axis beginning at the origin with the time at which the temperature was between 27 and 28°.

To locate or *plot* a point corresponding to a reading of the time and the temperature, follow along the time axis to the line representing the time. Follow this line upward (parallel to the temperature axis) to the line representing the temperature. Place a dot on the paper to mark the point at which the two lines intersect. For example, if the temperature is 30.5° at 2:14 o'clock, the point representing this time-temperature reading is obtained as illustrated in Fig. 44. Plot the time-temperature data in this manner. After all of the

points have been located, draw a smooth curve through the points. Note that part of the curve is parallel to the time axis. This shows graphically or visually that the temperature remains constant during the passage of a certain period of time.

Draw a dotted line parallel to the time axis from the center of the *horizontal* part of the curve across to the temperature axis. Read the temperature corresponding to the

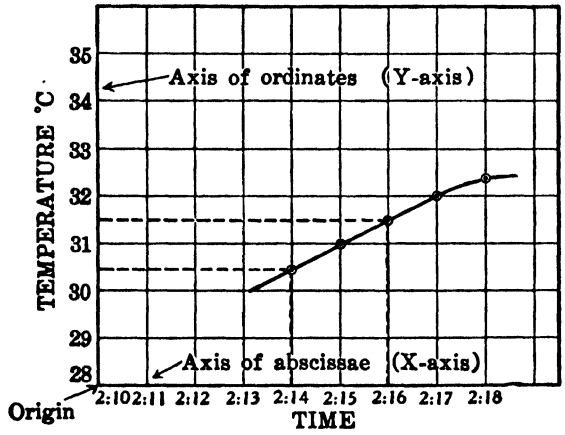


FIG. 44. Graphic representation of data

point at which this line cuts the temperature axis. Mark this temperature as the transition temperature and record its value on the report sheet.[3]

Plot the curve representing the data taken during the cooling of the salt. Record the transition temperature as determined from this curve.[4] If the transition temperature determined in this experiment is different from the accepted value (see **Discussion**), suggest some reasons which might account for the discrepancy.[5]

What is the requirement of this method with regard to the speed of transformation? [6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment VI

DETERMINATION OF THE BOILING POINT AND THE MELTING POINT. THE TRANSITION TEMPERATURE OF A HYDRATE

(A) Determination of the Boiling Point

1.

(B) Determination of the Melting Point of a Known Substance

1.

2.

3.

4. Approximate melting point =

5. Melting point range (more exact m.p.) =

6.

(C) Tentative Identification of an Unknown Substance

1.

2. The substance is

Name (last name first) _____ Desk No. _____ Date _____

Experiment VI (Cont'd)

(D) Positive Identification by Mixed Melting Point

1.

2.

3.

4.

(E) Determination of the Transition Temperature of Sodium Sulfate Decahydrate

1, 2.

Time	Temperature	Time	Temperature

Name (last name first) _____ Desk No. _____ Date _____

Experiment VI (Cont'd)

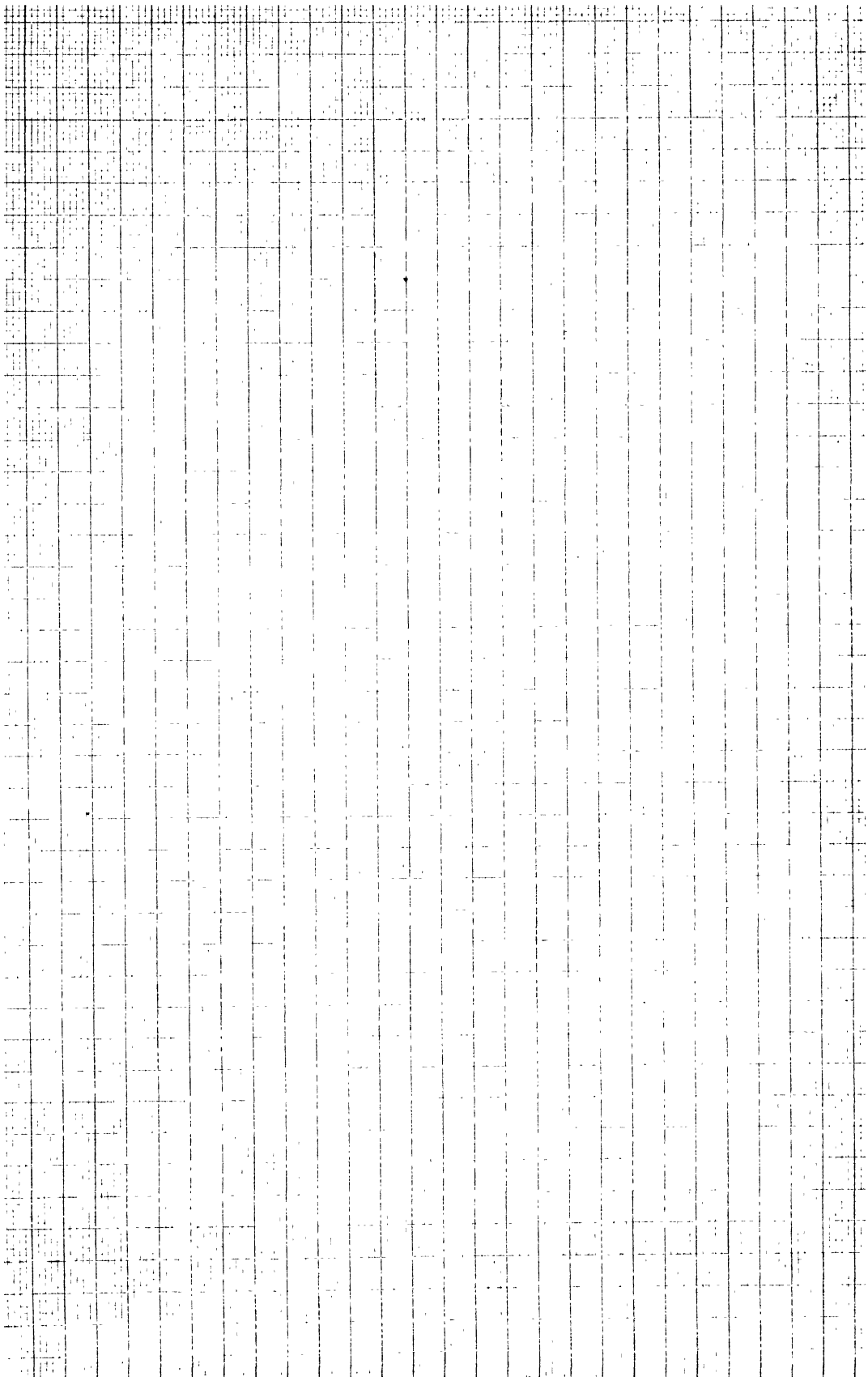
(E) Cont'd

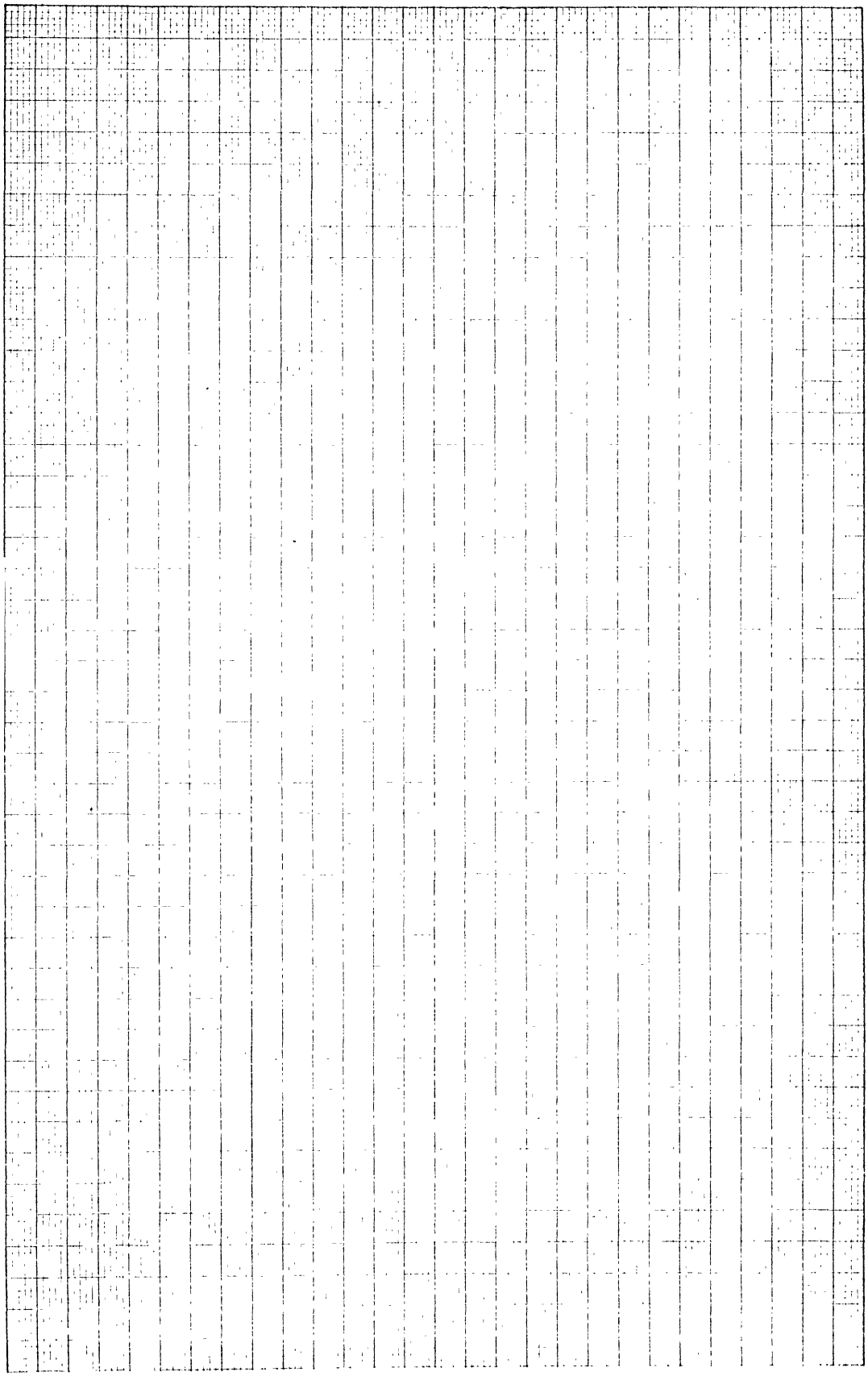
3.

4.

5.

6.





Experiment VII

CHARACTERIZATION OF A SUBSTANCE BY ITS PHYSICAL PROPERTIES

Discussion. The properties of a substance are the peculiar, inherent characteristics by which it is recognized and distinguished from other substances. Many varieties of matter possess such specific and marked properties that there is little chance for cases of mistaken identity. However, a large number of substances are similar in many respects. In these cases a complete system of characterization is necessary in order to distinguish one substance from all the others; as many physical properties as possible should be measured and described.

Apparatus: Watch; 250° thermometer.

(A) Qualitative Determination of Properties. Observe and record the odor,[1] color,[2] and malleability [3] (brittleness) of a small piece of roll sulfur.

1. Solubility. An important property of each substance is concerned with its behavior toward water and other liquids. If the material dissolves in the liquid, it is said to be *soluble;* the result is a *solution.* The substance that goes into solution is the *solute,* whereas the liquid is the *solvent.* An element or a compound is said to be *insoluble* in a given solvent if solution does not take place to any appreciable extent. Thus, sugar is soluble in water, but it is insoluble in gasoline. Tests of the solubility of sulfur in water and in carbon disulfide are made in this experiment.

Shake 0.5 g. of powdered sulfur and 10 ml. of water in a test tube. Is it possible to determine visually whether or not any sulfur has dissolved? [4] A physical method is used in this experiment to determine whether or not sulfur dissolves in water. The method takes advantage of the fact that water is readily volatile at temperatures at which the volatility of sulfur is extremely low. Thus, if a solution has been formed, the evaporation of the volatile solvent (water) should leave behind a residue of the nonvolatile solute (sulfur). If there is no residue when the solute is known to be nonvolatile, then the solute may be judged to be insoluble.

2. Filtration. Undissolved sulfur must be removed before the evaporation of the liquid portion of the mixture is carried out. Why? [5] Separation of the solid from the liquid is accomplished by filtration. This is a mechanical process in which a mixture of a liquid and a solid is allowed to flow through a sheet of *filter paper.* The pores of this specially prepared paper are so small as to prevent the passage of undissolved solids, but are large enough to permit liquids and dissolved material to pass through. A filter is prepared in the following manner.

A dry sheet of filter paper is folded in half. It is then folded again through the center, but this time the two halves of the first crease must not coincide (Fig. 45). Paper folded in this way will not exactly fit the walls of a 60° funnel at its apex, but it will fit snugly at the top. Such a paper filters more rapidly than one that adheres to the funnel over its entire area. No air is drawn between the funnel and the paper, and thus the liquid runs down freely in the narrow space between the paper and the glass. Do not flatten the creases too much; this weakens the filter at its tip.

FIG. 45. Folding a filter paper

Now tear a small piece from one of the corners of the paper (Fig. 45). Open the paper so that there are three thicknesses on one side and one on the other, and then place the cone in a funnel. The size of the paper should be such that the top of the filter falls from ½ to 1 cm. below the rim of the funnel. Moisten the paper with distilled water from the wash bottle, and press the upper third gently against the glass. Place the funnel with its properly fitted paper in a funnel arm which has been clamped to a ring stand (Fig. 46). A clean 50-ml. beaker is placed in position beneath the funnel. The stem of the funnel must touch the side of the beaker in order to prevent splashing during filtration, and it should be well above the bottom of the receiving vessel; *the funnel stem is never permitted to extend into the liquid collected in the receiver.* The filter is now ready for use.

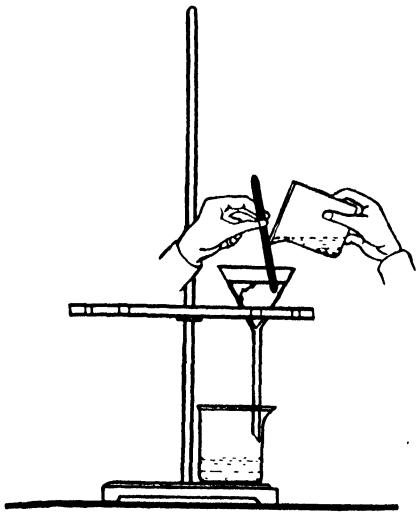


FIG. 46. Filtration

Hold a stirring rod so that its lower end is close to, but does not touch, the filter paper on the side having the three thicknesses of paper. The lip of the test tube containing the mixture of sulfur and water is placed against the rod, and the tube is inclined until the liquid flows down the rod without splashing. Pour the liquid so that the sulfur that has settled on the bottom of the tube is not disturbed. This procedure of pouring a *supernatant* liquid from an insoluble solid (a *precipitate*) is called *decantation.* It is used whenever possible because it reduces the time required for filtration. Why would the filtration time be longer if the precipitate was poured onto the filter at the beginning of the filtration? [6] Continue to pour liquid into the filter as long as a stream passes freely through the paper. However, the liquid should not occupy more than two thirds of the volume of the filter. If the liquid that has been filtered (the *filtrate*) is cloudy, it should be returned to the test tube and then poured through the same filter. The particles partly fill the pores in the paper during this process and the smaller openings do not permit the passage of those particles that were small enough to pass through the paper during the first filtration.

After a clear filtrate has been obtained, add 5 ml. of water to the test tube. Rinse the tube with this water and then pour it through the filter so that the precipitate is washed down into the bottom of the paper. (The wash water is allowed to flow into the original filtrate.) This step has for its purpose the removal of any solution that remains in the test tube, in the pores of the filter paper, and in the stem of the funnel. In most cases the washing is repeated two or three times with small volumes of wash liquid.

3. Evaporation over a Water Bath. Measure 200 ml. of water into the 400-ml. beaker. Set the beaker on a wire gauze placed on the tripod. Cover the beaker with a 10-cm. watch glass, and pour the filtrate onto it. Now boil the water vigorously in the beaker until the filtrate has been evaporated to dryness.

Remove the watch glass and examine it for a residue having the appearance of sulfur. Record the conclusion reached regarding the solubility of sulfur in water.[7]

4. Solubility of Sulfur in Carbon Disulfide. Pour 5 ml. of carbon disulfide into a test tube containing 0.2 g. of powdered sulfur. (**CAUTION!** Carbon disulfide is highly inflammable. It evaporates rapidly at ordinary temperatures to form a very explosive mixture with air. Do not bring the liquid near an open flame!)

Shake the test tube for a few seconds. What can be said regarding the solubility of sulfur in carbon disulfide? [8] Verify the answer just given by pouring the liquid through a *dry* filter. Do not wet the paper after it has been fitted into the funnel! Receive the fil-

trate on a dry 10-cm. watch glass, and permit evaporation to take place. What is the residue?[9] How does it differ in appearance from the original sulfur?[10] Is it necessary to modify the statement made in ([8])? If so, how?[11]

(B) Quantitative Determination of Properties. 1. Density. Determine the density of sulfur by finding the volume occupied by a known weight of the substance. Follow the procedure used in Exp. V. Use as many lumps of roll sulfur as are needed to make a total weight of approximately 15 g. *The lumps must be free from powder.* Why?[1] Record the density as it is obtained in this experiment, and place *in parentheses* alongside this value the density of rhombic sulfur as given in the Text.[2]

2. Melting Point. Place 12 g. of powdered sulfur in a 15-cm. (6-in.) test tube. Hold the latter with the test-tube holder and melt the sulfur slowly by moving the tube in and out of a burner flame. The flame should be from 8 to 10 cm. in height and should be burning quietly (not with a rustling sound). Place a 250° thermometer in the tube as soon as the sulfur begins to melt. Stir slowly with the thermometer and continue to heat until the contents of the tube reach a temperature of 125°. Discontinue the heating but continue to stir until all the sulfur has melted. Another student may be called in at this point to assist in taking time-temperature readings. The second student now calls for a temperature reading and notes the time at which the temperature is given. Both time and temperature are then recorded at 15-sec. intervals until the temperature has fallen to 110°.[3] Slow stirring must be continued throughout the entire time interval.

Plot the time against the temperature readings and construct a time-temperature curve (Exp. VI) on the sheet of graph paper furnished as one of the report sheets with this experiment (Exp. VII). Record the melting point.[4]

Summarize the physical properties of sulfur as determined in this entire experiment.[5]

Name (last name first) _____ Desk No. _____ Date _____

Experiment VII

CHARACTERIZATION OF A SUBSTANCE BY ITS PHYSICAL PROPERTIES

(A) Qualitative Determination of Properties

1.

2.

3.

4.

5.

6.

7.

8.

9.

10.

Name (last name first) _____ Desk No. _____ Date _____

Experiment VII (Cont'd)

(A) Cont'd

11.

(B) Quantitative Determination of Properties

1.

2.

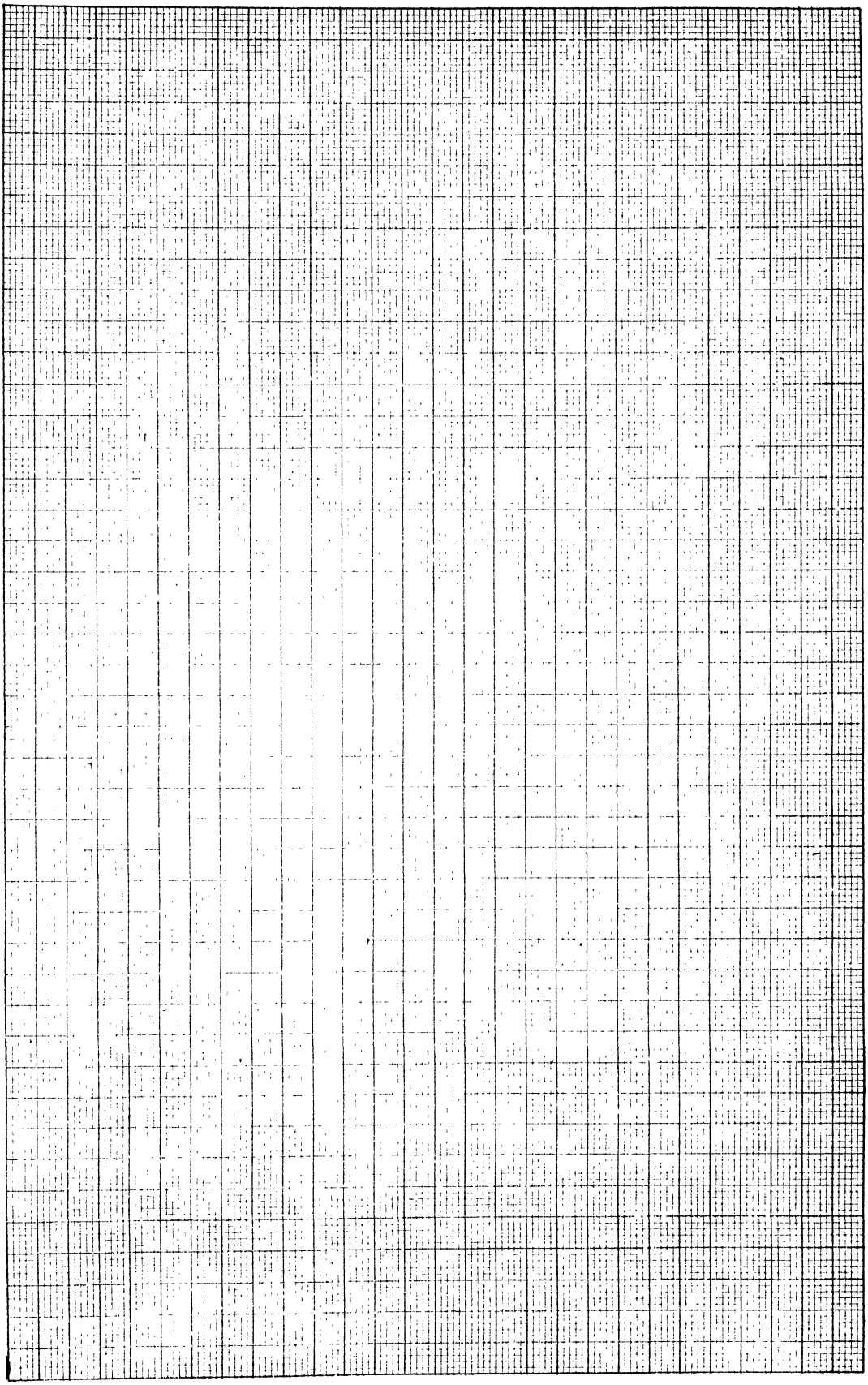
3.

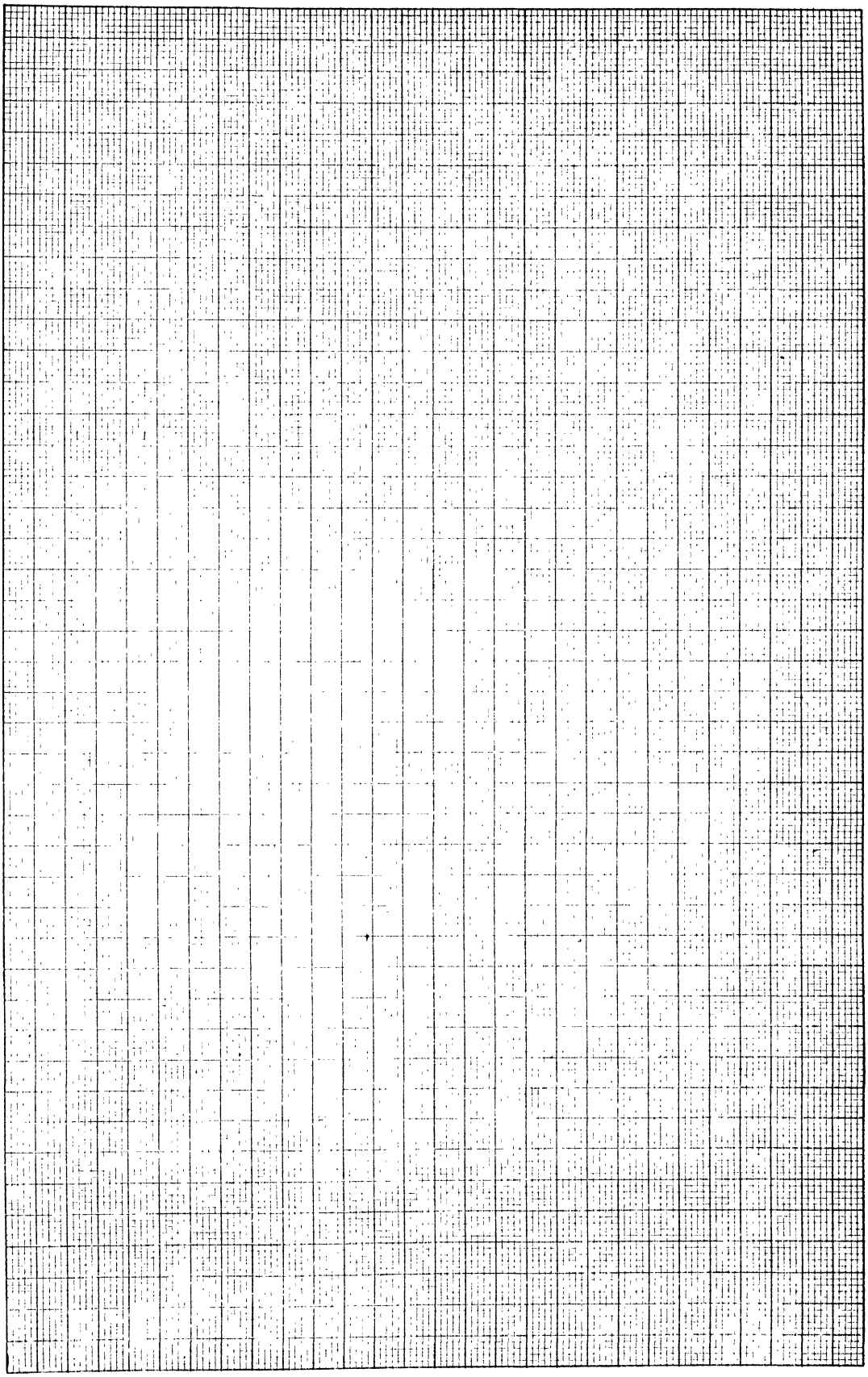
Name (last name first) _____ Desk No. _____ Date _____

Experiment VII (Cont'd)

(B) Cont'd

5.





Experiment VIII

SEPARATION OF THE COMPONENTS OF A MIXTURE

Discussion. A material composed of two or more different substances is called a *mixture;* each of the different substances is a *component* (ingredient) of the mixture. Inasmuch as matter exists in solid, liquid, and gaseous forms, a variety of types of mixtures is possible. Thus, a two-component mixture may be of the solid-solid, liquid-solid, or any one of the other possible types.

An important distinguishing characteristic of mixtures is their lack of homogeneity. Each of the components taken separately is homogeneous, but their mixture is heterogeneous except in the cases of solutions and mixtures of gases. In certain mixtures the separate particles of each component may be seen under a microscope, or even with the naked eye. The latter statement is true of granite, which is a mixture. A *description* of granite, as well as of any other mixture, should contain the name of each component in addition to the general appearance, the density, the hardness, and other physical properties.

In order to be able to name the components of a mixture, each substance must be identified. The first step in the identification involves the separation of the various components from one another. It is generally a much simpler matter to identify a *pure* substance than it is to identify that same substance in the presence of other materials. As a matter of fact, it is extremely difficult to determine the identity of certain substances in the presence of certain others.

Differences in the physical properties of the components of a mixture are taken advantage of wherever possible in order to bring about a separation. For example, one of the components of a solid-solid mixture dissolves in a liquid solvent, while the other is insoluble. It is a relatively simple problem to separate these substances by the processes of solution and filtration, followed by the evaporation of the filtrate. What is the purpose of the final operation? [1]

Separations based upon differences in chemical properties are many in number, and vary widely in character. In fact, one of the major branches of chemistry has for its purpose the separation, identification, and quantitative determination of the components of mixtures. This branch of the science is called *analytical chemistry.* Its processes are based upon differences in the chemical and physical properties of elements and compounds.

Materials: Barium sulfate, $BaSO_4$ (1 g.); sodium chloride, NaCl (0.3 g.); powdered wood charcoal, C (0.5 g.); iodine, I_2 (0.1 g.).

Experimental Procedure. Obtain the stated quantities of the substances listed in the preceding section on materials. At this time put aside on a watch glass a small amount of the barium sulfate for use in the last part of this experiment. Iodine is secured from the stockroom; the element should be carried to the desk on a watch glass, and *not* on a piece of paper. Note the odor of iodine, and be prepared to recognize the element later on by its odor. Grind the four substances together in a mortar until the mixture assumes a uniformly gray appearance. Use a steel spatula to scrape the powder off the surface of the mortar, and then transfer the material to a 150-ml. beaker

A 100-ml. beaker containing 70 ml. of cold water is now placed inside the 150-ml. beaker. The bottom of the smaller beaker will be about 1 cm. above that of the larger beaker. Place this "nest" of beakers on a wire gauze supported on a tripod. Heat the

apparatus gently for 3 min. Observe carefully all that occurs during this time. Remove the flame, and then describe what has taken place.[2] Resume the heating for another minute. Now allow the apparatus to stand until the purple vapor is no longer visible.

Remove the inner beaker and pour out the water. Describe the appearance of the deposit on the under side of the beaker.[3] Identify the crystals by their odor.[4] Scrape some of the crystals into a clean porcelain crucible, and heat it with a low flame (Fig. 47). Does the substance melt before it vaporizes? Name and define this type of change.[5] None of the other components undergoes this change at the temperature used in this experiment.

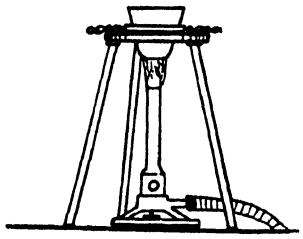


FIG. 47. Heating a crucible

Now add 15 ml. of water to the contents of the 150-ml. beaker. Heat the resulting mixture, and stir it with a thermometer. Discontinue the heating when the temperature reaches 70°, and then allow the mixture to stand until most of the undissolved material has settled to the bottom of the beaker. Decant (pour) the liquid through a filter. Receive the filtrate in a 100-ml. beaker. If the filtrate is not clear, pour it back through the same filter.

Add 5 ml. of water to the residue in the beaker and then heat the mixture to 70°. Again allow undissolved material to settle before decanting the liquid, and then filter it as soon as the original 15 ml. of solution has drained from the funnel. When the 5-ml. portion is poured into the filter, direct its flow down the sides of the filter paper so as to wash the material there as well as that which is at the bottom of the cone. Allow this filtrate, as well as those following, to run into the original filtrate. Repeat the entire operation twice with 5-ml. portions of water. However, instead of decanting the last portion of water, swirl it with the insoluble material so that when the liquid is poured into the filter it will carry with it most of the undissolved substances.

Particles of solid remaining in the beaker are washed onto the filter in the following manner. Place a stirring rod across the top of the beaker so that the rod rests against the lip of the beaker and projects from about 2 to 3 cm. beyond it. Now hold the stirring rod in position by placing the index finger of the left hand across the rod and at right angles to it; grasp the beaker with the other fingers and the thumb. Incline the beaker over the funnel so that liquid can flow out of the beaker down the rod into the paper (Fig. 48). Now grasp the wash bottle in the right hand and force a stream of water against the inside of the beaker so that particles of solid are washed into the filter (Fig. 48). Do not use more than 10 ml. of water for this purpose. The total volume of the filtrate should now measure about 40 ml.

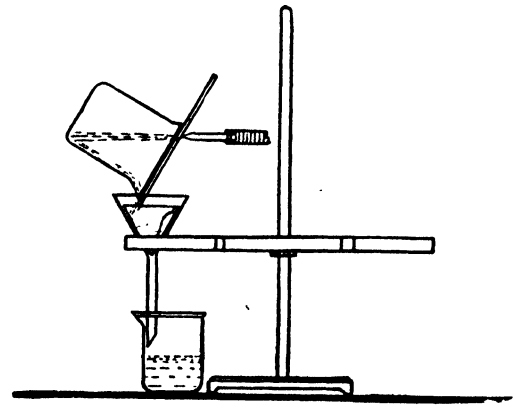


FIG. 48. Removing a residue from a beaker

The preceding series of operations with water have served to dissolve a water-soluble substance from the material which remained after the sublimation of the iodine. Why was the residue from the treatment with 15 ml. of water washed repeatedly with separate portions of water?[6] The water-soluble component is said to have been *dissolved out of* or *extracted from* the mixture; the solution is the *extract*.

Boil the extract until a solid begins to settle from the solution. Keep the beaker covered with a watch glass during this operation. Why?[7] Compare the appearance of the crystals formed in the solution with the appearance of charcoal. What physical property

is used as the basis of differentiation between these two substances?[8] This same basis cannot be used to distinguish barium sulfate from sodium chloride; solubility in water can, however, be used. The solubility of sodium chloride (common salt) in water is a matter of common knowledge. Test the solubility of barium sulfate in the same solvent by shaking a small quantity (set aside at the beginning of the experiment) with 10 ml. of water in a test tube. Result?[9] What is the conclusion regarding the identity of the water-soluble component?[10]

The separation of barium sulfate and carbon is accomplished by means of a chemical change. Carefully loosen the filter paper containing the two substances, and lift it from the funnel without tearing the paper. Fold the edges of the paper down and over so as to completely enclose the residue on the paper. Gently press this package down into a crucible which is then supported on a clay triangle placed on the tripod. Heat the crucible over a small flame until all the moisture has been driven out, and then use the hottest flame obtainable. Break up the mass of solid from time to time with a glass rod. Continue the heating until the contents of the crucible are pure white. Which of the components has disappeared?[11]

One of the chemical properties of carbon is to burn in the air. Barium sulfate does not do this. Carbon reacts readily with the oxygen of the air at high temperatures to form carbon dioxide (CO_2). Write the equation that expresses this reaction.[12] An apparatus could be arranged in which the carbon dioxide formed could be identified by means of its chemical properties. The experiment just carried out serves merely to separate the carbon from the barium sulfate.

In a series of brief statements summarize the procedure used to separate the four components of the mixture prepared at the beginning of this experiment.[13]

Name (last name first) _____ Desk No. _____ Date _____

Experiment VIII

SEPARATION OF THE COMPONENTS OF A MIXTURE

1.

2.

3.

4.

5.

6.

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment VIII (Cont'd)

8.

9.

10.

11.

12.

13.

Experiment IX

CHEMICAL CHANGE. COMBINATION AND DECOMPOSITION

Discussion. Substances are identified by the specific properties they possess. Properties are of two kinds. A *physical* property is one that may be described or measured without causing the substance to change its chemical identity or without reference to any substance other than the one under consideration. For example, the density of a substance may be determined independently of the density of any other variety of matter. Furthermore, a substance may undergo a physical *change* such as the alteration of its color or its physical state without involving the presence of other substances and without change of its chemical identity.

The determination of a *chemical* property, on the other hand, usually involves one or more substances in addition to the one under consideration. Thus a chemical property of oxygen is its ability to react with various metals; the interactions always involve chemical *changes*. Hence a chemical property is described in terms of chemical reactions.

Effect of Physical and Chemical Change upon Properties. A physical change does not necessarily affect all the properties of a substance. In addition, this type of change is of a temporary nature in the sense that, when the original conditions (*e.g.*, temperature and pressure) are restored, the properties return to their original values. However, a chemical change alters all of the properties of a substance to a greater or lesser extent; the original properties do not reappear upon the restoration of the original conditions. Thus, physical changes always accompany chemical changes, and such physical changes are frequently accepted as evidence of a chemical change.

The Basis for the Recognition and Classification of Chemical Change. It is important to be able to recognize and to classify chemical changes. They are recognized by certain characteristics that accompany them, and they are classified according to the nature of the process involved in the change. However, it is inadvisable to make a rigid distinction between physical change and chemical change. Many processes, for example, the melting of solids and the vaporization of liquids, are usually classified as physical changes, but in a number of cases these changes show some of the characteristics of chemical change.

Materials: 5 g. of iron filings (Fe); 2.9 g. powdered sulfur (S); 3-cm. length of magnesium ribbon (Mg); a small globule of mercury (Hg); 0.2 g. of iodine (I_2); 0.1 g. sugar ($C_{12}H_{22}O_{11}$); a small crystal of cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$); 0.1 g. of mercuric oxide (HgO); 0.5 ml. of 95 per cent alcohol (C_2H_5OH); 4 ml. of carbon disulfide (CS_2).

(A) Combination. 1. Mercury and Iodine. Obtain from the stockroom a small globule of mercury and 0.2 g. of iodine (the mercury should be obtained in a small beaker; the iodine is to be carried on a watch glass). Observe and describe the appearance, physical state, and odor of each of these substances.[1] Are they elements or compounds?[2] Place the mercury and the iodine in a mortar. Note any change in the appearance of the mercury after it has come into contact with a crystal of iodine.[3] Now add 0.5 ml. of 95 per cent alcohol, and vigorously grind the contents of the mortar until all the alcohol has evaporated. Examine the product for droplets of mercury and for unchanged particles of iodine. What conclusion regarding the nature of the change can be drawn from the complete disappearance of either one or both of the original substances?[4]

If the experiment is properly carried out, no visual evidence can be obtained for the existence of mercury or of iodine in the final product. In this instance mercury and iodine have united to form a single, entirely different substance called mercuric iodide. The change is represented as follows:

$$\text{Mercury} + \text{iodine} \rightarrow \text{mercuric iodide}$$

This type of chemical reaction is called combination. It is characterized by the formation of a single, new substance from two or more different substances. A chemical reaction has occurred in which mercury and iodine (called the *reacting substances* or *reactants*) have combined to form mercuric iodide (the *reaction product* or simply *the product*).

2. Magnesium and Oxygen. Hold a strip of magnesium ribbon in the burner flame by means of crucible tongs. Describe the change that occurs.[5] Contrast the physical properties (color, hardness) of the product with those of the magnesium.[6] Aside from the change in physical properties, what are the most obvious characteristics of this combination that were not apparent in the reaction between mercury and iodine? [7]

A chemical change is always accompanied by an energy change. Energy in the form of heat is either absorbed or evolved (given off) during a chemical change. Which is the case in this reaction? [8] If a great amount of heat is evolved in a short time, then a chemical change is accompanied by the production of light.

Magnesium and oxygen (present in air) are the reactants in this combination. The reaction is represented by the following equation:

$$2Mg + O_2 \rightarrow 2MgO$$

Examine the reaction product to determine whether there is any evidence of fusion having taken place during the reaction. As a result of the examination, what can be said about the relative melting point of magnesium oxide? [9] One of the uses of magnesium oxide is based in part upon the value of its melting point. Refer to the Text, and then record this use.[10]

3. Iron and Sulfur. Grind together in a mortar 5 g. of iron filings and 2.9 g. of powdered sulfur. Is there any evidence of chemical change? [11] Verify the conclusion by the following procedure.

Recall the solubility of sulfur in carbon disulfide (Exp. VII). Obtain 4 ml. of carbon disulfide, and test the solubility of iron in this liquid by shaking two or three particles of the metal with 2 ml. of carbon disulfide (use a test tube). *Decant* (pour off) the carbon disulfide from the iron and allow the liquid to evaporate on a watch glass. Make a statement regarding the solubility of iron in carbon disulfide.[12]

Now test the action of 5 ml. of dilute ($4N$) hydrochloric acid on a few iron filings. Note any visible evidence of a chemical change. Can an odor be detected at the mouth of the test tube? Make a statement regarding the action of hydrochloric acid on iron.[13] Repeat the procedure but use sulfur instead of iron. Result? [14]

On the basis of the data obtained in the two preceding paragraphs, devise a procedure for verifying the statement made in ([11]). Write out the plan of the procedure [15] and submit it to the laboratory instructor for approval. Put the scheme into operation as soon as it is approved, and record the conclusion reached after the experimental work has been carried out.[16] (**Note:** *Use only a small part of the material prepared in the mortar.*)

Transfer the remainder of the material in the mortar to a Pyrex test tube. Heat the tube in the hottest part of the burner flame until the contents begin to glow. Quickly remove the tube from the flame at this time, and observe the behavior of the reaction mixture. Note that the mixture continues to glow even after the tube is removed from the flame. What conclusion is to be reached regarding the kind of change that leads to the

evolution of such a large amount of heat? [17] Allow the tube and its contents to cool to room temperature.

Place the lower end of the tube in a mortar, and use the pestle to break the glass. Pick out a number of pieces of the product that are free from glass, and use them to verify the conclusion reached in ([17]). Try the action of carbon disulfide. Does the solid contain free sulfur? [18] Test a *very small* piece of the black solid with dilute hydrochloric acid. Note the odor of the gas that is evolved. What does this indicate with regard to the presence or absence of free iron in the solid reactant? [19]

Summarize the evidence that will prove that a chemical change takes place when a mixture of iron and sulfur is heated.[20]

(B) Decomposition. 1. Cupric Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$). Obtain a small crystal of this salt, and grind it thoroughly in a mortar. Examine the powder to determine whether or not it is wet or even moist. Result? [1] Loosen the powder with the steel spatula and then transfer it to a test tube. Heat the tube gently. Note any change in the appearance of the salt.[2] What evidence is there that a volatile product is driven off from the salt? [3] What is the product? [4]

The fact that cupric sulfate always crystallizes with a definite number of molecules of water (5) marks the substance $CuSO_4 \cdot 5H_2O$ as a true chemical compound; it is not simply a mixture of cupric sulfate and water. This type of compound is called a *hydrate.* Thus, a chemical change occurs when the water is driven off. This type of chemical change in which one substance gives rise to the formation of two or more different substances is known as decomposition. Heat is absorbed when this decomposition takes place.

Add a drop of water to the white powder in the test tube. Interpret the result.[5] What type of chemical change is represented? [6]

The changes observed in this experiment with $CuSO_4 \cdot 5H_2O$ are summarized in the expression:

$$CuSO_4 \cdot 5H_2O \underset{\text{combination}}{\overset{\text{decomposition}}{\rightleftharpoons}} CuSO_4 + 5H_2O$$

2. Mercuric Oxide. Test the action of heat on 0.1 g. of mercuric oxide contained in a Pyrex test tube. Result? [7] Identify the product that has condensed on the upper part of the wall of the test tube.[8] The chemical change that has taken place is a decomposition and, according to definition, at least one other product must have been formed. Was there any visible evidence of the formation of another product? [9] In view of this answer, what must be the nature of any other product formed in the reaction? [10]

The decomposition of mercuric oxide is represented in the following manner:

$$2HgO \rightarrow 2Hg + O_2$$

The other product of this reaction is seen to be oxygen. Look up the physical properties of oxygen in the text, and pick out all those that cause the element to be overlooked as one of the reaction products in this experiment.[11]

Note that, although oxygen is one of the components of air, the mercury on the wall of the tube does not tend to combine with oxygen at ordinary temperatures to form mercuric oxide. If this change *were* taking place, what evidence would there be for it? [12]

Name (last name first) _____ Desk No. _____ Date _____

Experiment IX

CHEMICAL CHANGE. COMBINATION AND DECOMPOSITION

(A) Combination

Mercury and iodine

1.

2.

3.

4.

Magnesium and oxygen

5.

6.

7.

8.

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IX (Cont'd)

(A) Cont'd

10.

Iron and sulfur

11.

12.

13.

14.

15.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IX (Cont'd)

(A) Cont'd

16.

17.

18.

19.

20.

(B) Decomposition

Cupric sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$

1.

2.

3.

4.

5.

6.

Mercuric oxide, HgO

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment IX (Cont'd)

(B) Cont'd

8.

9.

10.

11.

12.

Experiment X

ILLUSTRATIONS OF THE LAW OF DEFINITE PROPORTIONS

Discussion. One of the most fundamental of the laws of chemistry deals with the proportion by weight of elements in compounds, and with weight relationships in chemical and physical changes. It has been found that *any sample of a pure compound always contains the same elements united in the same definite proportions by weight.* This statement is sometimes called *the Law of Constant Composition.* Thus, sodium chloride contains 39.34 per cent of sodium and 60.66 per cent of chlorine whether the salt is obtained from the salt wells of Michigan, the waters of Great Salt Lake, or from the oceans. Analysis of many compounds has verified the law.

An approach to the above law is possible from a different point of view. Experiment shows that *when elements react to form a particular compound, they do so in the same definite proportions by weight.* This statement is the *Law of Definite Proportions.* Hence, when sodium and chlorine react to form sodium chloride, the weights of the elements entering into the reaction are in the ratio of 39.34 to 60.66 respectively. It is to be remembered that the isotopes (Text) of an element have different combining weights.

The two statements given above describe a fundamental principle of chemical combination. Either statement necessarily follows from the other; the one more frequently used is the law of definite proportions.

Two syntheses and one decomposition are offered in this experiment. The preferred synthesis, that of cupric sulfide, must be carried out in a ventilating hood. If satisfactory equipment is not available, the synthesis of magnesium oxide is to be used inasmuch as it may be carried out in the open laboratory.

The decomposition referred to in the preceding paragraph involves the breaking up of a single compound into two other compounds rather than into its elements. Certain compounds, especially salts, combine with definite weights of water to form a class of compounds called *hydrates.* Thus, a gram-molecular weight of a given salt combines with a definite number of gram-molecular weights of water. This water is generally driven off completely when the hydrate is heated. These definite proportions by weight may be verified by quantitative determination; hence the study of the decomposition of a hydrate illustrates the law of definite proportions.

Apparatus and Materials: Beam balance; 1 g. of No. 18 copper wire; 15 g. of powdered sulfur; 38 cm. of magnesium ribbon; 1.5 g. of $BaCl_2 \cdot 2H_2O$; 1.5 g. of a hydrate of unknown composition. (See part D.)

(A) The Synthesis of Cupric Sulfide. This experiment must be carried out in a ventilating hood. Support a *clean* porcelain crucible on a clay triangle which has been placed on a tripod (Fig. 47). Heat the crucible for 5 min. in the hottest flame obtainable with the gas burner. At the end of this time allow the crucible to cool; do not remove it from the triangle. While the crucible is cooling, obtain about 1 g. of No. 18 copper wire from the stockroom. Use a clean towel to wipe the wire, and then weigh the wire on a small beam balance; record this value as "weight of copper wire." [1] Now bend the wire into a flat spiral that will fit into the bottom of the crucible.

Place the wire in the cool crucible and determine their combined weight on the beam balance. *Use a crucible tongs to transfer the crucible from the triangle to the balance.* Before

using the tongs inspect the tips to make certain that there is no material on them which might adhere to the crucible. No object to be weighed should be handled directly with the fingers because oil and moisture from the skin may increase the apparent weight. Record the weight of the crucible and wire.[2] The difference between values (1) and (2) is recorded as the weight of the crucible.[3]

Set up the tripod, triangle, and crucible containing the wire (Fig. 47) in the ventilating hood. Cover the wire in the crucible with approximately 1.5 g. of powdered sulfur, and then heat the crucible gently until the sulfur melts and begins to burn. Remove the flame, and permit the sulfur to burn for about 5 min. At the end of this time place the porcelain cover on the crucible. Heat intensely as long as sulfur continues to burn around the edges of the crucible cover. Lift the cover from time to time to ascertain whether any sulfur remains. When all the sulfur has burned, continue heating intensely for a 3-min. period. Do not remove the cover during this time. After the last period of heating allow the crucible to cool with the cover on.

Weigh the cooled crucible *without its cover*. Record the weight.[4] Calculate the weight of cupric sulfide formed in the reaction.[5] Determine the weight of sulfur that has combined with the copper.[6]

How many grams of sulfur would have combined with exactly 1 g. of copper? [7]; with a gram-atomic weight of copper? [8] How does the latter weight compare with the atomic weight of sulfur? [9] On the basis of the experimental data, how many gram-atomic weights of copper have combined with 1 gram-atomic weight of sulfur? [10] What is the simplest formula of cupric sulfide? [11] Write the equation for the reaction between copper and sulfur, and list all the facts expressed by the equation.[12]

(B) The Synthesis of Magnesium Oxide. Support a *clean* porcelain crucible and its cover on a clay triangle which has been placed on a tripod. Heat the crucible and cover for 5 min. in the hottest flame obtainable with the gas burner. At the end of this time allow the crucible to cool. Do not remove it from the triangle during the cooling period. While the crucible is cooling, obtain a beam balance from the stockroom. About 10 min. is required to cool the crucible to room temperature.

Transfer the cooled crucible from the triangle to a small beam balance. In making this transfer use a crucible tongs. Before using the tongs, inspect the tips to make certain there is no material on them that might adhere to the crucible. No object to be weighed should be handled directly with the fingers because oil and moisture from the skin can increase the apparent weight. Weigh the crucible and cover; record the weight.[1]

Break a 38-cm. (15-in.) length of magnesium ribbon into two approximately equal lengths. Roll these pieces into fairly tight coils, and place them well down in the crucible. Measure and record the combined weight of the crucible, the cover, and the coils.[2] What is the weight of the ribbon? [3]

Now replace the covered crucible and its contents on the clay triangle. Heat the crucible strongly for about 2 min., then remove the flame, and lift the cover slightly with the tongs. The magnesium should glow as the air strikes it (if it does not, the heating should be resumed for about $\frac{1}{2}$ min.). Replace the cover after a few seconds, or at once if white fumes begin to escape from the crucible. After about 10 sec. lift the cover again; if the magnesium glows again, replace the cover before white fumes have a chance to escape. However, if the magnesium does not glow, heat the crucible for a 20-sec. period. Continue the alternate heating and admission of air * until the magnesium no longer glows when the cover is raised. The cover is now removed, placed underside up on a wire gauze, and allowed to cool. Be careful not to lose any magnesium oxide which may adhere to the underside of the cover. Heat the uncovered crucible intensely for 3 min. and allow it to cool.

* This may be facilitated by holding the burner in the left hand and the tongs in the other hand.

Add 3 or 4 drops of water to the cooled crucible. This reacts with the small amount of another magnesium compound (Mg_3N_2) formed in the combustion, and converts it into magnesium hydroxide. This is decomposed by heat to magnesium oxide. Heat very slowly to evaporate the water without spattering, and then use the hottest flame obtainable to keep the crucible red-hot for 3 min. Replace the cover, heat for another minute, and then allow the covered crucible to cool to room temperature. Weigh the crucible with its cover and contents.[4] Calculate the weight of the magnesium oxide formed.[5] What weight of oxygen combined with the magnesium during the reaction? [6]

How many grams of oxygen would have combined with exactly 1 g. of magnesium [7]; with a gram-atomic weight of magnesium? [8] How does the latter weight compare with the atomic weight of oxygen? [9] Calculate the percentage difference.[10] On the basis of the experimental data, decide upon the number of gram-atomic weights of oxygen combined with 1 gram-atomic weight of magnesium. What, therefore, is the simplest formula for magnesium oxide? [11] Write the equation for the reaction between magnesium and oxygen, and list all the facts expressed by the equation.[12]

(C) The Decomposition of a Hydrate. Heat a clean, dry porcelain crucible and its cover for 5 min. Weigh the crucible and cover on a beam balance as soon as they have cooled to room temperature.[1] Grind about 1.5 g. of the hydrate of barium chloride ($BaCl_2 \cdot 2H_2O$) in a mortar. Transfer the finely ground hydrate to the crucible, and accurately weigh the covered crucible with its contents.[1] Calculate the weight of the hydrate.[1]

Heat the covered crucible *gently* for a few minutes in order to avoid loss of material by spattering during the initial stage of the decomposition of the hydrate. If any of the solid is thrown out of the crucible, do not carry the experiment further but obtain a new sample. When the crackling noises in the crucible are no longer heard, the temperature is raised as high as is possible with the burner flame. Continue the heating about 15 min. Weigh the covered crucible after it has cooled.[1] Now reheat the covered crucible for about 5 min. and then weigh it again after it has cooled.[1] If the two weighings agree within 0.02 g., take the average as the accepted or constant weight.[1] However, if the two weights do not agree within 0.02 g., the reheating process must be continued until two consecutive weighings fall within the required range of agreement. The weight of the water lost is the difference between the weight of the hydrate and the weight of the anhydrous salt.[1]

Calculate the number of grams of water united with 1 g. of $BaCl_2$.[1] How many grams of water are indicated for a gram-molecular weight of $BaCl_2$? [1] How many gram-molecular weights of water are represented by the preceding weight? [1] How closely does the experimental value agree with the formula of the salt? [2] What is the basis for the statement that hydrates are definite chemical compounds? [3]

(D) The Decomposition of a Hydrate of Unknown Composition. Obtain a 1.5-g. sample of an unknown hydrate.* Repeat the experimental work carried out in part (C), record the data in the spaces provided on the report sheet, and calculate the percentage of water in the hydrate.[1]

Calculate the percentage of water in each of the hydrates listed in the footnote to this part of the experiment.[2] With which of these hydrates does the value found in ([1]) agree? [3] Calculate from the *experimental data* the number of gram-molecular weights of water combined with a gram-molecular weight of the salt chosen in ([3]). Show these calculations.[4]

* The following hydrates are to be used as unknowns in this experiment: $BaCl_2 \cdot 2H_2O$ $CuSO_4 \cdot 5H_2O$, $MgSO_4 \cdot 7H_2O$, $SrCl_2 \cdot 6H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, and $ZnSO_4 \cdot 7H_2O$.

Name (last name first) _____ Desk No. _____ Date _____

Experiment X

ILLUSTRATIONS OF THE LAW OF DEFINITE PROPORTIONS

(A) The Synthesis of Cupric Sulfide

1.

2.

3.

4.

5.

6.

7. 8.

9.

10. 11.

12.

(B) The Synthesis of Magnesium Oxide

1.

2.

3.

4.

5. 6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment X (Cont'd)

(B) Cont'd

7. **8.**

9. **10.**

11. **12.**

(C) The Decomposition of a Hydrate

1.

Weight of crucible + cover + hydrate . . . . . .
Weight of crucible + cover . . . . . _____
Weight of hydrate . . . . . .

Weight of crucible + contents after heating . . . . . .
Weight of crucible + contents after reheating . . . . . .
Constant weight of crucible + contents . . . . . .
Weight of crucible + cover . . . . . _____
Weight of anhydrous salt . . . . . .

Weight of the hydrate . . . . . .
Constant weight of anhydrous salt . . . . . _____
Weight of water driven off . . . . . .

Number of grams of H_2O combined with 1 g. of $BaCl_2$ . . . . .
Number of grams of H_2O combined with 1 mole of $BaCl_2$ . . . . .
Number of moles of H_2O combined with 1 mole of $BaCl_2$ . . . . .

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment X (Cont'd)

(D) The Decomposition of a Hydrate of Unknown Composition

1.

Weight of crucible + cover . . . . . .
Weight of crucible + cover + hydrate . . . . . .
Weight of hydrate . . . . . .
Weight of crucible + contents after heating . . . . . .
Weight of crucible + contents after reheating . . . . . .
Constant weight of crucible + contents . . . . . .
Weight of water driven off . . . . . .
Weight of anhydrous salt . . . . . .
Number of grams of H_2O combined with 1 g. of the salt . . . . .
Per cent of water in the hydrate . . . . . .

2.

3.

4.

Experiment XI

THE PREPARATION OF OXYGEN

Discussion. Oxygen is the most abundant element associated with the earth. It occurs in the atmosphere as free oxygen, in water combined with hydrogen, and in many compounds with other elements. The preparation of oxygen requires its liberation from these compounds or its separation from air.

Oxygen may be obtained from certain oxides (binary compounds, one constituent of which is oxygen) by heating them to a sufficiently high temperature. Many oxides, particularly those of the very active metals and nonmetals, do not decompose at a sufficiently low temperature to serve as practical sources of oxygen. Other oxides give off only part of their oxygen. Oxides of the least active metals give off all of their oxygen to yield the free metal.

Other compounds containing oxygen, such as the nitrates (KNO_3) and the chlorates ($KClO_3$), also give off oxygen when heated. The nitrates yield only part of their oxygen while all of the oxygen may be obtained from the chlorates. Many compounds do not give off their oxygen even at the maximum temperature obtainable with a Bunsen or a Tirril burner. Certain compounds are decomposed by heat to give one or more substances that contain oxygen, but not free oxygen. For example, calcium carbonate ($CaCO_3$) will decompose to give solid calcium oxide (CaO) and a gas, carbon dioxide (CO_2). Therefore, if a gas is liberated from an oxygen-containing compound, the gas is not necessarily oxygen. Accordingly a *test* must be made to determine the presence of oxygen.

A *test* for a substance is a procedure that utilizes a characteristic property or reaction to detect the presence of the substance. The *test* for oxygen is made as follows: A glowing splinter of wood is thrust into a gas. If the splinter continues to glow or bursts into flame, oxygen is assumed to be present. Only one or two other easily recognizable substances support the combustion of wood. If there is no evidence of the presence of these other substances, then it may be concluded that oxygen is present. A glowing splint is rekindled only when the concentration of oxygen is about 30 per cent. Therefore, the fact that the splint does not burst into flame is not absolute proof that the oxide does not decompose at all.

Oxygen is obtained in certain instances as a product of the interaction of two other substances. Such reactions may be used as methods for the preparation of oxygen. Oxygen is also obtained at the positive electrode (anode) when an electric current is passed through water to which has been added a little sulfuric acid or sodium hydroxide.

Apparatus and Materials: 0.5 g. of each of the following compounds: lead dioxide (PbO_2), lead monoxide (litharge, PbO), barium peroxide (BaO_2), mercuric oxide (HgO), silicon dioxide (sand, SiO_2), ferric oxide (Fe_2O_3), manganese dioxide (MnO_2), potassium chlorate ($KClO_3$), potassium nitrate (KNO_3), potassium sulphate (K_2SO_4), calcium carbonate ($CaCO_3$), sodium peroxide (Na_2O_2); wooden splints; three or four 4-in. Pyrex test tubes.

(A) Preparation of Oxygen by Heating Oxides. Heat approximately 0.5 g. of each of the following oxides in small hard-glass (Pyrex) test tubes*: lead dioxide (PbO_2), lead

* The 6-in. Pyrex test tubes may be used, but small 75 × 10 mm. Pyrex test tubes are preferable. Suitable small test tubes may be prepared from 10-mm. soft-glass tubing (as described in Exp. II) or from 10-mm. Pyrex-glass tubing if blast lamps are available.

monoxide (litharge, PbO), barium peroxide (BaO_2), mercuric oxide (HgO), silicon dioxide (sand, SiO_2), ferric oxide (Fe_2O_3), and manganese dioxide (MnO_2). Continue the heating for 2 or 3 min. until the test tube has become dull red in color. This will be a minute or two after the intense yellow color is imparted to the flame. Test for oxygen intermittently, as follows: Light a wooden splint and then blow out the flame so that the end of the splint still glows. Thrust this into the test tube near the solid. If the splint continues to glow, or bursts into a flame, the presence of oxygen is indicated. The more quickly the splint bursts into flame, the greater is the rate of liberation of oxygen. If the splint merely glows more brightly without bursting into a flame, oxygen is being given off slowly and the test tube should be heated to a higher temperature if possible. The splinter will cease to glow if it is thrust into a test tube in which oxygen is not being given off from a material. Record the data on the form provided on the report sheet.[1]

What is the type of reaction that takes place in the above experiments?[2] Are they exothermic or endothermic?[3] Which of the above substances loses all of the oxygen combined with the metal?[4] Which ones lose only a part of the oxygen?[5] List the following compounds in the order of their stability at high temperature: SiO_2, HgO, and BaO_2.[6] Which of these three substances has the greatest heat of formation?[7] Which has the smallest heat of formation? (Text)[8]

(B) Preparation of Oxygen by Heating Oxygen-Containing Compounds. Obtain 0.5 g. of each of the following compounds: potassium chlorate ($KClO_3$), potassium sulfate (K_2SO_4), potassium nitrate (KNO_3), and calcium carbonate ($CaCO_3$). Clean the Pyrex test tubes used in part (A). Heat each of the above substances and test for oxygen by inserting a glowing splint into the test tube. Record the results in the same way as described in part (A).[1] Some of the above substances will melt. Continue the heating until no further reaction is noticed. Describe what happens to the potassium chlorate as the heating is continued.[2] What is the residue remaining in the test tube?[3]

(C) Preparation of Oxygen by the Reaction of Sodium Peroxide with Water. When sodium burns in air, sodium peroxide (Na_2O_2) is formed. This compound reacts with water to yield sodium hydroxide (NaOH) and oxygen (O_2).

Obtain 0.5 g. of sodium peroxide from the stockroom. (**CAUTION!** Do not allow the sodium peroxide to touch the hands. Do not throw any unused peroxide into the waste jars. Wash it down the sink with water.) Place the sodium peroxide in a test tube and add a few drops of water. Test for the evolution of oxygen.[1] Write an equation for the reaction.[2]

(D) Oxygen from the Air. Oxygen may be obtained from the air by chemical or by physical means. In order to obtain oxygen from the air by chemical means, the oxygen must first be made to form a compound from which the oxygen can be recovered. Suggest three methods for obtaining oxygen from the air chemically. Start with each of the following substances: mercury (Hg), barium oxide (BaO), and sodium (Na).[1]

Suggest a method of obtaining oxygen from the air physically (Text).[2]

(E) Preparation of Oxygen by the Electrolytic Decomposition of Water.* Draw a diagram of and explain the operation of an apparatus which might be used for the production of oxygen from water.[1] Can pure water be used? Why?[2] What are the relative volumes of hydrogen and oxygen obtained?[3] At which electrode is the oxygen liberated?[4] The valence of an element in the free state is zero. What is the valence of oxygen in water?[5] What is the change in valence of oxygen when it is liberated in the free state?[6] How many electrons are lost in the process?[7] What happens to these electrons?[8] (**Hint:** Consider what happens to the hydrogen.)

* If the apparatus is available, the students may operate it and measure the relative volumes of hydrogen and oxygen.

Name (last name first) Desk No. Date

Experiment XI

THE PREPARATION OF OXYGEN

(A) Preparation of Oxygen by Heating Oxides

1.

Material	Oxygen Obtained	Relative Ease of Decomposition	Change in Appearance of Solid	Equation for the Reaction
PbO_2				
PbO				
BaO_2				
HgO				
SiO_2				
Fe_2O_3				
MnO_2				

2.

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XI (Cont'd)

(B) Preparation of Oxygen by Heating Oxygen-Containing Compounds

1.

Material	Oxygen Obtained	Relative Ease of Decomposition	Change in Appearance of Solid	Equation for the Reaction
$KClO_3$ K_2SO_4 KNO_3 $CaCO_3$				

2.

3.

(C) Preparation of Oxygen by the Reaction of Sodium Peroxide with Water

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XI (Cont'd)

(D) Oxygen from the Air

1.

2.

(E) Preparation of Oxygen by the Electrolytic Decomposition of Water

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XI (Cont'd)

(E) Cont'd

3.

4.

5.

6.

7.

8.

Experiment XII

CATALYSIS

Discussion. The speed of a chemical reaction depends upon a number of factors: (1) the chemical nature of the reactants, (2) the temperature, (3) the concentration of the reacting substances, (4) the extent of surface or state of subdivision in the case of solids, and (5) the presence of a catalyst. A catalyst is a substance that changes the speed of a reaction without undergoing a permanent change, that is, the catalyst has the same chemical composition at the end of the reaction that it had at the beginning.

Catalysis is important in many chemical reactions. Certain reactions will not take place to any noticeable extent in the absence of certain catalysts. Other reactions are speeded up and proceed noticeably at much lower temperatures. Still other reactions may be slowed down by the presence of *negative* catalysts. Numerous examples of both *positive* and *negative* catalysts are encountered in the course of the study of a number of industrial processes.

When potassium chlorate ($KClO_3$) is heated, it melts at 368.4°. At 400° it begins to decompose, and at 600° the decomposition is complete. However, if a small amount of manganese dioxide is present, the potassium chlorate decomposes very rapidly at 270 to 300°. Certain other metallic oxides, for example, ferric oxide (Fe_2O_3) and cupric oxide (CuO), catalyze this reaction in the same way.

Apparatus and Materials: 8 g. of potassium chlorate; 0.5 g. of manganese dioxide; 0.5 g. of cupric oxide; 1.0 g. of ferric oxide (heated to redness before use); 0.5 g. of silicon dioxide. Three or four 6-in. hard-glass (Pyrex) test tubes; beam balance and weights.

(A) Catalytic Decomposition of Potassium Chlorate. Place about 1 g. of potassium chlorate ($KClO_3$) in each of two Pyrex test tubes. Add 0.1 g. of manganese dioxide (MnO_2) to one of the test tubes and shake it until the MnO_2 and the $KClO_3$ are thoroughly mixed. Put a flame spreader on the burner and hold the tubes in the flame in such a manner that both are heated at the same rate. Test intermittently for the evolution of oxygen. Which one gives off oxygen at the lower temperature? [1] Continue heating the test tube that contained only potassium chlorate and note how much longer it must be heated before the presence of oxygen can be detected.

Place about 1 g. of $KClO_3$ in another test tube and clamp it to the ring stand so that the test tube is slightly inclined from a vertical position. Heat the test tube until the $KClO_3$ melts. Apply the test for oxygen.[2] Note that only a few oxygen bubbles rise through the liquid. Now take about 0.2 g. of ferric oxide (Fe_2O_3) on the end of a spatula and drop the powder into the test tube. What happens? [3] Test for oxygen.[4] Compare the behavior of potassium chlorate when it is heated with and without a catalyst.[5]

Test the catalytic action of the following substances in the decomposition of potassium chlorate: cupric oxide (CuO) and silicon dioxide (SiO_2).[6] Follow the same procedure described for testing the catalytic action of Fe_2O_3. Do all oxides catalyze the decomposition of potassium chlorate? [7] What does this action show about the specific nature of catalysis? [8]

(B) Quantitative Study of the Catalytic Decomposition of Potassium Chlorate. Weigh a test tube to the nearest 10 mg. (0.01 g.) on a beam balance. Record this weight and all other weights obtained in part (B) on the form provided on the report sheet.[1] Place about 2 g. of potassium chlorate in the bottom of the test tube (Fig. 36) and weigh the test tube

with its contents. Now place about 0.5 g. of ferric oxide (Fe_2O_3) in the bottom of the test tube in the same manner. (Approximately 0.5 g. of Fe_2O_3 will be obtained if the end of the spatula is dipped well into a quantity of Fe_2O_3 once, or if the tip is dipped into it twice. The student should learn to judge the approximate weight of small quantities of solids.) Weigh the test tube plus its contents to obtain the weight of the Fe_2O_3 added.[1]

Shake the test tube until the $KClO_3$ and Fe_2O_3 are well mixed. Clamp the test tube to the ring stand as described in part (A). Heat the test tube carefully until all the potassium chlorate is decomposed and no further reaction is observed. Allow the test tube to cool, and then weigh it and the residue. What weight of oxygen was lost? [2]

Add from 5 to 7 ml. of water to the test tube and shake it to loosen the residue and to dissolve the soluble portion. Pour the mixture onto a filter paper as illustrated in Fig. 46. Add successive 3-ml. portions of distilled water to the test tube and pour each onto the filter paper. Continue until all of the Fe_2O_3 is transferred to the filter paper. Five or six such washings may be required. If difficulty is experienced in removing the Fe_2O_3 that clings to the glass, remove it by pushing a small piece of filter paper along the inside surface of the test tube with a stirring rod. This small piece of filter paper with the Fe_2O_3 on it is then added to the rest of the Fe_2O_3 in the funnel.

Now wash the filter paper twice to remove any of the original solution which may have been absorbed by the filter paper. To do this direct a small stream of water from the wash bottle around the upper edges of the filter paper. Do not let the filter paper become more than half full of water. Allow the water to drain into the beaker before the next washing is made. Do not discard the solution in the beaker.

While the filter paper is draining, heat a crucible to redness, allow it to cool, and then weigh it to the nearest 10 mg. on a beam balance.[1] Remove the filter paper from the funnel and tear off any of the filter paper which does not have Fe_2O_3 on it. Now fold the filter paper and place it in the crucible. Heat the crucible with a hot flame as illustrated in Fig. 47, but tilt the crucible well on its side. This allows a draught of air to pass into the crucible, thereby speeding up the process of burning off the filter paper. Proceed as directed in the next paragraph while the filter paper is burning. When the filter paper has been completely burned, cool the crucible and reweigh it in order to determine the weight of the Fe_2O_3.[1] Compare the weight of the Fe_2O_3 obtained from the residue with the original amount added.[3] Did the oxygen which was lost come from the Fe_2O_3? [4] Observe the color of the residue. Has there been any apparent change in the catalyst? [5]

While the filter paper is burning, weigh a small evaporating dish to the nearest 0.01 g. Transfer the filtrate from the beaker to the evaporating dish. Place the latter on a wire gauze which has been placed on a ring clamped to the ring stand. While the crucible is cooling, begin the evaporation of the filtrate. When the solid begins to crystallize, the heating must be done slowly and carefully, otherwise the solution will spatter out of the evaporating dish. After the water has evaporated and the salt has dried, allow the evaporating dish to cool. Weigh it and determine the weight of the residue.[1] What is this residue? [6] Does it weigh more or less than the potassium chlorate originally taken? [7] Add the weight of this residue to the weight of oxygen which was lost as a result of the heating.[8] Compare this combined weight with the weight of the potassium chlorate originally taken.[9] Explain how this experiment demonstrates that the Fe_2O_3 acts only as a catalyst.[10]

Problems. Write the equation for the decomposition of potassium chlorate.[1] Write under each substance the weight represented in the number of gram-formula weights indicated. It will be noted that 245.1 g. of potassium chlorate decomposes to give 149.1 g. of potassium chloride and 96 g. of oxygen. Calculate the number of grams of potassium chloride which would be obtained from 1 g. of potassium chlorate.[2] Now calculate the number of grams of potassium chloride that can be obtained from the weight of potassium

chlorate used in the above experiment.[3] Compare this weight with the weight of potassium chloride recovered.[4]

Calculate the number of grams of oxygen which may be obtained from 1 gram of potassium chlorate.[5] Calculate the number of grams of oxygen which may be obtained from the weight of potassium chlorate used in the above experiment.[6] Compare this value with the weight of oxygen liberated in the above experiment.[7]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XII

CATALYSIS

(A) Catalytic Decomposition of Potassium Chlorate

1. **2.**

3. **4.**

5.

6.

7.

8.

(B) Quantitative Study of the Catalytic Decomposition of Potassium Chlorate

1.

Weight of test tube + $KClO_3$ . . . . . .
Weight of test tube . . . . . _____
Weight of $KClO_3$ . . . . . .

Weight of test tube + $KClO_3$ + Fe_2O_3 . . . . . .
Weight of test tube + $KClO_3$ (Same as above) . . . . . _____
Weight of Fe_2O_3 at the beginning . . . . . .

Weight of test tube + $KClO_3$ + Fe_2O_3 . . . . . .
Weight of test tube + residue . . . . . _____
Weight of O_2 lost . . . . . .

Weight of crucible + Fe_2O_3 . . . . . .
Weight of crucible . . . . . _____
Weight of Fe_2O_3 at the end . . . . . .

Weight of evaporating dish + KCl . . . . . .
Weight of evaporating dish . . . . . _____
Weight of KCl. . . . . .

Name (last name first) _____ Desk No. _____ Date _____

Experiment XII (Cont'd)

(B) Cont'd

2.

3.

4.

5.

6. **7.**

8. **9.**

10.

Problems

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XII (Cont'd)

Problems (Cont'd)

3.

4.

5.

6.

7.

Experiment XIII

CHEMICAL PROPERTIES OF OXYGEN

Discussion. The relatively small quantities of oxygen used in this and in other laboratory experiments are obtained by the thermal decomposition of potassium chlorate in the presence of manganese dioxide. Because of several unfavorable factors involved, this method is not used to make large amounts of oxygen. One of these is the relatively high cost (from about 10 to 11 cents per pound) of potassium chlorate. Larger amounts of oxygen needed for experimental work are generally obtained from a tank containing the gas under high pressure. How is oxygen obtained in commercial quantities? [1]

The chemical properties of oxygen are described in terms of the reactions of this element with other elements and with compounds. Hence this experiment deals with reactions of these two types.

Apparatus and Materials: A 7.6-cm. (3-in.) length of magnesium ribbon; 12.7 cm. (5 in.) of picture wire; 0.1 g. powdered wood charcoal; 0.1 g. powdered sulfur; small piece of cotton; 0.3 to 0.5 g. steel wool; 0.1 g. sand; 2 iron nails (about 1.5 cm. in length); 0.5 g. mossy or granulated tin; 15 g. potassium chlorate; 0.5 g. manganese dioxide; 7.6 cm. (about 3 in.) of 7-mm. black rubber tubing; 20 cm. (8 in.) of No. 18 copper wire; pneumatic trough; beam balance.

(A) Preparation and Collection of Oxygen.* Heat about 0.2 g. of manganese dioxide in a crucible for 2 min. This serves to destroy any impurities that might cause an explosion

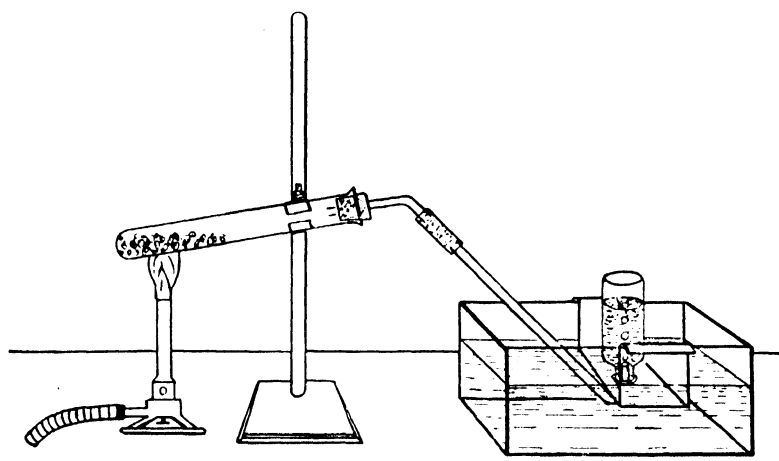


FIG. 49. Laboratory preparation and collection of oxygen

when the dioxide is heated with potassium chlorate. Allow the dioxide to cool, and then transfer it to a 15-cm. (6-in.) Pyrex test tube containing 7 g. of potassium chlorate. Mix the two compounds by shaking the test tube.

Now obtain a one-holed rubber stopper for the test tube, and insert in the stopper a short piece of glass tubing bent to an angle of 120° (prepared in Exp. II). The end of the

* Omit this preparation of the gas for use in parts (A), (B), (C), and (D) if oxygen is available from a cylinder.

tubing should project slightly below the bottom of the stopper. The test tube is now tightly stoppered and then connected by a short piece (7.6 cm.) of rubber tubing with the delivery tube constructed in Exp. II. Set up the apparatus used for the collection of a gas (Fig. 49). Use both of the 250-ml. wide-mouthed bottles supplied in the desk set. *The apparatus must now be checked by the laboratory instructor.*

Begin the generation of oxygen by heating the test tube, at first gently and then strongly, until bubbles rise in a steady stream through the water in the pneumatic trough. Do not begin the collection of gas until it has flowed steadily for about 20 sec. What is the reason for this? [1] Now fill the first bottle with oxygen. Discontinue the heating as soon as the bottle is completely filled, and then immediately remove the delivery tube from the trough. If this is not done, water will be forced up through the delivery tube into the hot test tube. Why must this be prevented? [2] Slide a glass plate over the mouth of the bottle while it is still immersed in the water. Then remove the covered bottle from the trough and place it right-side-up on the desk. Now resume the generation of oxygen so as to fill the second bottle. As soon as this has been done, discontinue the heating, remove the delivery tube as before, and place the covered bottle on the desk. *Do not dismantle the apparatus; it is to be used in parts (B), (C), and (D).*

(B) Reaction of Oxygen with Metals. 1. Magnesium. Use a burner flame to light a 7.6-cm. length of magnesium ribbon held at one end with crucible tongs. Observe the brilliance of this oxidation in the air, and then quickly thrust the burning ribbon into one of the bottles containing oxygen. (Continue to hold the ribbon with the tongs; do not drop the metal into the bottle.) What change, if any, is noted in the brilliance of the combustion? [1] Note and explain any change in the rate of oxidation.[2] Every chemical reaction may be put into one or the other of two classes, depending upon whether heat is released or absorbed during the reaction. (Text) Name these two classes, and tell in which one the oxidation of magnesium belongs.[3] Write the equation for this oxidation reaction.[4]

2. Iron. Unravel a 12.7-cm. (5-in.) length of picture wire about 1 cm. from one end and spread out the individual strands. Heat this end for about 15 sec. in the hottest region of the burner flame. Remove the wire, and then note the change in the appearance of the part that has been heated. Hold this over a piece of filter paper, and scrape the surface of the metal with a knife blade. Result? [5] The coating is an oxide of iron. Is its formation observable at ordinary temperatures? [6] What is the effect of a change in temperature upon the rate of a chemical reaction? [7] On the basis of this answer tell why the formation of the oxide is not observed at ordinary temperatures.[8]

Now obtain enough sand to cover completely the bottom of a 250-ml. wide-mouthed bottle with a layer that is 0.5 cm. thick. Add this sand to the covered bottle that contains oxygen. *This must be done very quickly so as to prevent the escape of any considerable part of the oxygen.* Reheat the picture wire (hold it with crucible tongs this time) to a red heat and then plunge it into the bottle. Do not *drop* the wire into the bottle, but hold it with the tongs. Describe everything that takes place, and tell what purpose is served by the sand in the bottle.[9] Classify this reaction from the standpoint of the thermal change involved, name the oxide formed, and write an equation for its formation.[10]

(C) Reaction of Oxygen with Nonmetals. Reheat the potassium chlorate-manganese dioxide mixture used in part (A) and collect two more bottles of oxygen.

1. Sulfur. Place 0.1 g. of powdered sulfur in a deflagration spoon. Does sulfur possess an odor? [1] Now heat the spoon until the element begins to burn. Describe the general size and color of the flame.[2] Is the combustion slow or rapid? [3] Endothermic or exothermic? [4] Note the odor of the oxidation product, and then make a statement regarding the rate of oxidation of sulfur at ordinary temperatures.[5] Plunge the spoon containing the burning sulfur into the bottle of oxygen. What evidence is there for a change in the rate of oxidation? [6] Write the equation for the reaction that takes place and name the product.[7]

2. Carbon (Charcoal). If any sulfur remains in the deflagration spoon it must be burned out. Place 0.1 g. of powdered charcoal in the clean deflagration spoon and heat it until the spoon reaches a dull-red heat. What evidence, if any, is there that the charcoal is being oxidized? [8] Thrust the hot spoon and its contents into the second bottle of oxygen. What can be said about the relative rates of oxidation of carbon in air and in oxygen? [9] What is the state (gaseous, liquid, or solid), the color, the odor, and the name of the oxidation product? [10] On the basis of general knowledge make a statement regarding the relative rate of oxidation of carbon (charcoal, coal, or coke) at ordinary temperatures.[11] Write the equation expressing the oxidation of carbon.[12] Classify this reaction on the basis of the thermal change that accompanies it.[13] To what universal use is this reaction put? [14]

(D) Reaction of Oxygen with Compounds. 1. Cotton. Collect two more bottles of oxygen, and then take down the apparatus. Ignite a pinch of cotton in a deflagration spoon. Make a statement regarding the rate at which the cotton burns.[1] Thrust the burning cotton into a bottle of oxygen. What is the evidence for a change in the rate of oxidation? [2] How should this reaction be classified on the basis of the thermal change accompanying it? [3] What, in general, are the products of the reaction of oxygen with a compound? (Text) [4] The simplest formula for cotton is $C_6H_{10}O_5$. What are the products of the combustion of this compound? Write the equation for this oxidation.[5] Write an equation to show what takes place when ethanol (grain alcohol, C_2H_5OH) burns in oxygen or in the air.[6]

2. Sand (Silicon Dioxide). Heat 0.1 g. of sand in a deflagration spoon until the latter is raised to a dull-red heat. Thrust the spoon quickly into the second bottle of oxygen. What is indicated by the result? [7] Advance an explanation for this observation.[8]

(E) Oxidation in a Combustion Tube. Tin. Heat 0.2 g. of manganese dioxide to destroy organic matter and then mix it in a 15-cm. Pyrex test tube with 7 g. of potassium chlorate. Now set up the apparatus shown in Fig. 50. (Students should work in pairs if

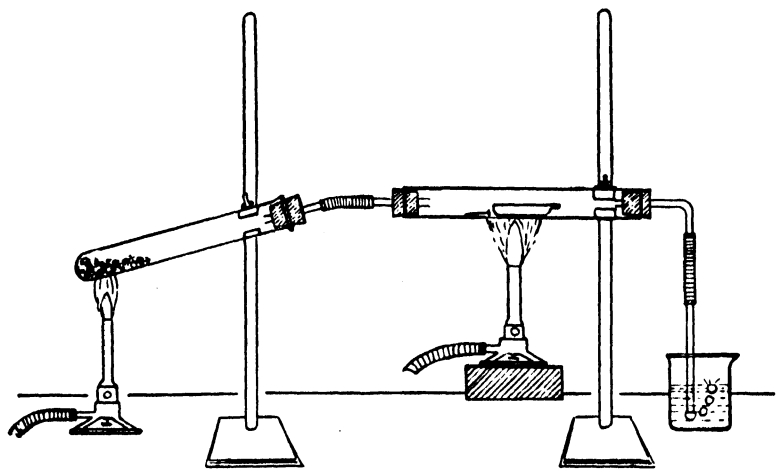


FIG. 50. Oxidation in a combustion tube

equipment is limited.) Place 0.5 g. of mossy tin in a porcelain combustion boat, and then use a 20-cm. (8-in.) length of copper wire (No. 18, B. & S. gauge) to push the boat into the central part of the tube. Now stopper the tube at its exit end with a right-angle glass bend and attach to the latter a straight piece of tubing which extends just below the surface of 100 ml. of water contained in the 150-ml. beaker.

Heat the combustion tube strongly under the boat, and begin the generation of oxygen as soon as the tin has melted. Continue the generation of oxygen and the heating

of the tin until the metal begins to glow. Remove the flame from under the combustion tube at once, and reduce the rate of flow of oxygen by heating the potassium chlorate less strongly. The rate of flow of the oxygen can be gauged by the rate at which the bubbles pass through the water in the beaker. *A flow of oxygen out of the exit tube must be maintained throughout the experiment.* If at any time the flow ceases, and water begins to rise in the exit tube, the latter should immediately be removed from the beaker. What is the melting point of tin? (Text) [1] What evidence is there for the rapid oxidation of the tin? [2] As soon as the oxidation is complete, remove the tube from the beaker, and discontinue the generation of oxygen. Why must the tube be removed from the beaker at this point? [3]

Allow the combustion tube to cool to room temperature. While the tube is cooling, make a hook that will serve to pull the boat out of the tube. The hook is made by making a short, right-angle bend at one end of the 20-cm. length of copper wire that was used to push the boat into the tube at the beginning of the experiment. If the boat sticks to the combustion tube it may be loosened by prying up one end with the handle of the deflagration spoon. ***Care!***

Examine the contents of the boat after its removal from the combustion tube. Contrast the physical properties of the product with those of tin.[4] On the basis of the thermal change that occurred, characterize the reaction.[5] Name the product and write an equation to show its formation.[6]

(F) Speed of Oxidation (Quantitative). Use the end of a file to remove as much as possible of the stannic oxide adhering to the porcelain boat that was used in the last experiment. The remainder of the oxide should be removed by boiling the boat for a few minutes in a solution of sodium hydroxide (use a 400-ml. beaker and enough solution to cover the boat). Wash the boat thoroughly with water, dry it with a towel, and then heat it strongly for 3 min. Allow the boat to cool to room temperature, and then weigh it carefully on a beam balance. Record the weight.[1]

Obtain from 0.3 to 0.5 g. of steel wool, and roll it between the fingers so that it fits into the boat. Do not allow loose strands to project from the boat. Weigh the boat and the wool.[2] Calculate the weight of the steel wool.[3]

Obtain the combined weight of two iron nails, each about 1.5 cm. in length.[4] Push these nails into the combustion tube ahead of the boat containing the wool until the nails and the boat occupy the central part of the tube. Fix the exit tube in place as shown in Fig. 50, and then heat both the nails and the boat until the bottom of the boat becomes dull-red in color. Maintain this temperature, and, at the same time, generate a rapid stream of oxygen. Watch the steel wool carefully for the appearance of a bright-red glow. The reaction is complete when the glow has spread throughout the entire mass of wool. Continue the heating of the combustion tube and the generation of oxygen for 1 min. after the reaction has occurred. At the end of this time stop the generation of oxygen, and remove the flame from under the combustion tube. Do not forget to take the outlet tube out of the water in the beaker! Allow the boat and nails to cool to room temperature.

Weigh the boat as soon as it has cooled.[5] Calculate the following values: the weight of the contents of the boat; [6] the increase in weight over the weight of the iron; [7] the percentage increase in weight.[8]

Now weigh the oxidized nails, and record their weight.[9] Calculate the following values: the increase in weight over the original weight of the nails; [10] the percentage of increase in weight.[11]

Compare the percentage of increase in the weight of the wool with that of the nails, and interpret this in terms of the rate of oxidation of the two samples of iron.[12] What was the determining factor in bringing about a difference in the rates at which oxidation took place? [13] What would have been the weight of the oxidized nails if they had reacted as rapidly, and to the same extent, as the wool? [14]

Calculate the percentage of oxygen and the percentage of iron (percentage composition) in the oxide prepared from the steel wool.[15] Compare the percentage composition of this oxide with those of the oxides Fe_2O_3 and Fe_3O_4. On the basis of this comparison decide which of these two oxides was formed by the combustion of iron in oxygen.[16]

(G) Characteristics of Oxidation. Summarize [1] the characteristics of oxidation with respect to the following points: relative rate of oxidation in air as compared with that in pure oxygen; thermal change accompanying oxidation; and influence of surface on the rate of oxidation.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIII

CHEMICAL PROPERTIES OF OXYGEN

Discussion

1.

(A) Preparation and Collection of Oxygen

1.

2.

(B) Reaction of Oxygen with Metals. *Magnesium*

1.

2.

3.

4.

Iron

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIII (Cont'd)

(B) Cont'd

6.

7.

8.

9.

10.

(C) Reaction of Oxygen with Nonmetals. *Sulfur*

1.

2.

3. **4.**

5.

6.

Name (last name first) Desk No. Date

Experiment XIII (Cont'd)

(C) Cont'd

7.

Carbon

8.

9.

10.

11.

12.

13.

14.

(D) Reaction of Oxygen with Compounds. *Cotton*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIII (Cont'd)

(D) Cont'd

2.

3.

4.

5.

6.

Sand

7.

8.

(E) Oxidation in a Combustion Tube

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIII (Cont'd)

(E) Cont'd

3.

4.

5.

6.

(F) Speed of Oxidation

1.

2.

3.

5.

6.

7.

8.

4.

9.

10.

11.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIII (Cont'd)

(F) Cont'd

12.

13.

14.

15.

16.

(G) Characteristics of Oxidation

1.

Experiment XIV

COMBUSTION

Discussion. Combustion is said to be taking place when oxidation is sufficiently rapid to produce both heat and light. Oxygen is only one of a number of substances that cause combustion to take place. The most common and the most useful cases of combustion result from the action of atmospheric oxygen on such fuels as coal, wood, petroleum products, and natural gas. When gaseous or volatilized substances burn with the production of heat and light, a *flame* is said to be produced. The light is not always visible.

It has been pointed out previously that the speed of oxidation depends upon the temperature, the concentration of the oxygen, and the concentration of the gas or volatilized substance which is to be oxidized, or upon the extent of surface or degree of subdivision as in the case of a solid. The substance burns when the speed of oxidation has become sufficiently rapid to produce heat and light and to maintain the remaining material at a temperature sufficiently high for the reaction to continue. It is obvious that the temperature required to start and maintain this condition will vary even for the same material under different conditions. However, if different materials are compared under as nearly the same conditions as possible, the temperature to which they must be heated to start and maintain combustion may be taken as a measure of their combustibility.

Two different temperatures are significant for liquids: the *flash point* and the *fire* or *burning point.* The flash point is the temperature at which a liquid, such as an oil, gives off vapor in sufficient concentration to flash or burn momentarily upon the application of a flame or spark. The flash point is used as a measure of the safety of a liquid in the neighborhood of flames or sparks. The *fire point* is the temperature to which the substance must be heated in order for it to ignite and burn continuously when its surface is touched with a flame. The *kindling temperature* of a solid under *specified conditions* is the temperature to which the solid must be heated in order for it to ignite and burn continuously.

Apparatus and Materials: 10 ml. of lubricating or transformer oil; 1 ml. of xylene; 1 ml. of kerosene; 1 ml. of carbon disulfide; small piece (0.2 g.) of each of the following: charcoal, magnesium turnings, wood, roll sulfur, and red phosphorus; thermometer (250°).

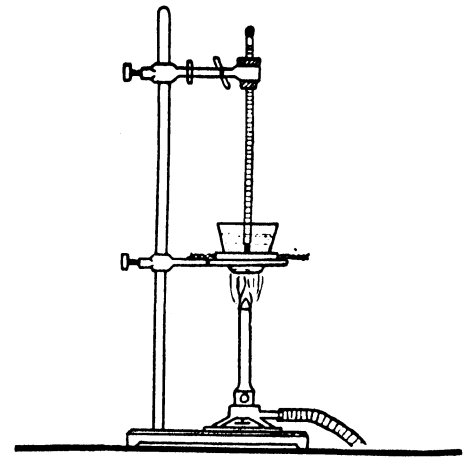


FIG. 51. Determination of the flash point

(A) Determination of the Flash Point. Obtain about 10 ml. of a lubricating or transformer oil. Pour it into a crucible and arrange an apparatus as shown in Fig. 51. Heat the crucible with a small flame (about 2 cm. high). Light a wooden splint and hold it momentarily over the top of the crucible (do not touch the liquid). Repeat this procedure at intervals until the vapor above the oil flashes. Note the temperature at which this first occurs.[1] This is the flash point. Remove the flame immediately and discontinue the heating. Do not pour the oil into the sink or waste jar; dispose of it in the bottle provided for this purpose.

Place a few *drops* of xylene (C_8H_{10}), carbon disulfide (CS_2), and kerosene on separate watch glasses. Heat the end of a stirring rod to redness and hold it over each of these substances. Do any of them flash or ignite? [2] Put out the flame immediately by covering the watch glass with a piece of cardboard. Hold a lighted wooden splint over the two other substances. Note any difference in their tendency to flash or ignite.[3] Arrange these three substances in the order of their flash points.[4] Which is the most dangerous to leave uncovered? [5]

(B) Kindling Temperature. Obtain *small pieces* (about 0.2 g.) of the following: charcoal, magnesium, wood (small piece broken from a wooden splint), roll sulfur, and red phosphorus. Place them in a row on a wire gauze which is on a ring attached to the ring stand. Place the flame spreader on the burner and set it under the wire gauze so that all of the materials receive about the same amount of heat. The ring should be at such a height that it is approximately an inch above the top of the flame. Note the order in which the materials ignite.[1] What is the order of their kindling temperatures? [2] Write the equations for the burning of magnesium, sulfur, and phosphorus.[3]

Give one or two examples which show that the kindling temperature of a substance is lower when it is broken into smaller pieces or is more finely divided.[4] Explain what is meant by *spontaneous combustion*, and give the conditions under which this is most likely to occur. (Text) [5]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIV

COMBUSTION

(A) Determination of the Flash Point

1. **2.**

3.

4. **5.**

(B) Kindling Temperature

1.

2.

3.

4.

5.

Experiment XV

THE WEIGHT OF A LITER OF OXYGEN

Discussion. The absolute density of a substance in the metric system is defined as the number of grams of a substance contained in a volume of 1 cc. (g./cc.). However, since the absolute density of a gas is generally small, it is more convenient to express the density of a gas by stating the number of grams of the gas contained in a volume of 1 liter.

Inasmuch as the volume of a given quantity of a gas varies with the temperature and pressure, the density will also depend upon these two factors. Therefore, the temperature and pressure of the gas must be stated when its density is reported. Standard conditions (0° and 760-mm. pressure) are the conditions chosen at which to compare the density of different gases. It is therefore necessary to calculate the density that the gas would have at standard conditions from the data taken in the laboratory. This calculation is made by applying Charles' law and Boyle's law to convert the measured volume of the gas to the volume that it would occupy at *standard conditions.*

The experimental determination of the density of a gas requires the determination of the *volume* of a *known weight* of a gas. The measurement of the weight of a gas by direct weighing is subject to a number of errors. Difficulties arise because gases are so light that a rather large volume must be weighed if the desired accuracy is to be attained. If the weight of the container is large compared with the weight of the gas, accuracy cannot be attained with the balances generally available in the laboratory. If the proper precautions are observed and if suitable apparatus is available, however, the density of a gas may be determined by the direct weighing of a known volume.

The weight of the gas may be determined more conveniently by weighing a generator before and after the gas has been evolved from it. This method is used in the present experiment.

The volume of the gas evolved can be measured in a eudiometer or in a container in which the gas is collected over a liquid. Another method used in this experiment measures the volume of water displaced during the collection of the gas.

As previously stated, the temperature and the pressure at which a gas is collected must be known. The gas is allowed to come to temperature equilibrium with the water over which the gas is collected. Its temperature is then determined by measuring the temperature of the water.

The pressure exerted by the gas is determined in the following manner. At the end of the experiment an adjustment is made to equalize the pressure of the collected gas with the pressure of the atmosphere. Thus, if the pressure of the latter is read on a barometer, this value also represents the total pressure exerted by the gas in the collecting flask. However, when the gas is collected over water, the space contains water vapor as well as the gas. Therefore, the partial pressure of the water vapor must be subtracted from the total pressure (atmospheric or barometric pressure) to give the partial pressure exerted by the gas. The partial pressure of the water vapor in the space is equal to the vapor pressure (aqueous tension) of water at the temperature of the water.*

The volume of the gas at the measured temperature and the "corrected pressure " may then be converted to the volume which the gas would occupy at 0° and 760-mm. pressure. The weight of the gas divided by its volume at 0° and 760 mm. times 1000 gives the density

* The value of the vapor pressure of water at different temperatures is given in Appendix C.

of the gas at standard conditions. The density thus determined may be used to characterize the gas, or to calculate its molecular weight. If the molecular weight is known, as is the case with oxygen, the volume of 1 gram-molecular weight at standard conditions may be calculated. This volume is known as the gram-molecular volume (G.M.V.). It is the volume occupied by 1 mole of any gas at standard conditions.

Apparatus and Materials: 1.5 g. of potassium chlorate; 0.1 g. of manganese dioxide; glass wool; 6-in. Pyrex test tube; a No. 0 one-holed rubber stopper; 30 cm. (1 ft.) of 6-mm. rubber tubing; beam balance.

(A) Determination of the Density of Oxygen. Dry 0.1 g. of manganese dioxide by heating it in a porcelain crucible for 1 or 2 min. Heat 1.5 g. of potassium chlorate in an evaporating dish gently with a small flame to drive off any moisture. Do not fuse the potassium chlorate.

While the crucible and evaporating dish are cooling to room temperature, set up an apparatus illustrated in Fig. 52. Use a 6-in. Pyrex test tube and the wash bottle prepared

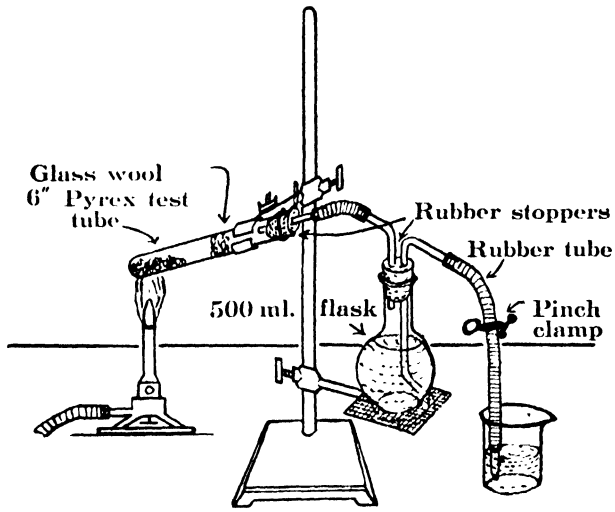


FIG. 52. Weight and volume of a gas by displacement

in Exp. II. Fill the flask with distilled water to the level indicated on the diagram. Attach an empty test tube to the apparatus and make the following test to determine whether the apparatus is airtight. Open the pinch clamp and blow a *few bubbles* of air through the exit tube into the flask. Note that the water rises in the exit tube which extends to the bottom of the flask. Why? [1] The apparatus is airtight if the level of the water does not fall.

Remove the test tube and place the 1.5 g. of dried potassium chlorate in the bottom of the tube. Next add 0.1 g. of the manganese dioxide (a *small* amount on the end of a spatula) to the test tube. Shake the tube to mix the two substances. Place a loose plug of glass wool (**DANGER!** not cotton!) in the position indicated. The glass wool is used to prevent the escape of a finely divided potassium-chloride dust which is produced when the potassium chlorate decomposes too rapidly. Weigh the test tube and its contents to the nearest 0.01 g. (10 mg.) on a beam balance. Record the data in the proper places on the report sheet.[2]

Fill the exit tube with water by opening the clamp and blowing into the other tube. Allow a small amount of water to run into a 100-ml. beaker; then stop the flow of water with the pinch clamp. Allow the end of the exit tube to remain in the water. Attach the test tube. Open the pinch clamp and slip it over the glass tube so that it will not be necessary to hold the clamp open. Raise the beaker containing the water until the level of the

water in the beaker coincides with the level in the flask. Keep the end of the exit tube below the surface of the water. This procedure allows water to flow in either direction until the pressure of the gas above the water is the same as the atmospheric pressure. Hold the beaker at this height from 2 to 3 min. Now clamp the rubber tube with the pinch clamp while the beaker is held in this position.

Clean and dry a 400-ml. beaker and place it under the exit tube. Begin to heat the test tube gently and immediately open the pinch clamp. Why? [3] Why is water displaced into the beaker before oxygen is evolved? [4] Continue to heat the test tube until oxygen is given off and until water is displaced into the beaker. Heat the test tube slowly, otherwise oxygen may be liberated faster than water can escape through the nozzle, and the pressure developed may blow out the stopper.

Discontinue the heating after about 300 ml. of water has been driven over. The water in the flask should not be allowed to fall below the end of the tube which extends to the bottom of the flask. Why? [5] Allow the test tube to cool with the clamp open and with the end of the exit tube under the surface of the water in the beaker. As the test tube cools to room temperature part of the water will return to the flask. Why? [6]

While the test tube is cooling, read the barometer and correct the observed height of the mercury to the calculated height at 0°. (Tables for the correction are to be found in Appendix D.) Record the values in the spaces provided on the report sheet.[2] Measure the temperature of the water which has been displaced (be careful not to spill or to lose any of the water from the beaker). The temperature of the water and the gas *in the flask* is assumed to be the same as the temperature of this displaced water. What is the difference between this temperature and the room temperature? [7] The temperature of the water in the beaker will more closely represent the temperature of the gas if the temperature of the water is nearly the same as that of the room. Consider the construction of the apparatus and suggest why the above statement is true.[8] Subtract the vapor pressure of water from the barometric pressure to obtain the partial pressure of the oxygen in the flask.[2]

When the test tube has cooled to room temperature, raise the beaker so that the level of the water in the flask is the same as the level of the water in the beaker. Hold the beaker in this position 2 or 3 min. Why? [9] Close the clamp on the rubber tube. Measure the volume of the water in the beaker as carefully as possible by means of a 100-ml. graduated cylinder.[2] This volume represents the volume of oxygen at the measured temperature and at a pressure equal to the partial pressure of the oxygen in the flask.

Weigh the test tube with the residue.[2]

Calculate the density of oxygen at the temperature and pressure of the oxygen collected in the experiment.[2] Calculate the volume that the dry oxygen would occupy at standard conditions (0° and 760-mm. pressure).[2] Then calculate the weight of 1 liter of oxygen under these conditions.[2] The accepted value of the density of oxygen at standard conditions is 1.429 g./l. What is the percentage error of the density determined in this experiment? [2]

(B) Questions and Problems

1. Calculate the volume which would be occupied by 1 mole of oxygen (32 g.) at 0° and 760-mm. pressure. Use the value for the density obtained in this experiment. What is the name given to this volume?

2. Why was it necessary to dry the potassium chlorate and the manganese dioxide? Would errors from this source cause the result to be too high or too low? Explain.

3. If fine particles had escaped from the test tube during heating, would the value of the density be too high or too low? Explain.

4. Would the result be too high or too low if the test tube had not been allowed to cool sufficiently? Explain.

5. Does the fact that oxygen dissolves in water to some extent have any effect upon the accuracy of the experiment? How does it affect the result?

6. Suggest other possible sources of error in the experiment. Which of these or which of the above errors account for the largest part of the percentage error of the result of this experiment?

7. Does the amount of gas originally present in the test tube and flask introduce any error? Why?

8. Calculate the weight of 100 ml. of oxygen at standard conditions.

9. What volume would be occupied by 5 g. of oxygen at standard conditions?

10. What weight of potassium chlorate will be required to yield 5 g. of oxygen?

Name (last name first) _____ Desk No. _____ Date _____

Experiment XV

THE WEIGHT OF A LITER OF OXYGEN

(A) Determination of the Density of Oxygen

1.

2.

Weight of test tube + contents before heating . . . . . .
Weight of test tube + contents after heating . . . . . _____
Weight of oxygen evolved . . . . . .
Volume of water displaced (Volume of O_2) . . . . . .
Temp. of water displaced (Temperature of O_2) . . . . . .

Barometer reading . . . . . .
Correction . . . . . _____
Barometric pressure . . . . . .
Vapor pressure . . . . . .
Pressure of oxygen . . . . . .
Density of O_2 at observed pressure and temperature . . . . . .

Volume of O_2 at standard conditions . . . . . .
Density of O_2 at standard conditions . . . . . .
Percentage error . . . . . .

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XV (Cont'd)

(A) Cont'd

7.

8.

9.

(B) Questions and Problems

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XV (Cont'd)

(B) Cont'd

5.

6.

7.

8.

10.

Experiment XVI

METHODS OF PREPARING HYDROGEN

Discussion. Hydrogen is obtained by a variety of reactions from compounds containing this element. Before any one of these methods is used to make hydrogen, a number of factors must be considered. Some of these are: cost of the reactants involved; type of apparatus required; conditions of temperature and pressure that are necessary; the total amount of hydrogen needed; the rate at which the hydrogen must be produced.

Some of the methods best suited for the production of large quantities of hydrogen at a rapid rate do not, for one reason or another, lend themselves to the preparation of the relatively small amounts of the gas needed in the laboratory. For example, hydrogen may be prepared quickly by passing steam through a layer of white-hot coke. Would this method be best suited to industrial operations or to work in the laboratory? Advance reasons to justify the conclusion reached.[1] On the other hand, tin reacts slowly with hydrochloric acid to yield hydrogen and stannous chloride. Give several reasons to show why this method is unsuited either for industrial or for laboratory operations.[2]

The most commonly used sources of hydrogen are water, and the appropriate acids and bases. Certain methods used to prepare hydrogen from these compounds are illustrated in this experiment.

Apparatus and Materials: Nickel or iron crucible; small pieces of sodium and calcium; 13 cm. (about 5 in.) of magnesium ribbon; 0.3 g. of aluminum turnings; 0.2 g. of each of the following metals: magnesium (turnings), zinc (mossy), iron (nail), tin (mossy), lead (granulated), and copper (turnings); 2 g. of sodium hydroxide (pellets or flakes).

(A) Hydrogen from Water. 1. Electrolysis. If a Hofmann apparatus (Fig. 53) is available in the laboratory, connect it to a 6-volt storage battery or to a 110-volt D.C. line with a 60-watt lamp in series with the apparatus. Determine the time required to liberate several milliliters of hydrogen and then calculate the rate (in ml. per hour) of the formation of the hydrogen and the oxygen.[1] Write the equations for the electrode reactions * taking place.[2]

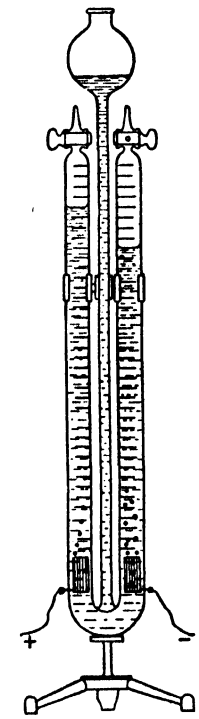


FIG. 53. Hofmann apparatus

Large amounts of industrial hydrogen are produced as a by-product in the electrolytic preparation of chlorine and of sodium hydroxide.

2. The Action of Metals on Water. Drop a very small piece (0.05 g.) of *sodium* into a 100-ml. beaker containing 50 ml. of water.† Tell what occurs.[3] An explosion results when a large piece of sodium is placed on water. What can be concluded regarding the density of sodium relative to that of water? [4] Write an ionic equation to express the reaction that takes place.[5] Test the effect of the solution upon blue litmus paper and upon red litmus paper. Result? [6] This behavior is characteristic of the hydroxide ion (OH^-) found in aqueous solutions of all *bases*. Classify the action of sodium with water on the basis of the thermal change accompanying the reaction.[7] If sodium is

* Ask the instructor for information about the electrolyte being used in the apparatus.

† Sodium metal is to be made available to the student only from the stockroom.

amalgamated (alloyed) with mercury, the resulting *amalgam* yields the same products with water as those formed when sodium alone reacts with water. The mercury remains unaffected. However, the reaction between sodium amalgam and water is much less vigorous than that between sodium and water. Give a reason for this difference.[8]

Test the action of *calcium* with water. Write the ionic equation for the reaction.[9] Draw a conclusion regarding the degree of chemical activity of this metal as compared with that of sodium. Upon what experimental fact is the conclusion based? [10]

3. Aluminum Amalgam. Prepare aluminum amalgam by placing a few pieces of aluminum turnings in a test tube with 5 ml. of water to which 10 drops (0.5 ml.) of a 0.1*N* solution of mercuric chloride (laboratory reagent shelf) have been added. The amalgam is formed as a result of the reaction:

$$2Al + 3Hg^{++} \rightarrow 2Al^{+++} + 3Hg$$

Mercury is liberated on the surface of the aluminum, and at once amalgamates with this metal. Watch the surface of the aluminum for several minutes. Tell what takes place.[11] Write an ionic equation to show the reaction between aluminum and H_3O^+.[12] What can be said about the relative rate of this reaction? [13]

4. The Action of Metals on Steam. Boil 30 ml. of water in a 250-ml. Erlenmeyer flask. Heat strongly to insure a rapid flow of steam from the flask. Then light a 10-cm. length of magnesium ribbon (hold it with a crucible tongs) and quickly thrust it as far down into the flask as possible. Do not drop the burning ribbon into the water. Is there any apparent change in the rate of oxidation? [14]

Thrust a burning wood splint into the steam. What does the result indicate regarding the amount of free oxygen in the atmosphere in the flask? [15] From what source does the magnesium obtain the oxygen necessary for its continued combustion? [16] Write an equation to represent the combustion of magnesium in steam.[17]

Other metals when heated also react with steam. Recall the action of iron with steam (Text). Write the equation for the reaction.[18]

(B) Hydrogen from Acids. Most acids react with certain metals to yield hydrogen, but in some cases the gas is not liberated because it is involved in secondary reactions before it has a chance to escape from the reaction mixture. On the other hand, certain metals are incapable of reacting with any acid to give hydrogen as one of the products.

The rate at which hydrogen is liberated from an acid by a metal depends upon a number of factors, one of which concerns the chemical activity of the metal. The more active a metal is, the more rapidly does it liberate hydrogen from acids. Thus, if a comparison is made of the rates at which different metals liberate hydrogen from acids, it is possible to place the metals in a series in which they are arranged in the order of their activity. What name is given to this series? [1]

Place a 0.2-g. portion of each of the following metals in separate test tubes: aluminum (turnings), copper (wool), zinc (mossy), lead (granulated), iron (nail), tin (mossy), magnesium (turnings). As a means of identifying the contents of the tubes label each test tube and then add 10 ml. of dilute (4*N*) hydrochloric acid to each tube. Note any immediate effect.[2] Thrust a burning splint into the test tube in which the most rapid evolution of gas is taking place. A slight explosion indicates the presence of hydrogen.

CAUTION! Although hydrogen and oxygen do not react with each other at ordinary temperatures, they do so very rapidly if a burning substance or a body at red heat is introduced into the mixture of the two gases. *The interaction is so rapid and so highly exothermic as to cause an explosion.* *Pure* hydrogen from a jet, or *pure* hydrogen in a test tube, burns quietly in air. However, it is extremely dangerous to ignite an amount of hydrogen larger than that contained in a test tube. Before hydrogen is lighted at a jet, its purity must be tested by collecting a test tube full of the gas and then testing this with a flame. If the gas

burns quietly, it is sufficiently pure to be lighted; if there is an explosive pop, the hydrogen is mixed with a dangerously large quantity of oxygen (air). It cannot be emphasized too strongly that extreme caution must be used in carrying out experiments dealing with the generation of hydrogen and with the investigation of its physical and chemical properties.

Observe the test tubes containing the metals and hydrochloric acid, and compare the rates of evolution of hydrogen at the end of 1 min., and again at the end of 3 min. If there are cases in which apparently no reaction occurs, try the effect of raising the temperature of these mixtures. Do not raise the temperature to the boiling point!

On the basis of the visual observations just made, arrange the elements in the order of the *decreasing* rates at which hydrogen was liberated in the various reaction mixtures.[3] This is also the arrangement in the order of decreasing chemical activity. Write an ionic equation for each reaction.[4]

Write a molecular equation for the reaction between zinc and hydrochloric acid.[5] Heat the test tube containing zinc and hydrochloric acid to a temperature of about 80°. Allow the reaction to continue 5 min. and then filter the contents of the tube. Receive the filtrate in a small evaporating dish. Now cover the dish with a watch glass and evaporate the solution just to dryness. Use a small gas flame. Do not heat so rapidly toward the end of the process as to cause loss of the dissolved substance by spattering. Name the residue and describe its appearance.[6] To what class of compounds (acids, bases, or salts) does it belong? [7] Write a *general* statement covering the action in which hydrogen is liberated from an acid by a metal.[8] This type of reaction is called *displacement*. It involves a reaction between a free element and an ion. The latter is reduced or oxidized, as the case may be, to the free state while the original element becomes ionic by a corresponding loss or gain of electrons.

(C) Hydrogen from Bases. Fuse 2 g. of sodium hydroxide in the form of pellets or flakes in a nickel or iron crucible; a porcelain crucible may be used, but its glaze is attacked by fused sodium hydroxide. When the compound is entirely melted, drop into it a little powdered zinc (zinc dust) from the end of a steel spatula. Note the escape of a gas. Test this for hydrogen by bringing the burner flame down to the top of the crucible, and then quickly withdrawing the burner. A slight explosion signifies the presence of hydrogen. Is hydrogen present? [1] Allow the crucible to cool, and then remove its contents by placing it in a stream of running water. A final treatment with dilute hydrochloric acid may be necessary.

Try the action of 10 ml. of a 4*N* solution of sodium hydroxide with a few pieces of aluminum turnings and with a small amount of zinc dust. Warm the reaction mixtures, and test the escaping gas for hydrogen. Results? [2]

Write equations for the reactions of aluminum and zinc with sodium hydroxide.[3] The reaction between molten sodium hydroxide and zinc follows essentially the same course as that taking place in solution.

(D) Other Methods of Preparing Hydrogen. The action of a nonmetal on steam at a high temperature has been mentioned in the **Discussion** at the beginning of this experiment as a method suitable for the industrial preparation of hydrogen. Write an equation to express the reaction.[1]

Hydrogen combines with the most active metals to form binary compounds called *metal hydrides*. When these compounds, such as LiH (lithium hydride) and CaH_2 (calcium hydride), are fused, the liquids conduct the electric current. The metallic ions are the cations, while the hydride ion (H^-) is the anion.

Write equations for the electrode reactions in the electrolysis of calcium hydride.[2] Hydrogen is one of the products formed by the action of a metal hydride on water. Write a molecular and an ionic equation to express the reaction.[3, 4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVI

METHODS OF PREPARING HYDROGEN

Discussion

1.

2.

(A) Hydrogen from Water.. *Electrolysis*

1.

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVI (Cont'd)

(A) Cont'd

The action of metals on water

6.

7.

8.

9.

10.

Aluminum amalgam

11.

12.

13.

Name (last name first) Desk No. Date

Experiment XVI (Cont'd)

(A) Cont'd

The action of metals on steam

14.

15.

16.

17.

18.

(B) Hydrogen from Acids

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVI (Cont'd)

(B) Cont'd

5.

6.

7.

8.

(C) Hydrogen from Bases

1. **2.**

3.

(D) Other Methods of Preparing Hydrogen

1.

2.

3.

4.

Experiment XVII

FACTORS INFLUENCING THE RATE OF DISPLACEMENT OF HYDROGEN BY METALS

Discussion. Hydrogen gas is evolved when metals more active than hydrogen are placed in contact with certain acids:

$$Zn + 2H_3O^+ + SO_4^= \rightarrow Zn^{++} + SO_4^= + H_2\uparrow + 2H_2O$$

This type of reaction is known as displacement. It should be distinguished from combination and decomposition reactions.

The rate of the displacement of hydrogen by a *given sample of a metal* depends upon several factors:

1. Hydronium Ion Concentration. The concentration of the hydronium ions varies with the concentration of a given acid. If the same concentration of two different acids is used, however, the rate of displacement of hydrogen will be greater for the stronger acid, that is, the acid which is ionized to the greater extent.

2. Temperature. A rise in temperature increases the rate of displacement reactions. The rate of most chemical reactions is doubled for each 10° rise in temperature. However, for certain reactions the rate is more than doubled. If the reaction is exothermic, and if the heat is not conducted away at a sufficient rate to maintain a uniform temperature, the reaction tends to become more and more rapid. The higher the temperature at which the reaction takes place, the more pronounced is this effect.

3. Surface. The greater the surface of the metal exposed to the acid, the greater will be the rate of displacement. Thus if a given weight of a metal be subdivided so that its surface area is twice that of the original surface, the rate of displacement should be doubled. Similarly, if the weight of a metal in the same state of subdivision is doubled, then twice the surface is presented and the rate of displacement is twice the initial rate.

4. Couples (Catalysts). The rate of displacement of hydrogen proceeds much more rapidly when the metal (zinc) is in contact with a less active metal (copper, platinum, etc.). The zinc ions go into solution and the hydrogen is liberated at the surface of the less active metal. The two electrons lost by each zinc atom as it goes into solution move through the remaining metal to the copper where they attract and discharge the hydronium ions. This process prevents the accumulation of a film of hydrogen on the zinc (polarization) and thereby allows better contact of the metal with the solution. None of the less active metal is used up in the process. The less active metal, therefore, acts as a catalyst.

5. The Activity of the Metal. If different metals are compared, the rate of displacement of hydrogen from an acid of a given concentration will be found to depend upon the activity of the metal. The higher the metal is in the electromotive series, the more rapidly will it displace hydrogen from the acid. This is true only if all other factors are the same. Metals below hydrogen in the electromotive series will not displace hydrogen from acids. The relative activity of the metals was studied qualitatively in Exp. XVI, part (B).

Measurement of the Rate of Displacement. Whenever it is desired to study the influence of one factor on the rate of a reaction, all other variable factors must be held constant. Thus, in order to study the influence of the concentration of an acid upon the rate of displacement of hydrogen by a *given metal*, the temperature, the surface, and the presence of couples or catalysts must be the same for each concentration of acid compared. If the

effect of the activity of the metal upon the rate of displacement is studied, then all four of the other factors must be the same for each metal.

Apparatus and Materials: 5 g. of powdered zinc; * beam balance; 50-ml. Mohr-type burette; 90 cm. (3 ft.) of small rubber tubing; two one-holed rubber stoppers (No. 0 and No. 00).

(A) The Effect of the Concentration and Strength of the Acid. Obtain a Mohr-type burette, a burette clamp, and about 90 cm. (3 ft.) of small rubber tubing (7 mm.). Arrange an apparatus as illustrated in Fig. 54. The section of rubber tubing attached to the funnel

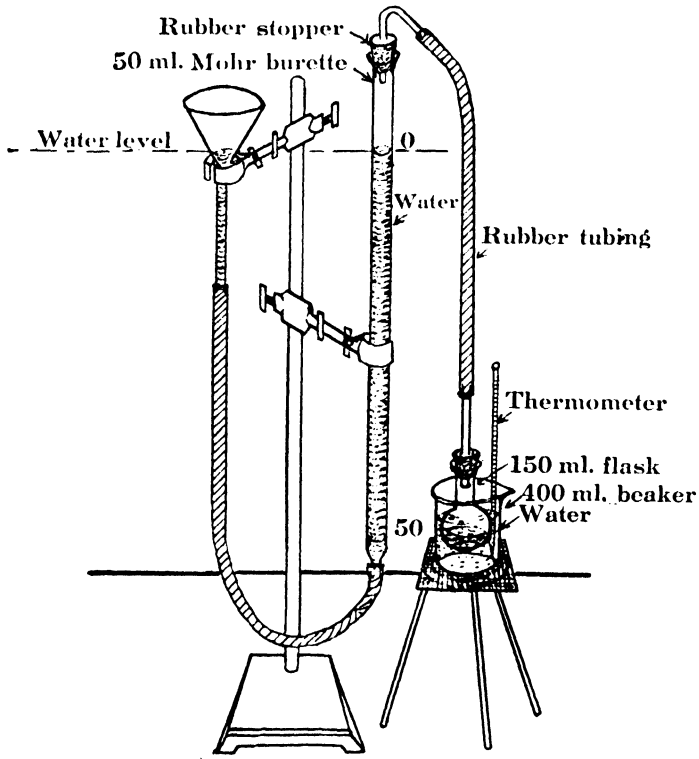


FIG. 54. Apparatus for determining the rate of evolution of hydrogen

should be long enough to allow the funnel to be raised to the top of the burette (about 45 cm.). Fill the burette with water by pouring water into the funnel until the water levels are as indicated in Fig. 54. If the rod of the ring stand is not sufficiently long to support the funnel at the height indicated, the funnel should be held in position while the burette is being filled with water.

Make up 300 ml. of *2-normal* † (2*N*) hydrochloric acid by diluting 50 ml. of concentrated hydrochloric acid (12*N*) with 250 ml. of distilled water. Prepare 120 ml. of 3*N* hydrochloric acid by adding 30 ml. of concentrated hydrochloric acid to 90 ml. of water. Dilute 45 ml. of 4*N* acetic acid with distilled water to obtain 60 ml. of 3*N* acetic acid.

Weigh out six 0.50-g. portions of powdered zinc to the nearest 0.01 g. (10 mg.) on the

* Because of the variable degree of purity of zinc, depending upon its source, the metal available in the laboratory should be tested by the instructor to determine whether the rate at which it liberates hydrogen is too rapid to permit the making of measurements. If this is the case, the acid concentrations should be decreased by one half (or more) in order to obtain a slower rate of evolution of hydrogen.

† A 1-normal (1*N*) solution of an acid contains 1 gram-equivalent weight of the acid in 1 liter of solution. A 2*N*-solution contains 2 gram-equivalent weights of the acid in 1 liter of solution. The method of expressing the concentration of electrolytes in terms of their normality is discussed later on.

beam balance; also a 1.00-g. portion. Place each of these on a small square of paper so that they will be ready for use.

1. Reaction between Powdered Zinc and 2*N* Hydrochloric Acid. Remove the stopper from the reaction flask and measure 50 ml. of the 2*N* hydrochloric acid into the flask. Raise the funnel with the left hand until the water rises to the zero mark on the burette. The water should not be above the top of the stem of the funnel when this adjustment is made. Now with the right hand pour one of the 0.50-g. portions of powdered zinc into the acid in such a way as to prevent the powder from adhering to the sides of the flask. Insert the stopper and note the time and the position of the meniscus. Record these data on the report sheet.[1] Keep the water in the funnel at the same level as it is in the burette. At the end of 1 min. read and record the position of the water level. Continue to take readings at the end of every minute until 50 ml. of gas have been evolved. If 50 ml. have not been evolved in 20 min., discontinue the readings and use the data collected during this time. Record the temperature several times during the determination.

2. Reaction between Powdered Zinc and 3*N* Hydrochloric Acid. Repeat the above procedure, but this time use 50 ml. of the 3*N* hydrochloric acid instead of the 2*N* hydrochloric acid. The volume should be read at consecutive intervals of *30 sec. each.* Record the data in the same manner described above.[2]

3. Reaction between Powdered Zinc and 3*N* Acetic Acid. Repeat the same experiment, but this time use 3*N* acetic acid and 0.50 g. of powdered zinc. It is not necessary to read the volume more frequently than every *2 min.* The funnel may be rested in the burette clamp between readings. However, the levels of the water must be the same at the time a reading is made. Make certain that the stoppers are tight, otherwise air may leak into the burette. Record the data in the same manner as described above.[3]

(B) The Effect of Couple Action (Catalysis). Repeat the general procedure described in part (A), but modify it as follows: Add a 0.50-g. portion of powdered zinc to the empty reaction flask. Dilute 5 ml. of 0.1*N* cupric nitrate ($Cu(NO_3)_2$) solution to 17 ml. with distilled water. Add this to the powdered zinc. Note the change in color of the zinc. Explain this behavior and write an equation for the reaction.[1]

Place the reaction flask in position, and, after raising the level of the water to the zero mark, pour 33 ml. of the 3*N* hydrochloric acid into the reaction flask. This makes a total volume of 50 ml. of solution which is now 2*N* with respect to hydrochloric acid. Stopper the flask immediately and record both the time and the level of the water at 30-sec. intervals.[2] Record the temperature several times during the experiment.[2]

(C) The Effect of Surface. The effect of increased surface of the zinc could be studied best by measuring the rate of evolution of hydrogen from an acid by equal weights of zinc in different states of subdivision. However, since different samples of zinc differ so widely in the amount of impurities present (especially those metals less active than zinc which form couples), this method is often unsatisfactory. The effect of increased surface on the rate of displacement of hydrogen may be studied by employing different weights of the zinc in the same state of subdivision. The comparison of the rates should be made before the reactions have proceeded too far (before 30 to 40 ml. of hydrogen have been evolved). These comparisons are sufficiently reliable for this experiment if the weights of zinc are 0.50 g. or greater.

Repeat the first experiment described (part (A)), except that the 1.00-g. portion of powdered zinc is used with 50 ml. of 2*N* hydrochloric acid. Record the data in the same manner.[1]

(D) The Effect of Temperature. Add 50 ml. of 2*N* hydrochloric acid to the reaction flask and place it in the beaker of water (Fig. 54). Heat the water until its temperature is 10° above the temperature recorded in part (A). Maintain the water at this temperature from 5 to 10 min. in order to establish temperature equilibrium with the solution in the flask. Raise the water in the burette to the zero mark, pour a 0.50-g. portion of powdered

zinc into the flask, and then push into place the stopper which is attached to the rubber tube. Record the time and the position of the water level at consecutive intervals of 30 sec. each.[1] If the temperature begins to fall, warm the water with a *small flame* and then move the flame away from the flask.

(E) The Effect of the Activity of the Metal. It is generally difficult to obtain two metals in the same state of subdivision. Furthermore, some metals may be covered with an oxide film or a layer of grease. Certain metals react much more rapidly than zinc while others react more slowly. Consequently the same concentration of acid cannot be employed with all metals to give a convenient rate of displacement. Quantitative measurements are, therefore, not carried out in this experiment. However a qualitative comparison was made in Exp. XVI, part (B). Reproduce on the report sheet the relative rates of displacement of hydrogen from acids as observed in that experiment.[1]

(F) Questions and Problems

1. Plot the data obtained in parts (A), (B), (C), and (D) on the sheet of graph paper provided with the report sheets. Plot the *time* readings as abscissae along the longer side of the sheet of paper. Let each centimeter division be equivalent to 1 min. Plot the *volumes of hydrogen evolved* [1] (reading of the water level minus the initial reading) as ordinates. Let each centimeter division be equivalent to 3 ml.

Label each curve so as to include the following data: grams of zinc, name and normality of the acid, temperature, and presence of a catalyst. For example, the curve for part (C) should be labelled "0.50 g. Zn, 2*N* HCl, 5 ml. 0.1*N* $Cu(NO_3)_2$, 25° ". Why is it more convenient to compare sets of data by means of curves rather than by inspection of the numerical values recorded in the experiment?

2. Follow up the line on the graph paper that represents 2 min. on the time axis. The intersection of this line with each of the curves gives the volume of hydrogen liberated in 2 min. in each of the experiments. Record these values in the table provided on the report sheet.[2]

3. How many times faster does 0.50 g. of powdered zinc displace hydrogen from 3*N* hydrochloric acid than from 2*N* hydrochloric acid? [3]

4. How many times faster does 3*N* hydrochloric acid react with zinc than does 3*N* acetic acid? Draw conclusions as to the relative strength of these two acids.[4]

5. How many times faster is the reaction of 0.50 g. of powdered zinc with 2*N* hydrochloric acid in the presence of the copper displaced from 5 ml. of 0.1*N* cupric nitrate solution than with 2*N* hydrochloric acid in the absence of the catalyst? [5]

6. How many times does a rise in temperature of 10° increase the rate of displacement of hydrogen under the conditions of this experiment? What is the increase for most reactions? Predict the volume of gas which would probably be obtained in 2 min. at temperatures that are 20° and 30° above the temperature recorded in part (A).[6]

7. Does twice the weight of powdered zinc double the rate of displacement of hydrogen? Record the increase in rate observed in this experiment.[7]

8. Determine the time required in each of the experiments to obtain 25 ml. of hydrogen. Record the values in the table provided on the report sheet.[8]

9. Write the equation for the reaction of zinc with hydrochloric acid. What weight of hydrogen would be obtained by the complete reaction of 0.5 g. of zinc with excess hydrochloric acid? What volume would this weight of hydrogen occupy at 760 mm. pressure? (The density of hydrogen at 0° and 760-mm. pressure is 0.0899 g. per liter.)[9]

10. What weight of zinc chloride could be recovered by evaporating to dryness the solution obtained in the above reaction? [10]

11. Would the volume of hydrogen obtained by the reaction of an excess of acetic acid with 0.5 g. of zinc be greater, smaller, or equal to the volume of gas obtained by the reaction of excess hydrochloric acid on the same weight of zinc? Why? [11]

Name (last name first) Desk No. Date

Experiment XVII

FACTORS INFLUENCING THE RATE OF DISPLACEMENT OF HYDROGEN BY METALS

(A) The Effect of the Concentration and Strength of the Acid

1. $2N$ HCl **2.** $3N$ HCl **3.** $3N$ CH_3COOH

Time	Vol.	Temp.	Time	Vol.	Temp.	Time	Vol.	Temp.

(B) The Effect of Couple Action (Catalysis)

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVII (Cont'd)

(B) Cont'd

2. 2*N* HCl, 5 ml. 0.1*N* $Cu(NO_3)_2$

Time	Vol.	Temp.	Time	Vol.	Temp.	Time	Vol.	Temp.

(C) The Effect of Surface

1. 2*N* HCl, 1.0 g. powdered Zn

Time	Vol.	Temp.	Time	Vol.	Temp.	Time	Vol.	Temp.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVII (Cont'd)

(D) The Effect of Temperature

1. 2*N* HCl, 10 degrees above the temperature in part (A).

Time	Vol.	Temp.	Time	Vol.	Temp.	Time	Vol.	Temp.

(E) The Effect of the Activity of the Metal

1.

(F) Questions and Problems

1. Graph

Name (last name first) Desk No. Date

Experiment XVII (Cont'd)

(F) Cont'd

2. Read from the plotted curves.

Zn	Acid	Temp.	Catalyst	Volume of H_2 evolved in 2 min.
0.50 g.	2*N* HCl			
0.50 g.	3*N* HCl			
0.50 g.	3*N* CH_3COOH			
0.50 g.	2*N* HCl		Cu	
1.00 g.	2*N* HCl			
0.50 g.	2*N* HCl			

3.

4.

5.

6

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVII (Cont'd)

(F) Cont'd

8. Read from the plotted curves.

Zn	Acid	Temp.	Catalyst	Time to evolve 25 ml. of H_2
0.50 g.	2*N* HCl		——— ———	
0.50 g.	3*N* HCl		———	
0.50 g.	3*N* CH_3COOH		———	
0.50 g.	2*N* HCl		Cu	
1.00 g.	2*N* HCl		———	
0.50 g.	2*N* HCl		———	

9.

10.

11.

Experiment XVIII

PROPERTIES OF HYDROGEN

Discussion. Hydrogen is rather inactive at ordinary temperatures unless it has been activated by an electrical discharge at reduced pressures or by alpha particles from radium emanations (Text); occluded hydrogen, or hydrogen at the instant of its liberation on the surface of a metal, is also more active than ordinary molecular hydrogen. The element is characterized by its extremely rapid union with oxygen at high temperatures to form water. Hydrogen also acts with combined oxygen, especially in the case of oxides, and with both free and combined chlorine and the other *halogens* (Text). In these reactions hydrogen is said to be a *reducing* agent; it *reduces* metallic oxides and chlorides. What process is considered to be the reverse of reduction? Illustrate.[1]

Apparatus and Materials: Pneumatic trough; anhydrous calcium chloride (granular).

(A) Laboratory Preparation of Hydrogen. Fit a 250-ml. wide-mouthed bottle * with a two-holed rubber stopper that carries a thistle tube and a delivery tube as shown in Fig. 55. Obtain a pneumatic trough, and fill it with water. Now place 15 g. of mossy zinc and

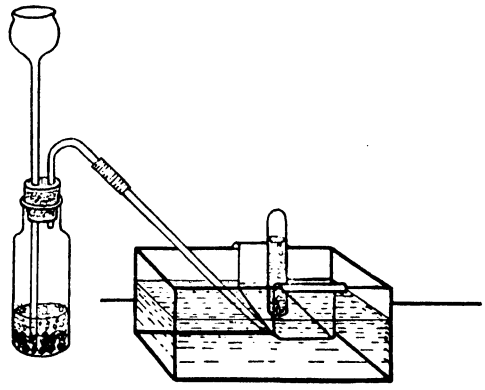


FIG. 55. Generation and collection of hydrogen

100 ml. of dilute sulfuric acid (4*N*) in the bottle, and set up the apparatus as shown in Fig. 55. *Lighted gas burners must be kept at least 2 ft. away from the trough.*

Fill a test tube with water and invert the tube in the trough. *Air must not enter the test tube during this operation!* Fill the tube with hydrogen and then bring it quickly (mouth downward) to a burner flame. A sharp explosive pop shows that the tube contains a mixture of air and hydrogen. Only a very small amount of air enters the tube during the quick transfer from the trough to the flame; in what other way is air introduced into the tube? [1] Continue to collect test tubes full of gas at 2-min. intervals until the gas burns *quietly* when lighted at the burner flame. Note the color of the flame.[2] The hydrogen is now of sufficiently high purity to be used in the following experiments.

* The thick glass of this bottle is not so apt to be shattered by an explosion as is the thinner glass used in the construction of flasks.

(B) Physical Properties. What does the collection of the gas over water show with regard to the relative solubility of hydrogen in water? [1]

Gases lighter than air may be poured *upward* from one container into another. Fill a test tube with hydrogen and then attempt to pour the gas upward into a test tube containing air (Fig. 56). After a few seconds bring the upper tube (mouth downward) to a burner flame. What does the result indicate regarding the relative density of hydrogen as compared with that of air? [2]

Fill a test tube with hydrogen and then quickly bring it down over the mouth of a test tube containing air (Fig. 57). Keep the tubes in this position 30 sec., and then quickly

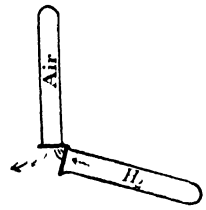


FIG. 56. Pouring hydrogen upward

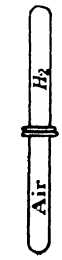


FIG. 57. Diffusion of hydrogen

test each tube for hydrogen. How does the result seemingly contradict the conclusion reached in the preceding paragraph? [3] What can be said about the rate of the process that must have occurred to bring about the observed result? [4]

Summarize the physical properties of hydrogen determined in this experiment, and add any others that may be observed visually.[5] (Odor, color, and solubility in water)

(C) Chemical Properties. 1. The Combustion of Hydrogen. Push a small piece of cotton into a drying tube so as to prevent the passage of solid particles from the bulb into the small tube at the end of the bulb. Do not wad the cotton tightly. Fill the tube with granular *anhydrous* calcium chloride to a distance of 2 cm. from the mouth. Place another

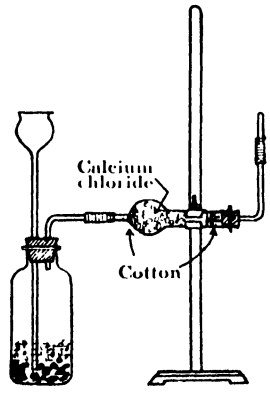


FIG. 58. Preparation of dry hydrogen

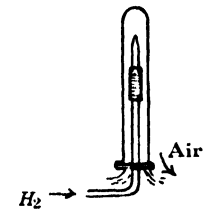


FIG. 59. Collection of hydrogen by downward displacement

plug of cotton in the tube to hold the column of calcium chloride in place. Now fit the mouth of the drying tube with a one-holed rubber stopper which carries a right-angle bend of glass tubing. Attach a glass nozzle or jet (prepared in Exp. II) to the bend as shown in Fig. 58. The distance from the tip of the nozzle to the point at which the tubing is bent should not be less than 15 cm. This distance is specified because a test tube is to be placed over the nozzle in the position shown in Fig. 59.

Remove the delivery tube and the 120-degree bend from the hydrogen generator. Substitute a right-angle bend for the 120-degree bend, and then set up the apparatus as shown in Fig. 58. Allow the generator to work for several minutes, and then test the purity of the hydrogen issuing from the jet. Keep flames at least 2 ft. from the jet. Collect hydrogen for the test by *downward* displacement of the air from a test tube (Fig. 59); allow a minimum time of 2 min. for the displacement. Bring the filled tube (mouth downward) to a burner flame. Proceed with the remainder of the experiment as soon as a sample of hydrogen burns quietly in a test tube.

The stream of hydrogen coming from the generator bottle carries with it water vapor and spray from the acid. Dry hydrogen is obtained by passing the gas through a layer of calcium chloride. This salt reacts readily with water (vapor or liquid) to form *hydrates* that are stable at room temperatures. Is this drying process physical or chemical in nature? Explain.[1] Lower a clean dry 150-ml. beaker down over the jet to test the dryness of the hydrogen. Does a film of water collect on the inner walls of the beaker? [2]

Now test the purity of the hydrogen. When the gas burns quietly, thrust a lighted splint up into the test tube and then quickly withdraw it. Note what occurs as the splint enters the tube, and, on the basis of this observation, make a statement regarding the ability of hydrogen to support combustion.[3] Why does the splint burst into flame again as it leaves the tube? [4]

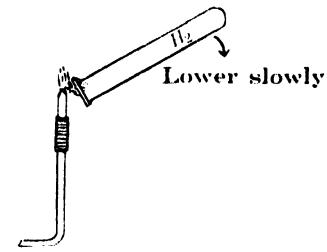


Fig. 60. Lighting a jet of hydrogen

Fill another test tube with hydrogen, and, if it burns quietly, use it as a torch to light the hydrogen issuing from the jet (Fig. 60). **NEVER LIGHT A HYDROGEN GENERATOR BY ANY OTHER METHOD.** Hold a clean dry 150-ml. beaker over the hydrogen flame. Note the deposit formed on the inner walls of the beaker, and write an equation to show how it is formed.[5] Blow out the hydrogen flame.

2. Reduction with Hydrogen. Remove the stopper carrying the right-angle tube with its jet, and connect a Pyrex combustion tube with the drying tube as shown in Fig. 61. Push a combustion boat containing a thin layer of cupric oxide into the central portion of the combustion tube. Attach the right-angle bend with its jet (Fig. 61).

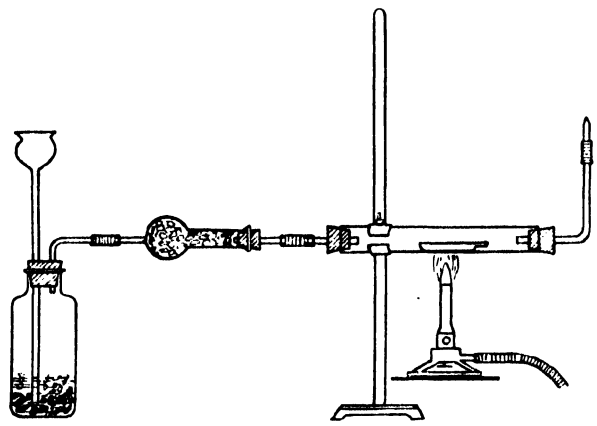


Fig. 61. Reduction with hydrogen

If the hydrogen generator has been operating for a period as long as a half-hour, the supply of acid must be replenished by the addition of 20 ml. of dilute (4*N*) sulfuric acid. Pour the acid through the thistle tube into the generator bottle. The apparatus now contains a dangerously large amount of air which must be expelled before the reduction is

begun. *If the combustion tube is heated previous to the expulsion of air, the apparatus may blow up.* It is therefore necessary to delay the reduction until the hydrogen issuing from the jet burns quietly in a test tube. As soon as this test shows the hydrogen to be free from oxygen, light the gas at the jet with a test tube in which hydrogen is burning.

Now heat the combustion tube strongly under the boat; use a burner equipped with a flame spreader. Note and record any change in the appearance of the cupric oxide.[6] Discontinue the heating after a period of 5 min., and allow the tube to cool in a stream of hydrogen. Blow out the hydrogen flame as soon as the tube is cool and then remove the boat by means of the hook used in Exp. XIII. Lighted gas burners in the vicinity should be turned off before the boat is removed.

Contrast the appearance of the material in the boat with that of cupric oxide.[7] Write an equation to express the chemical change that has occurred.[8] What has been oxidized in the reaction? [9]

3. Reduction in Solution. Place 5 ml. of a 0.1*M* solution of chromic chloride ($CrCl_3$) in each of two separate test tubes. To one of these add 2 ml. of concentrated (12*N*) hydrochloric acid. Now replace the right-angle bend and the jet in the combustion tube, but turn the tube downward so that hydrogen may be bubbled through each of the solutions in the test tubes. (Do not heat the combustion tube.) Pass the gas through each solution for a period of 5 min. Is a change noted in either solution? [10]

Remove the jet from the right-angle bend. Lubricate the hole of a No. 00 one-holed rubber stopper with glycerol, and then insert the jet in the stopper so that the wider end of the tube projects just below the bottom of the stopper. Now drop a 0.5-g. portion of mossy zinc into each of the solutions of chromic chloride. Place the stopper holding the jet in the test tube containing the solution to which 2 ml. of concentrated hydrochloric acid was added; fit a solid stopper into the other test tube. Observe both solutions and record any evidence of chemical change.[11] Now set the tubes aside for a period of 10 min.

During the 10-min. interval dismantle the apparatus used throughout this experiment. Pour the acid into the sink and wash the liquid down the drain with running water; dispose of the zinc in a waste jar provided at the end of the laboratory desk.

Note and record the color of the solutions at the end of the 10-min. interval.[12] Which solution is apparently unchanged? [13] Aside from the action of zinc on hydrochloric acid is there any evidence showing a chemical change in the other solution? [14] Write and balance molecular and ionic equations to express the reaction.[15] Which element is oxidized in this reaction? [16] Which one is reduced? [17] Which one is the oxidizing agent? [18] Which one is the reducing agent? [19]

Now decant several milliliters of the solution of chromous chloride into another test tube. Shake the solution vigorously about 10 sec. What change occurs? [20] What can be assumed to have taken place? [21] Write an ionic equation to express the reaction.[22] How does the relative rate of this reaction compare with that of the reduction of chromic chloride with mossy zinc and hydrochloric acid? [23] Zinc *dust* and the acid cause the reduction to take place much more rapidly. Explain.[24]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVIII

PROPERTIES OF HYDROGEN

Discussion

1.

(A) Laboratory Preparation of Hydrogen

1.

2.

(B) Physical Properties

1.

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVIII (Cont'd)

(C) Chemical Properties. *The combustion of hydrogen*

1.

2.

3.

4.

5.

Reduction with hydrogen

6.

7.

8.

9.

Name (last name first) Desk No. Date

Experiment XVIII (Cont'd)

(C) Cont'd

Reduction in solution

10.

11.

12.

13.

14.

15.

16. **17.**

18. **19.**

20.

21.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XVIII (Cont'd)

(C) Cont'd

22.

23.

24.

Experiment XIX

THE VALENCE AND THE EQUIVALENT WEIGHT OF A METAL BY DISPLACEMENT OF HYDROGEN

Discussion. The valence of an element or a radical is that number which represents the number of atoms of hydrogen or other univalent element that the radical or 1 atom of the element combines with or displaces. All atoms do not have the same capacity to displace or to combine with other atoms. Thus 1 atom of sodium or potassium displaces only 1 atom of hydrogen or combines with only 1 atom of chlorine. On the other hand, 1 atom (or 1 atomic weight) of aluminum will displace 3 atoms (or 3 atomic weights) of hydrogen. Therefore the valence of sodium and potassium is 1, and the valence of aluminum is 3.

The equivalent weight of an element is that weight of it which combines with or displaces an atomic weight of hydrogen or any other univalent element (or $\frac{1}{2}$ atomic weight of oxygen). If 1 atomic weight of a given element displaces 2 atomic weights of hydrogen, then the equivalent weight of the element is one half its atomic weight. It follows that the equivalent weight is equal to the atomic weight divided by the valence. Thus the equivalent weight is that weight of an element associated with a single valence. The *gram-equivalent weight* is the equivalent weight expressed in grams.

Similarly, the equivalent weight of an ion or a radical is that weight of it which combines with or displaces 1 atomic weight of hydrogen or any other univalent element. Since the valence of an ion or radical is numerically equal to the charge associated with it, that is, to the number of electrons lost or gained in its formation, the equivalent weight is equal to the formula weight of the ion or the radical divided by its charge. The equivalent weight of an ionic compound is that weight containing 1 equivalent weight of the anion or the cation in question (Text). The equivalent weight of a compound, a radical, or an ion taking part in an oxidation-reduction reaction is shown later to be equal to the formula weight divided by the change in oxidation state of the element, the ion, or the radical concerned.

One of the most direct methods of determining the equivalent weight and the valence of a metal measures the volume of hydrogen displaced by a known weight of a metal. The equivalent weight of the metal is then obtained by calculating the weight of the metal which will displace 1.008 g. of hydrogen. The valence is equal to the atomic weight divided by the equivalent weight.

Apparatus and Materials: 10 cm. of magnesium ribbon; 3 cm. of fine copper wire; 15 cm. (6 in.) of small rubber tubing; 0.5 g. of an unknown metal (aluminum, magnesium, zinc, or iron).

(A) Determination of the Equivalent Weight of Magnesium. Set up an apparatus as illustrated in Fig. 62. If the ring available in the desk set is too large to support the funnel, a clay triangle is placed on the ring, or a second burette clamp may be used.

Weigh 0.1 g. (10 to 12 cm.) of magnesium ribbon to the nearest 0.0005 g. on an *analytical balance.* If an analytical balance is not available, the weight of 1 cm. of the ribbon may be obtained from the laboratory instructor. In this case measure the length of the magnesium ribbon and calculate its weight. Record this weight in the proper place on the report sheet.[1] Fold up the magnesium ribbon and wrap it with a short piece of fine copper wire.

Place the folded ribbon in the test tube and fill the funnel with water. Now open the pinch clamp in order to fill the entire apparatus. All air bubbles must be removed before the reaction is started. Keep part of the liquid in the funnel to prevent air bubbles from being carried down the stem into the apparatus. The exit tube should not extend below the bottom of the stopper. Why? [2]

Fill a 100-ml. graduated cylinder with water and invert it in a 400-ml. (or larger) beaker which is about two thirds full of water. A small square of paper held over the completely filled graduate is more convenient than a glass plate as a means of holding the water in the graduate while it is being inverted.

Pour from 10 to 15 ml. of concentrated (12*N*) hydrochloric acid into the funnel. Open the pinch clamp and allow some of the acid to run into the test tube. Close the pinch clamp

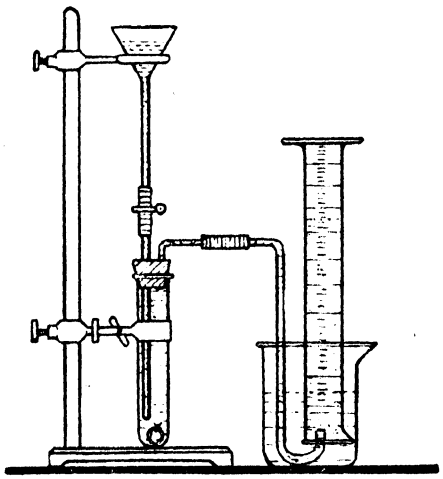


FIG. 62. Determination of the equivalent weight

and allow the reaction to continue until all the magnesium has reacted. Fill the funnel with water, open the pinch clamp and allow the flowing water to drive all of the gas from the test tube and the delivery tube into the graduated cylinder. Do not allow all of the water to run out of the funnel. Add more water if necessary.

Allow the graduated cylinder containing the hydrogen to stand from 5 to 10 min. Why? [3] Measure the temperature of the water in the beaker.[1] Why should the water in the beaker be at about the same temperature as that of the room? [4]

Adjust the graduate so that the level of the water inside is the same as that outside. Why? [5] Read the volume as accurately as possible.[1] Read the barometer and make the necessary correction to obtain the barometric pressure (Appendix D). Subtract from this value the vapor pressure of water (Appendix C) at its present temperature to obtain the pressure of hydrogen in the graduated cylinder. On the basis of what law is this calculation made? [6]

Reduce the volume of hydrogen obtained in the experiment to the volume that dry hydrogen would occupy at standard conditions.[1] The weight of 1 liter of hydrogen at standard conditions is 0.0899 g./*l*. Calculate the weight of hydrogen obtained in the experiment.[1] Then calculate the number of grams of magnesium required to displace 1 g. of hydrogen.[1] Multiply the latter value by 1.008 to obtain the equivalent weight of magnesium.[1] Look up the accepted value for the atomic weight of magnesium and calculate the valence of the metal.

Compare the equivalent weight determined above with the theoretical value and calculate the percentage error of the result.[1]

What would be the effect on the result of the experiment if the level of the water in the graduate had been higher than the level outside? Explain.[7] State the effect of the following operative errors on the result: 1. The apparatus was not airtight and part of the hydrogen escaped. 2. A few bubbles of air were not displaced from the rubber tube. 3. Part of the magnesium remained undissolved.[8]

Look up the solubility of hydrogen in water. Estimate the total volume of water in the test tube plus the volume of water originally present in the graduated cylinder. Calculate the volume of hydrogen that would dissolve in this quantity of water at saturation. What percentage is this of the total volume of hydrogen displaced? [9] Since the solution of a gas in a liquid approaches saturation slowly, the value represents the maximum source of error from this cause rather than the actual error.

Explain the purpose of the copper wire.[10] Write the equation for the reaction of magnesium with hydronium ion.[11] How could magnesium chloride be obtained from the solution in the test tube and in the beaker? [12]

Which of the following metals might be used in this experiment: calcium, copper, lead, aluminum, zinc, silver, iron, potassium, and tin? [13]

(B) Determination of the Equivalent Weight of an Unknown Metal. Repeat the procedure described in part (A) using an unknown metal obtained from the stockroom. Record the number of the unknown, and weigh out about 0.1 g. of the metal to the nearest 0.0005 (0.5 mg.) on an *analytical balance*.[1] The precision of the weighing is then $(\pm 0.0005 \div 0.1) \times 100 = \pm 0.5\%$. This is about the same as the precision attained in measuring the volume of the displaced hydrogen by means of a 100-ml. graduated cylinder—$(\pm 0.2$ ml. $\div 100) \times 100 = \pm 0.2\%$.

If the weighings are made on a small beam balance to the nearest 0.01 g. (10 mg.), the precision in weighing 0.1 g. is only $(\pm 0.01 \div 0.1) \times 100 = 10\%$. Obviously greater precision than this is required. Greater precision may be attained with the small beam balance by weighing out a larger quantity of the metal. Thus if 0.5 g. is weighed to the nearest 0.01 g., the precision is 2%. However, this weight of aluminum (if that metal should be the unknown) displaces 600 to 650 ml. of hydrogen. Carry out this calculation.[2] Therefore a container larger than the 100-ml. graduate must be used to collect the gas.

In case the small beam balance is used, weigh out about 0.5 g. of the metal, obtain a pneumatic trough from the stockroom and collect the gas in a 1000-ml. bottle or flask. After the reaction is complete, and the water levels are equalized, cover the mouth of the bottle tightly and remove it from the trough. Measure the volume of water required to fill the bottle. This volume is equal to the volume of the hydrogen collected. Measure the temperature of the water over which the hydrogen was collected. Determine the pressure of the hydrogen and carry out the calculations indicated on the report sheet.[1]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIX

THE VALENCE AND THE EQUIVALENT WEIGHT OF A METAL BY DISPLACEMENT OF HYDROGEN

(A) Determination of the Equivalent Weight of Magnesium

1. Weight of magnesium . . . . . .

Temperature of the water (hydrogen) . . . . . .

Volume of hydrogen . . . . . .

Barometer reading . . . . . .
Correction . . . . . _____
Barometric pressure . . . . . .

Vapor pressure of water at _____ °C . . . . . .
Partial pressure of hydrogen . . . . . .

Calculated vol. of H_2 at standard conditions . . . . . .

Weight of hydrogen . . . . . .

Grams of Mg to displace 1 g. of H_2 . . . . . .

Grams of Mg to displace 1.008 g. of H_2 (equiv. wt.) . . . . . .

Atomic weight of Mg (atomic wt. table) . . . . . .
Valence of Mg . . . . . .

Percentage error in equiv. wt. . . . . .

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIX (Cont'd)

(A) Cont'd

6.

7.

8.

9.

10.

11.

12.

13.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XIX (Cont'd)

(B) Determination of the Equivalent Weight of an Unknown Metal

1. Number of unknown. . . . . .
Weight of metal . . . . . .
Temperature of water (hydrogen) . . . . . .
Volume of hydrogen . . . . . .

Barometer reading . . . . . .
Correction . . . . . _____
Barometric pressure . . . . . .

Vapor pressure of water at _____ °C . . . . . _____
Partial pressure of hydrogen . . . . . .

Calculated vol. of H_2 at standard conditions . . . . . .
Weight of hydrogen . . . . . .

Grams of metal to displace 1 g. of H_2 . . . . . .

Grams of metal to displace 1.008 g. of H_2 (equiv. wt.) . . . . . .

2.

Experiment XX

PHYSICAL PROPERTIES OF WATER

Discussion. Water holds the position of greatest importance among all liquids. This substance is the most abundant and the most widely distributed liquid in nature; it has an intimate connection with nearly all life, geologic, and industrial processes; and it acts as a medium in which a large number of chemical reactions are carried out.

Chemical properties and processes are concerned in a number of the foregoing considerations. The physical properties of water must also be emphasized, particularly in the natural sciences, because of the use of water as a standard in the determination of a number of important physical constants.

This experiment is concerned especially with the determination of the *heat of vaporization* of water and the *heat of fusion* of ice. Define each of these terms.[1]

Apparatus and Materials: Stop watch or wrist watch; ice.

(A) Specific Gravity and Specific Heat. Water is the reference standard for the specific gravities of liquids and solids. Explain the following statement: [1]

Sp. gr. 18°/18° of substance "X" = 2.630

The density of water at 18° is 0.9986. Calculate the *density* of "X" at 18°.[2] (See Exp. IV.)

The amount of heat necessary to raise the temperature of 1 gram of water 1° C (from 14.5 to 15.5°) is the *small calorie.* This is the most commonly used unit of heat. Explain the meaning of the term "specific heat," and give the specific heat of water.[3] How does the latter value compare with those for the specific heats of the metals? [4]

(B) Heat of Vaporization. Prepare a 45-degree bend of glass tubing with the dimensions shown in Fig. 63. Now fold a piece of note paper of standard size ($8\frac{1}{2}$ by 11 in.) so that it measures $5\frac{1}{2}$ by $8\frac{1}{2}$ in. Wrap this strip tightly around the long arm of the glass bend, and hold the paper in place by two narrow sections of rubber tubing cut from the tubing used on the gas burner.

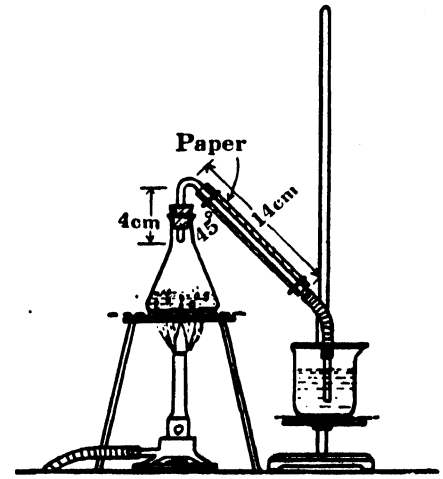


FIG. 63. Determination of the heat of vaporization

Fire-polish both ends of a 9-cm. length of glass tubing and attach it to the long arm of the 45-degree bend with a piece of small rubber tubing 9 cm. in length. Insert the short arm of the bend into a one-holed rubber stopper selected to fit the 250-ml. Erlenmeyer flask. Place the latter on a wire gauze over a tripod, measure out 125 ml. of distilled water into the flask and then fit it with the one-holed rubber stopper which holds the 45-degree bend and the attached 9-cm. length of glass tubing. Now heat the flask so that the water boils vigorously. Adjust the burner to give the maximum amount of heat of which it is capable.

While the water is being raised to the boiling point, support a 400-ml. beaker on a wire gauze placed on an iron ring clamped onto the ring stand. Adjust the position of the ring

stand and the height of the ring until the delivery tube from the Erlenmeyer flask hangs centrally in the beaker with the end of the tube about 4 cm. above the bottom of the beaker (Fig. 63). Remove the beaker and carefully measure into it exactly 300 ml. of distilled water. Record this volume * as V_0.[1] Determine the temperature of the water and record the value as T_0.[2]

Allow the water in the Erlenmeyer flask to boil vigorously. Note the fact that both steam and water issue from the delivery tube. The presence of liquid water is evidence for the condensation of part of the steam in the delivery tube. Measure the *rate* at which condensation occurs by directing the delivery tube over the mouth of a 5-ml. graduate at such an angle that the steam passes over the graduate but the water drops into it. Collect water in the graduate for 1 min. Allow the water to cool, and then measure and record its volume as "rate of condensation in ml./min." [3]

Continue to boil the water vigorously in the Erlenmeyer flask. Grasp the delivery tube at the point at which it is insulated with paper, and turn both the tube and the flask so that the beaker containing 300 ml. of water may be brought up until the tube is immersed in the water. Place the beaker (with the tube in it) on the ring stand and allow steam to bubble into the water 40 sec. *The time interval begins at the moment the delivery tube is immersed in the water.* Stir the water with a thermometer throughout the 40-sec. period. At the end of this time turn the delivery tube and the beaker so that the latter may be moved off the wire gauze and then lowered away from the delivery tube. Measure and record the temperature at once. Stir constantly while making this reading, and be certain that the maximum temperature reached is the one recorded as T.[4] Now discontinue the generation of steam.

Carefully determine the volume of the water in the beaker. Use the 100-ml. graduate to measure three 100-ml. portions; the small residual volume is measured in the 5-ml. graduate. Record the total volume as V.[5] Correct this volume for the number of milliliters of steam condensed to water in the delivery tube during the time interval of 40 sec. Record it as $V_{corr.}$.[6]

Calculate the following values:

The weight of $V_{corr.}$ at T (Appendix E). Record this value as W.[7]
The weight of V_0 at T_0 (Appendix E). Record as W_0.[8]
The number of grams of steam condensed. This is $W - W_0$. Record as G_s.[9]
The rise in temperature, $T - T_0$, produced by the condensation of $W - W_0$ grams of steam in W_0 grams of water. Record as Δt.[10]
The number of calories necessary to raise the temperature of W_0 grams of water through a temperature change of Δt. Record as H.[11]
The number of calories given up during the cooling of $W - W_0$ grams of water from 100° to T. Record as H_c.[12]

The heat of vaporization of water in calories per gram is calculated from the above data. An analysis of the experiment shows that the value actually being determined is the amount of heat liberated by the *condensation* of steam to water. Expressed in calories per gram, the quantity is known as the *heat of condensation.* However, since the latter value is numerically equal to the heat of vaporization, the result obtained in this experiment may be used as the value for the heat of vaporization.

Calculation of the number of calories involved in the condensation (or vaporization) of a gram of steam at 100° to water at 100° requires the formulation of a *heat balance* equation which sets up an equality between the heat liberated and the heat absorbed in a system.

* Direct weighing should be substituted for volume measurements throughout the experiment if balances of the proper type are available.

In the system under consideration, heat is evolved by the condensation of steam at 100° to water at 100°, and by the cooling of this water at 100° to the final temperature (T). All of the heat liberated is absorbed by the original weight of water (W_0) with a resultant rise in temperature of Δt. However, that fraction of Δt contributed by the cooling of the condensed water at 100° to the temperature T is not part of the heat of condensation (or vaporization), and therefore the proper correction must be made for this fact. Thus, the heat-balance equation becomes:

$$\left.\begin{array}{l}\text{Calories gained by } W_0 \text{ grams of} \\ \text{H}_2\text{O in the temperature change, } \Delta t\end{array}\right\} = \left\{\begin{array}{l}\text{Calories lost by } G_s \text{ grams of steam +} \\ \text{calories lost in cooling of } G_s \text{ grams} \\ \text{of water from 100° to } T\end{array}\right.$$

In terms of the experimental data the equation is:

$$W_0\Delta t = LG_s + G_s(100 - T)$$

in which L = the heat of vaporization. This equation may now be written in the following form:

$$L = \frac{(W_0\Delta t) - G_s(100 - T)}{G_s}$$

Solve for the heat of vaporization (L) by substituting the proper experimental values in the above equation.[13] Calculate the percentage error.[14] Systematic errors of three classes may contribute to the observed deviation from the accepted value (Appendix A). Point out an error from one of these classes that may have influenced the result of this experiment.[15]

(C) Heat of Fusion. Place 300 ml. of tap water in a 400-ml. beaker, and then paste a small gummed label on the beaker to indicate the position of the water level. Empty the beaker, dry it carefully with a towel, and then accurately measure into it 200 ml. of distilled water. Record the volume as V_0 and the temperature as T_0.[1, 2]

Warm the water to a temperature of about 40°. Record the exact temperature as T.[3] Now quickly add as many pieces of ice as are necessary to bring the water level to approximately the 300-ml. mark. Use a towel to dry each piece of ice just before it is placed in the water. Now stir the mixture of ice and water to hasten the process of melting. Read the *minimum* temperature reached after all of the ice has melted. Record as T_1.[4] Calculate the lowering in temperature ($T - T_1$) and record it as Δt.[5]

Raise the temperature of the water to about 25°.* Record the exact temperature as T_2.[6] Measure the volume of the water at this temperature; record as V.[7]

Calculate the following values:

The weight of V_0 at T_0 (Appendix E). Record as W_0.[8]
The weight of V at T_2. Record as W.[9]
The number of grams of ice melted. This is $W - W_0$. Record as G_i.[10]
The number of calories lost by W_0 grams of water in cooling through the temperature change of Δt. Record as H_c.[11]
The number of calories required to raise the temperature of G_i grams of water from 0° to T_1. Record as H.[12]

The expression for the heat balance is:

$$\left.\begin{array}{l}\text{Calories lost by } W_0 \text{ grams of water} \\ \text{in the temperature change } \Delta t\end{array}\right\} = \left\{\begin{array}{l}\text{Calories required to melt } G_i \text{ grams of} \\ \text{ice + calories required to raise the} \\ \text{temperature of } G_i \text{ grams of water} \\ \text{from 0° to } T_1\end{array}\right.$$

* This step is taken to eliminate the changes in volume that would otherwise take place during the measurement of a volume of water whose temperature is considerably below that of the laboratory.

In terms of the experimental data the equation is:

$$W_0\Delta t = L_f G_i + G_i T_1$$

in which L_f is the heat of fusion. This equation is written in its final form as:

$$L_f = \frac{W_0\Delta t - G_i T_1}{G_i}$$

Solve for the heat of fusion after the proper experimental values have been substituted in the last equation.[13] Calculate the percentage error.[14]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XX

PHYSICAL PROPERTIES OF WATER

Discussion

1.

(A) Specific Gravity and Specific Heat

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XX (Cont'd)

(B) Heat of Vaporization

1. V_0 =
2. T_0 =
3. Rate of condensation in ml./min. =
5. V =
4. T =
6. $V_{corr.}$ =
7. W =
8. W_0 =
9. G_s =
10. Δt =
11. H =
12. H_c =
13. L =
14.
15.

(C) Heat of Fusion

1. V_0 =
2. T_0 =
3. T =
4. T_1 =
5. Δt =
6. T_2 =
7. V =
8. W_0 =
9. W =
10. G_i =
11. H_c =
12. H =
13. L_f =
14.

Experiment XXI

PURIFICATION OF WATER BY DISTILLATION

Discussion. Distillation is the process of driving off gas or vapor from a liquid by heating it in a still and then condensing all or some of the products in a condenser or in a cool receiver. This operation is used to separate volatile substances from less volatile ones. If there is a relatively great difference in volatility between two substances, the less volatile one may remain completely in the still during the vaporization of the more volatile component.

The nonvolatile components may be either liquids or solids, whereas the gases dissolved in a liquid are always found in the vapor which escapes from a liquid during the process of distillation. Certain gases are driven out of solution at rates which are so much greater than the rate of vaporization of the liquid that, after a time, the liquid undergoing distillation is found to be free from these gases. Certain other gases do not show this behavior since they are found to be present both in the liquid being distilled and in the distillate throughout the course of the distillation.

Water obtained from lakes, rivers, and wells contains varying amounts of soluble salts of potassium, sodium, calcium, magnesium, and iron. The gases of the air and accidental components, such as ammonia and hydrogen sulfide, are also found in natural water. What other substances are carried by natural water?[1] What impurities are found in rain water?[2] (Text)

Apparatus: Liebig water-jacketed condenser; 250-ml. distilling flask; 110° thermometer.

(A) Nonvolatile Material (N.V.M.) in Tap Water and in Distilled Water. Pour a 10-ml. portion of tap water and an equal volume of distilled water onto separate watch glasses. Use the latter to cover two beakers, each of which contains about 100 ml. of distilled water. Boil the water vigorously until the liquid on each watch glass has evaporated to dryness. What do the results show regarding the amount of N.V.M. in each sample of water?[1]

(B) Distillation. This process is carried out most efficiently in the apparatus shown in Fig. 64. If condensers and distilling flasks are not available, set up an apparatus according to the design given in Fig. 65.

Place 100 ml. of distilled water and *1 drop* of concentrated (15*N*) ammonium hydroxide in the distilling flask or in the 250-ml. Erlenmeyer flask. Fit the flask with the stopper holding the delivery tube. Now fill the beaker with cold water from the tap. Place a clean 6-in. test tube in the beaker and insert the delivery tube in the test tube.

Heat the water in the flask so that it boils slowly. As soon as the volume of the distillate becomes approximately 10 ml., remove the test tube, and substitute an empty one for the collection of a second 10-ml. fraction. Repeat this process until eight fractions have been collected. Arrange the fractions in the order of their collection. Stir the cooling bath from time to time with a thermometer. If, after the collection of any fraction, the temperature of the water in the bath is found to be as high as 60°, replace the warm water with cold water from the tap.

Add *one drop* of a solution of phenolphthalein to the liquid in each of the eight test tubes and to the water remaining in the Erlenmeyer flask. Results?[1] The development of a color denotes the presence of hydroxide ion. Explain its presence in the distillate.[2] What

evidence verifies the statement that ammonia is completely removed from its aqueous solution when the latter is boiled?[3] Approximately what percentage of the original volume of

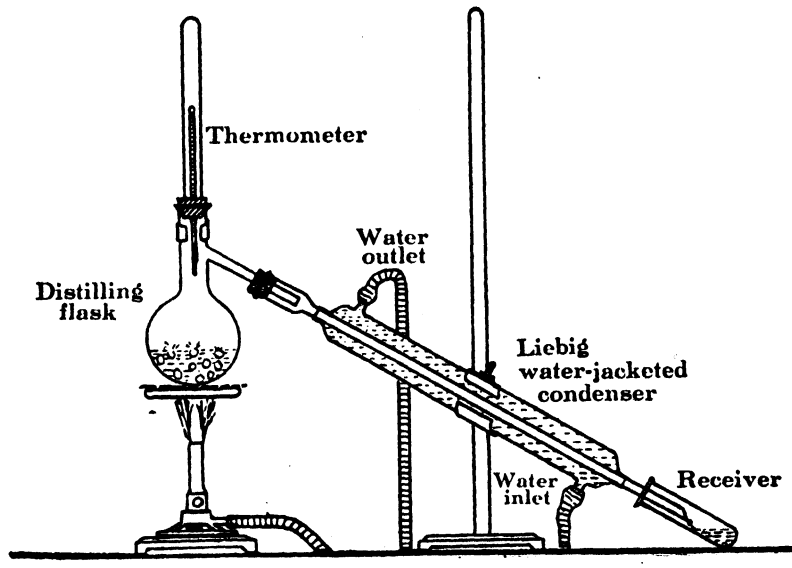


FIG. 64. Distillation

water has to be distilled before the distillate is found to be free from ammonia?[4] Would this be an economical method for obtaining ammonia-free water? Explain.[5]

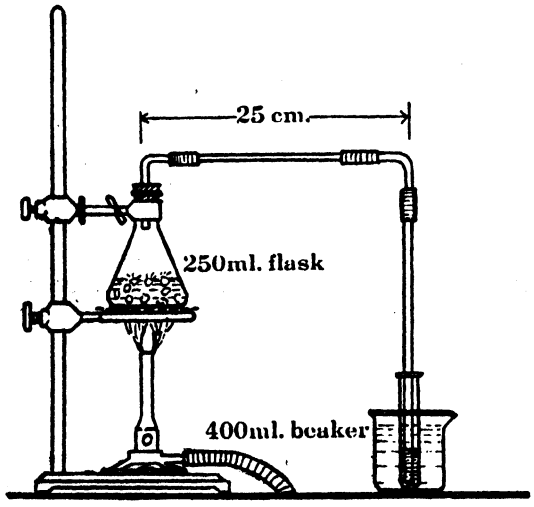


FIG. 65. Distillation

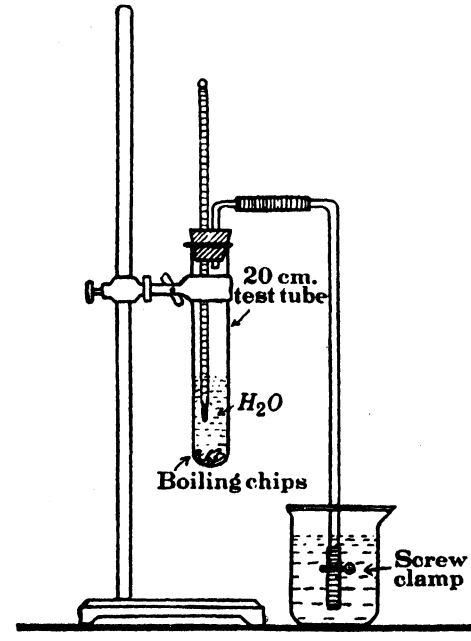


FIG. 66. Boiling under reduced pressure

(C) Relation of Boiling Point to Pressure. Set up the apparatus shown in Fig. 66. Place 25 ml. of water and a few chips of marble in the 20-cm. (8-in.) Pyrex test tube. The chips * cause the water (or other liquids) to boil steadily. Without this aid to boiling,

* Glass beads or small pieces of broken glass or porous clay plate may be substituted for the marble chips.

liquids show a tendency to boil with a series of violent bumps caused by the sudden evolution of relatively large amounts of vapor. Use 6-mm. rubber tubing for the connections. It is essential that the connections be gastight.

Boil the water in the test tube until bubbles no longer issue from the delivery tube and rise to the surface of the water in the beaker. Continue the boiling until a characteristic crackling sound shows steam to be issuing from the delivery tube. Read the temperature of the boiling water and then *remove* the flame from under the test tube. Close the screw clamp *immediately* without removing the delivery tube from the water in the beaker. Note that the water in the test tube continues to boil. Read and record the temperature at the end of successive 10-min. intervals until boiling ceases.[1] Record the minimum temperature at which boiling occurs.[2]

What is the general effect of a change in pressure upon the boiling point of a liquid?[3] What does the change in boiling point of the water indicate with regard to the change in pressure within the apparatus after the removal of the flame and the closing of the screw clamp?[4] Give the reason for the change in pressure.[5] Define boiling point in terms of vapor pressure.[6]

Use the values given in Appendix C to construct a graph showing the vapor pressure of water in the temperature range between 35 and 100°. Plot the temperatures as abscissae along the shorter dimension of the graph paper and the vapor pressures as ordinates. Let 1 cm. on the temperature axis be equivalent to 5°, and 1 cm. on the vertical axis be equivalent to 40 mm. Draw a smooth curve through all of the points.

Read from the curve the pressure prevailing in the apparatus at each of the temperatures recorded in (1).[7] What pressure corresponds to the lowest temperature at which boiling was observed to occur?[8] Extend the curve to the line indicating a pressure of 840 mm. What is the indicated boiling point of water at this pressure?[9]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXI

PURIFICATION OF WATER BY DISTILLATION

Discussion

1.

2.

(A) Nonvolatile Material (N.V.M.) in Tap Water and in Distilled Water

1.

(B) Distillation

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXI (Cont'd)

(B) Cont'd

3.

4.

5.

(C) Relation of Boiling Point to Pressure

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXI (Cont'd)

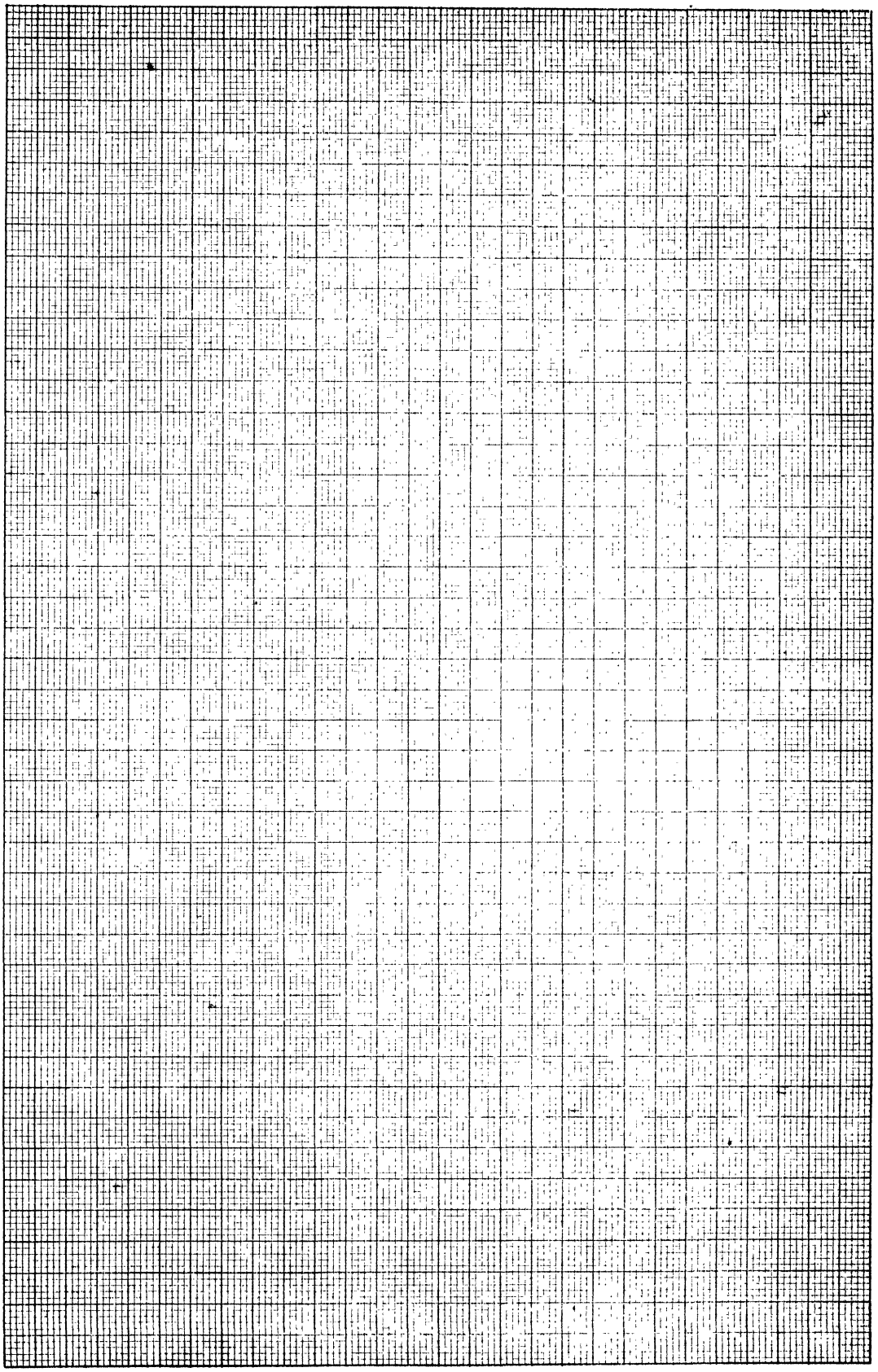
(C) Cont'd

5.

6.

7.

8.



Experiment XXII

CHEMICAL PROPERTIES OF WATER. HYDRATES

Discussion. Water not only reacts with many elements and compounds but it is also an important medium in which other chemical reactions take place. Many reactions are catalyzed by small quantities of water.

Water forms an important class of compounds called hydrates. These must be distinguished from other crystalline substances and from substances which contain the elements of water as water of hydroxylation (hydroxides, for example). In certain solids the water molecules occupy holes in the crystal lattice. Water combined in this way is known as zeolitic water. Hydrous materials adsorb water which can be removed only by heating or by intensive drying.

In order to *dry* gases or liquids it is necessary to choose suitable drying agents. These may be anhydrous salts (those from which the water of crystallization has been removed), substances that react chemically with water to give compounds containing water of hydroxylation, substances that take up water as zeolitic water, or substances that are deliquescent. Physical methods, such as adsorption or refrigeration, may also be employed. The following table gives a comparison of the effectiveness of various drying agents and refrigeration methods used to remove water vapor from the air:

Drying Agent	Mg. of H_2O left in 1 liter of gas
$CuSO_4$ (anhyd.)	1.4
Ice (0°)	0.5
$CaCl_2$ (anhyd.)	0.14
H_2SO_4 (conc.)	0.003
KOH (fused)	0.002
$Mg(ClO_4)_2$ (anhyd.)	less than 0.0002
P_2O_5	less than 0.00002
Dry ice (−80°)	3×10^{-7}
Liquid air (−196°)	3×10^{-23}

Classify each of the above substances according to the manner in which it acts as a drying agent.[1]

Materials: 0.5 g. of potassium iodide; 0.5 g. of tartaric acid; 0.2 g. of phosphorus pentoxide; 15 g. of plaster of Paris; 0.5 g. of zeolite (Permutit).

(A) Water as a Medium for Chemical Changes. 1. Reaction of Lead Nitrate with Potassium Iodide. Mix 0.5 g. of dry pulverized lead nitrate with 0.5 g. of potassium iodide. Is there any noticeable reaction?[1] Add 5 ml. of water to the mixture of salts. Write the equation for the reaction and explain the function of the water.[2]

2. Reaction of Sodium Bicarbonate with Tartaric Acid. Mix about 0.5 g. of solid sodium bicarbonate with 0.1 to 0.2 g. of dry tartaric acid. Now add water. What happens?[3] Thrust a glowing splinter into the test tube. What happens?[4] What gas is evolved?[5] Some baking powders are mixtures of sodium bicarbonate (soda) and a solid acid such as tartaric acid. Explain the use of baking powder in cooking.[6]

3. Reaction of Ammonium Carbonate with Cupric Nitrate. Pulverize about 0.5 g. of ammonium carbonate in a mortar. Heat about 0.5 g. of cupric nitrate in a crucible several

minutes until all of the water of crystallization has been driven off. Allow the salt to cool and then pulverize it in the mortar. Thoroughly mix the two pulverized salts.

Do the salts react?[7] Transfer the mixture to a hard-glass test tube and heat it strongly. (**DANGER!** Do not point the mouth of the tube toward near-by students.) Describe what takes place.[8] Try the reaction of 5 ml. of a 0.1*N* *solution* of ammonium carbonate with an equal volume of 0.1*N* cupric nitrate *solution.* Write the equation for this reaction and explain why it differs so markedly from the reaction between the dry salts.[9]

(B) Dissociation of Water by Heat. Write the equation for the dissociation of water.[1] Define dissociation.[2]

Look up in the textbook the values for the percentage of water dissociated at temperatures above 1500°. Plot these values on graph paper as ordinates (let 1 cm. represent 1 per cent dissociation) and plot the corresponding temperatures as abscissae along the longer side of the sheet of graph paper (let 1 cm. represent 100°). Draw a smooth curve through all of the points.[3] Extend the curve past the line for 3000° and predict the percentage dissociation at 2000° and at 3000°.[4] (**Note:** If the temperatures are given in degrees absolute, they should be changed to degrees centigrade by subtracting 273 from the temperatures recorded.)

(C) Reaction of Water with Elements. Recall the reaction of metals with water to give hydrogen (Exp. XVI). Write equations for the reaction of two metals with cold water.[1] Name two metals which react with water at higher temperatures. Equations.[2] How does the presence of a less active metal influence the reaction of a given metal with water? Give an example.[3]

Name two nonmetallic elements which react with water. What are the products of the reactions? Equations.[4]

(D) Reaction of Water with Metallic Oxides. Add a small piece (about 0.5 g.) of calcium oxide to 10 ml. of water in a 50-ml. beaker. Describe the reaction.[1] Is heat liberated or absorbed?[2] Test the solution with litmus paper.[3] Write the equation for the reaction.[4] Write the equations for the reactions of sodium oxide and sodium peroxide with water.[5] How do the resulting solutions affect litmus?[6] Add about 0.5 g. of cupric oxide to 10 ml. of water. Test the solution with litmus paper. Explain the result.[7]

Aqueous solutions of ammonia (ammonium hydroxide) are made by dissolving the gas in water. Test the solution in the reagent bottle with litmus.[8] Moisten a piece of red litmus paper with water and place it on the convex side of a watch glass. Place the watch glass over a beaker containing 10 ml. of the solution of ammonia. Explain what happens to the litmus paper.[9] Write an equation for the reaction of ammonia with water.[10]

Summarize the properties of hydroxide bases learned thus far (Text).[11]

(E) Reaction of Water with Nonmetallic Oxides. 1. Phosphorus Pentoxide. Obtain about 0.2 g. of phosphorus pentoxide (P_2O_5) from the stockroom. Add it in small portions to about 10 ml. of water. Describe the reaction.[1] Test the resulting solution with litmus paper.[2] Write the equation for the reaction.[3]

2. Sulfur Dioxide. Place 0.2 g. of sulfur in a deflagration spoon. Hold the spoon in a flame until the sulfur begins to burn. Insert the spoon in a wide-mouthed bottle. Why does the sulfur cease to burn after several minutes?[4] Remove the deflagration spoon, cover the bottle with a glass plate, and then add 1 to 2 ml. of water. Shake the bottle and test the solution with litmus.[5] Write the equation for the burning of sulfur and for the reaction of the product with water.[6]

3. Carbon Dioxide. Remove the remaining sulfur from the deflagration spoon. Fill the spoon about three fourths full of wood charcoal. Heat the spoon to *redness* in a flame and insert the glowing charcoal in another wide-mouthed bottle in which 5 ml. of saturated calcium hydroxide solution (lime water) has been shaken. Note the change in appearance

of the drops of lime water adhering to the side of the bottle. Explain.[7] Write the equations for the following reactions:[8] the oxidation of carbon, the reaction of the product with water and with calcium hydroxide.

Summarize the properties of acids learned thus far. (Text)[9] Write the equation for the neutralization of an acid by a base.[10] What is obtained by evaporating the resulting solution to dryness? [11]

(F) Water in Hydrates. 1. A Test for Hydrates. Heat 0.5 g. of the following crystalline substances in separate Pyrex test tubes: borax (sodium tetraborate), potassium chloride, barium chloride, magnesium sulfate (Epsom salts), sodium sulfate (Glauber's salt), and potassium dichromate. Note whether water collects in the cooler part of each test tube. Which of the above substances are hydrates? [1] Are all crystalline substances hydrates? Illustrate.[2]

2. Cupric Sulfate. Heat about 1 g. of cupric sulfate crystals (blue vitriol) in a crucible until all of the water is driven off. Describe the change in appearance of the crystals.[3] Add from 2 to 3 ml. of water and heat the mixture until the water boils. Allow the solution to cool. If crystals do not form, boil off part of the water. Describe the crystals and compare their appearance with the original crystals.[4] Write the equations for the reactions.[5]

3. Cobaltous Chloride. Invisible Ink. Heat about 0.5 g. of crystalline cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) in a crucible. Describe what takes place.[6] Dissolve the residue in from 1 to 2 ml. of water. Dip the end of a match or wooden splint into the solution and write on a piece of filter paper. Warm the filter paper over a small flame. Now breathe upon the heated filter paper. Describe and explain the changes that occur in the appearance of the characters.[7] Write equations for the reactions.[8]

4. Plaster of Paris. Mix 15 to 20 g. of plaster of Paris thoroughly with enough water to form a paste. Transfer the mixture to a funnel which has been fitted with a wet filter paper. Wrap the bulb of a thermometer with a piece of paper and insert it in the mixture. The paper will prevent the thermometer from sticking in the plaster of Paris when the latter sets. Record the temperature every 2 min. for about 10 min.[9] Is the reaction exothermic or endothermic? [10] What time was required for the plaster of Paris to set? [11] What practical use is made of plaster of Paris and its property of setting to a solid mass during hydration? [12]

(G) Water of Hydroxylation and Zeolitic Water. 1. Hydroxides and Hydrous Oxides. Heat about 0.5 g. of solid calcium hydroxide in a Pyrex test tube. What evidence is there for the liberation of water? [1] Write the equation for the reaction.[2] The most active metals form hydroxides which do not decompose in this manner. Heat 0.5 g. of commercially impure aluminum oxide or ferric oxide in a Pyrex test tube. Explain the presence of the water on the cooler part of the test tube.[3]

Explain the difference between hydrates and hydroxides by listing the characterizing features of each.[4]

2. Sugar. Place about 0.5 g. of sugar in a Pyrex test tube and heat the test tube carefully in a flame. Where does the water which condenses on the cooler parts of the tube come from? [5] If water is added to the residue, is sugar re-formed? [6] How does this behavior differ from that of hydrates? [7]

3. Zeolitic Water. Heat 0.5 g. of a zeolite (natural greensand or an artificial zeolite such as Permutit). Is water given off? [8] What is the fundamental difference between zeolites and hydrates? [9]

(H) Drying Agents. Substances which have a marked affinity for water are used to dry gases, liquids, and solids. List the types of substances which may be used [1] (Text and Discussion).

A gas is dried by passing it through a tube or bottle containing anhydrous calcium chloride or some other drying agent. The latter should not react chemically with any of the

components of the gas except water. List a few drying agents other than calcium chloride which might be used to dry air.[2]

Write the equation for the reaction involved when anhydrous calcium chloride is used as the drying agent.[3] What is the relation of this reaction to the dehydration of the hydrate?[4] Write the equation involved when phosphorus pentoxide is used as a drying agent.[5] What component of air other than water vapor would be removed if air is passed through a mixture of sodium hydroxide and calcium oxide (soda lime)?[6] (**Hint:** Recall the use of calcium hydroxide in part (D) of this experiment.)

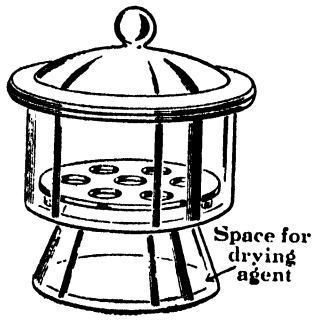


FIG. 67. Desiccator

What difficulty is encountered if anhydrous calcium chloride is used to dry a liquid containing ammonia and alcohol in addition to water?[7]

Solids are very often dried by placing them in a desiccator (Fig. 67) which contains a suitable drying agent. If moist crystals of cupric sulfate are to be dried without dehydration of the hydrate, a drying agent must be chosen that will not reduce the partial pressure of the water vapor in the desiccator below the stability range of the hydrate. What would take place if moist crystals of $CuSO_4 \cdot 5H_2O$ were placed in a desiccator over P_2O_5?[8]

(I) Efflorescence. Hydration and Deliquescence. When the partial pressure of the water vapor in the air is less than the vapor pressure of a hydrate at the existing temperature, dehydration will take place spontaneously and the hydrate is said to *effloresce.*

Will $CuSO_4 \cdot 5H_2O$ effloresce at 30° if the relative humidity is 60 per cent? The vapor pressure of the system $CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 3H_2O$ is 12.5 mm. Record the calculations upon which the conclusion is based.[1] (**Note:** The relative humidity is the ratio, expressed in per cent, of the partial pressure of the water vapor in the air to the vapor pressure of water at the existing temperature, that is, the relative humidity is the percentage saturation of the air with water vapor.)

Water vapor will not react with an anhydrous salt to form a hydrate, or with a lower hydrate to form a higher hydrate unless the partial pressure of the water vapor is at least equal to the vapor pressure of the hydrate. During the process of hydration the partial pressure of the water vapor remains equal to the vapor pressure of the hydrate. When hydration is complete, water vapor will not react to yield the next higher hydrate unless the pressure of the water vapor is equal to the vapor pressure of the higher hydrate.

Given:

Temperature	System	Vapor Pressure
50°	$CuSO_4 \cdot 3H_2O - CuSO_4 \cdot H_2O$	30 mm.
50°	$CuSO_4 \cdot 5H_2O - CuSO_4 \cdot 3H_2O$	47 mm.

If the relative humidity is 50 per cent at 50°, will either or both of these systems react with water vapor under the conditions given?[2] If a mixture of $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$ is placed in an atmosphere with a partial pressure of water vapor equal to 40 mm., will $CuSO_4 \cdot 5H_2O$ form after all of the $CuSO_4 \cdot H_2O$ has been converted to $CuSO_4 \cdot 3H_2O$? Why?[3]

Whenever the partial pressure of the water vapor in the air is greater than the vapor pressure of a saturated solution of a salt or a hydrate, water condenses on the solid to form a saturated solution. When this occurs, the substance is said to *deliquesce.* A very soluble salt is more likely to deliquesce than is a slightly soluble one. Why?[4] Highly deliquescent salts are sometimes employed as drying agents. Name one.[5]

Explain why a saturated solution of a salt in contact with excess solid salt, or a mixture of two hydrates, such as $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$, maintains a constant pressure of water vapor in a closed system.[6]

Experimental Procedure. Place about 0.5 g. of the following substances on a glass plate with a label pasted near each substance to identify it: anhydrous calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), cupric sulfate ($CuSO_4 \cdot 5H_2O$), sodium sulfate ($Na_2SO_4 \cdot 10H_2O$), sodium carbonate ($Na_2CO_3 \cdot 10H_2O$). Place the glass plate on the desk top and observe the appearance of the substances from time to time. List those substances which deliquesce and those which effloresce.[7] Which ones remain unchanged? [8] Remove those compounds which deliquesce and allow the other substances to remain on the glass plate until the next laboratory period. Describe the results.[9]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII

CHEMICAL PROPERTIES OF WATER. HYDRATES

Discussion

1.

(A) Water as a Medium for Chemical Changes. *Reaction of lead nitrate with potassium iodide*

1.

2.

Reaction of sodium bicarbonate with tartaric acid

3. **4.**

5.

6.

Reaction of ammonium carbonate with cupric nitrate

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(A) Cont'd

9.

(B) Dissociation of Water by Heat

1.

2.

3. Graph

4.

(C) Reaction of Water with Elements

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(D) Reaction of Water with Metallic Oxides

1.

2.

4.

5.

6.

7.

8.

9.

10.

11.

(E) Reaction of Water with Nonmetallic Oxides. *Phosphorus pentoxide*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(E) Cont'd

2. **3.**

Sulfur dioxide

4.

5.

6.

Carbon dioxide

7.

8.

9.

10. **11.**

(F) Water in Hydrates. ***A test for hydrates***

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(F) Cont'd

2.

Cupric sulfate

3.

4.

5.

Cobaltous chloride. Invisible ink

6.

7.

8.

Plaster of Paris

9.

10. **11.**

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(F) Cont'd

12.

(G) Water of Hydroxylation and Zeolitic Water. *Hydroxides and hydrous oxides*

1. **2.**

3.

4.

Sugar

5.

6.

7.

Zeolitic water

8.

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(H) Drying Agents

1.

2.

3.

4.

5.

6.

7.

8.

(I) Efflorescence. Hydration and Deliquescence

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXII (Cont'd)

(I) Cont'd

2.

3.

4.

5.

6.

7.

8.

9

Experiment XXIII

THE PREPARATION AND PROPERTIES OF HYDROGEN PEROXIDE

Discussion. Hydrogen peroxide may be prepared by the reaction of an acid with a metallic *peroxide*. Simple oxides or dioxides do not yield hydrogen peroxide.

Solutions of hydrogen peroxide *slowly decompose*. This decomposition is accelerated by light, by solutions of certain salts, and by finely divided substances such as manganese dioxide or platinum.

Hydrogen peroxide can act either as an oxidizing agent or as a reducing agent. Reactions of both types are studied in this experiment. The most common test for hydrogen peroxide is its reaction with potassium dichromate to produce a blue compound (called peroxychromic acid). The blue compound is more soluble in ether than in water. An excess of either the dichromate or the hydrogen peroxide renders the test less sensitive or may even entirely destroy the blue compound.

Materials: 2 g. of sodium peroxide; 0.5 g. of barium peroxide; 3 ml. of ether.

(A) Preparation of Hydrogen Peroxide. 1. From Sodium Peroxide. Measure out 10 ml. of 4*N* sulfuric acid and add it to 95 ml. of cold water contained in a 150-ml. beaker. Stir the acid solution and add about 2 g. of sodium peroxide in small portions. Test the solution with litmus paper. If it is not acid, add more of the diluted sulfuric acid. Name the substances present in the resulting solution.[1] Write the equation for the reaction.[2] What reactions occur when sodium peroxide is added to water? Equations.[3] Reserve the peroxide solution for use in the remaining parts of this experiment. Test 2 ml. of the solution for the presence of hydrogen peroxide according to the procedure described in part (B).[4]

2. From Barium Peroxide. Suspend about 0.5 g. of barium peroxide in 5 ml. of cold water. Add 1 ml. of 4*N* sulfuric acid and shake the mixture. What is the precipitate?[5] Write the equation for the reaction.[6] Filter the solution and test it for hydrogen peroxide as directed in part (B).[7] What advantage is there in using barium peroxide instead of sodium peroxide for the preparation of hydrogen peroxide?[8] Repeat the experiment using PbO_2 and MnO_2 in place of BaO_2. Test for hydrogen peroxide as directed in part (B). Explain the results.[9]

(B) Test for Hydrogen Peroxide. To 5 ml. of a solution to be tested for hydrogen peroxide add 3 ml. of ether. **(DANGER!** Ether is inflammable. It must be kept away from flames.) Add *two drops* of 0.1*M* potassium dichromate and then a few drops of 4*N* sulfuric acid if the solution does not already contain a slight excess of the acid. Close the mouth of the test tube with the thumb, and then shake the tube. Now allow the layers to separate. Explain the result.[1] The reaction of hydrogen peroxide with a dichromate in acid solution to form a blue compound soluble in ether may be used as a test for a peroxide or, conversely, as a test for a dichromate.

(C) Oxidizing Properties of Hydrogen Peroxide. 1. Reaction with a Starch-iodide Solution. Prepare a starch-iodide solution by adding 1 ml. of potassium iodide solution (0.1*N*) to 5 ml. of starch solution. If the starch solution is not already prepared, mix about 0.5 g. of starch (preferably soluble starch) with a sufficient quantity of water to make a paste. Add this paste to 50 ml. of boiling water and allow the solution to cool. Filter it if insoluble material is visible in the solution.

Add 2 ml. of the starch-iodide solution to 5 ml. of the solution of hydrogen peroxide prepared in part (A). What takes place? [1] Write the equation for the formation of iodine in this reaction and explain the appearance of the blue color.[2]

Starch-iodide paper is often used to test for oxidizing agents that will oxidize iodide ion to free iodine. Prepare pieces of starch-iodide paper by immersing strips of filter paper in the starch-iodide solution. Allow the strips to dry and then place them in a corked test tube for use in later experiments. Add a few drops of the hydrogen peroxide solution to one of the pieces of starch-iodide paper (it is not necessary to dry it). What takes place? [3]

2. Oxidation of Lead Sulfide. Cut a narrow strip of filter paper and moisten it with 0.1*N* lead acetate solution. Hold the paper above 5 ml. of a 0.1*N* solution of ammonium sulfide in a 50-ml. beaker. Ammonium sulfide decomposes to give ammonia and hydrogen sulfide. Cautiously smell the gas above the solution. What happens to the strip of moist filter paper? Write the equation for the reaction.[4] Dip the blackened filter paper into a portion of the hydrogen peroxide solution prepared in part (A). Explain the result and write the equation for the reaction.[5]

White lead (basic lead carbonate $[Pb_3(OH)_2(CO_3)_2]$) is an important pigment often used in paints. Hydrogen sulfide in the air gradually converts this compound to lead sulfide. Explain how hydrogen peroxide could be used to restore old paintings.[6]

(D) Reducing Properties of Hydrogen Peroxide. 1. Reaction with Potassium Permanganate. Dilute 10 drops of 0.1*M* potassium permanganate solution to 5 ml. with distilled water. Add about 1 ml. of 4*N* sulfuric acid. Note the color of the solution.[1] Pour this solution slowly into 5 ml. of the hydrogen peroxide solution prepared in part (A). Result? [2] Test the gas evolved with a glowing splinter. What is the gas? [3] Write the equation for the reaction.[4]

Continue to add the potassium permanganate solution. Note that the solution is colored as soon as all of the hydrogen peroxide has been used up. Explain how this procedure could be used to determine the amount of hydrogen peroxide in a given volume of the solution.[5]

2. Reaction with Manganese Dioxide in Acid Solution. Add 5 ml. of 4*N* nitric acid to a *small* quantity (0.05 g.—a quantity about equal in volume to that of a match head) of manganese dioxide in a test tube. Does it dissolve? [6] Now add 5 to 10 ml. of the hydrogen peroxide solution prepared in part (A). Result? [7] Write the equation for the reaction.[8]

(E) Acid Properties of Hydrogen Peroxide. An acid reacts with a hydroxide base to form water and the ions of a salt. Obtain 5 ml. of 3 per cent hydrogen peroxide solution and add to it 5 ml. of a saturated solution of barium hydroxide. What is the precipitate? [1] Allow the solution to stand 5 min., filter it, and then wash the precipitate. Outline a method to determine whether or not the precipitate is a peroxide.[2] [See parts (A) and (B).] The method adopted should not require the removal of the precipitate from the filter paper. Proceed with the test and describe the result.[3] What complications would have been encountered if the solution of hydrogen peroxide prepared in part (A) had been used to carry out the reaction with barium hydroxide? [4]

(F) Catalytic Decomposition of Hydrogen Peroxide Solutions. Add a small amount of manganese dioxide to 5 ml. of the hydrogen peroxide solution prepared in part (A). Test the evolved gas with a glowing splinter.[1] Write the equation for the decomposition.[2] Explain the function of the manganese dioxide.[3] Why is hydrogen peroxide usually kept in brown bottles? [4]

(G) The Rate of the Catalytic Decomposition of Hydrogen Peroxide Solutions. 1. Positive Catalysis. Construct the apparatus illustrated in Fig. 68. Place 0.1 g. of manganese dioxide and 5 ml. of water in a large test tube. Fill the delivery tube by blowing into the open tube where the test tube is to be attached. Allow about 5 ml. of water to run into the graduated cylinder and then close the clamp. Pour 2 or 3 ml. of 3 per cent hydrogen

peroxide solution into the funnel. Remove the test tube and carefully open the pinch clamp until the solution has filled the stem of the funnel. Paste a label on the stem of the funnel near its apex. Allow the remainder of the solution to run out of the funnel until the level of the solution is at the position marked by the label, and then close the pinch clamp. Place the stopper in the test tube. Release the clamp on the delivery tube, equalize the water levels in the flask and in the graduate, and then close the clamp.

Now measure 5 ml. of the hydrogen peroxide solution into the funnel. Observe and record the level of the water in the graduate.[1] Open the pinch clamp on the delivery tube, observe and record the time,[1] and then allow the 5 ml. of hydrogen peroxide solution to flow into the test tube. Close the clamp when the level of the solution has reached the position marked by the label on the stem of the funnel. The oxygen which is evolved forces an

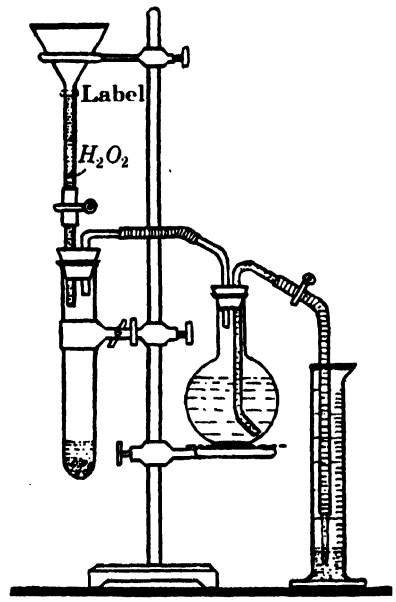


FIG. 68. Catalytic decomposition of hydrogen peroxide

equal volume of water out of the flask into the graduated cylinder. At the end of 1 min. and again at the end of 5 min. equalize the level of the water in the graduate with the level of the water in the flask. Read the volume of water in the graduate. The volume of oxygen evolved is obtained by subtracting 5 ml. (the volume of the hydrogen peroxide solution run into the test tube) from the volume of water displaced from the flask. Record the results on the report sheet.[1]

Allow the reaction to continue until the evolution of oxygen has ceased. What is the total volume of oxygen released?[1] The 3 per cent solution of hydrogen peroxide sold commercially is commonly referred to as a "10-volume solution" because 1 volume of this solution evolves 10 volumes of oxygen at room temperature. Estimate the percentage of hydrogen peroxide in the solution tested.[1]

Repeat the experiment, but use 5 ml. of 0.1*M* ferric chloride solution instead of MnO_2. Record the data in the table on the report sheet.[1] Discontinue the experiment after 5 min.

2. Negative Catalysis. The presence of an acid or of certain organic substances such as acetanilide retards the decomposition of dilute solutions of hydrogen peroxide. Sodium nitrate retards the decomposition of hydrogen peroxide by finely divided substances.

Repeat the experiment described above but this time use 0.1 g. of manganese dioxide and 0.5 g. of sodium nitrate. Record the results on the blanks provided on the report sheet.[1] Discontinue the experiment after 5 min.

What is the ratio of the volume of oxygen obtained in 1 min. with manganese dioxide in the presence of sodium nitrate to the volume of oxygen obtained in 1 min. with manganese dioxide alone? [2] Compare the catalytic activity of the ferric chloride solution and manganese dioxide.[3]

3. Strength of the Hydrogen Peroxide Solution Prepared in Part (A). Determine the total volume of oxygen liberated from 10 ml. of the hydrogen peroxide solution prepared in part (A).[4] Use about 0.5 g. of MnO_2 as a catalyst for the decomposition. Calculate the percentage of hydrogen peroxide in the solution.[5]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIII

THE PREPARATION AND PROPERTIES OF HYDROGEN PEROXIDE

(A) Preparation of Hydrogen Peroxide. *From sodium peroxide*

1.

2.

3.

4.

From barium peroxide

5. **6.**

7.

8.

9.

(B) Test for Hydrogen Peroxide

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIII (Cont'd)

(C) Oxidizing Properties of Hydrogen Peroxide. *Reaction with a starch-iodide solution*

1.

2.

3.

Oxidation of lead sulfide

4.

5.

6.

(D) Reducing Properties of Hydrogen Peroxide. *Reaction with potassium permanganate*

1. **2.**

3. **4.**

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIII (Cont'd)

(D) Cont'd

Reaction with manganese dioxide in acid solution

6. **7.**

8.

(E) Acid Properties of Hydrogen Peroxide

1.

2.

3.

4.

(F) Catalytic Decomposition of Hydrogen Peroxide Solutions

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIII (Cont'd)

(F) Cont'd

4.

(G) The Rate of the Catalytic Decomposition of Hydrogen Peroxide Solutions

1.

	Positive Catalysis		Negative Catalysis
	0.1 g. MnO_2	5.0 ml. of $FeCl_3$	0.1 g. MnO_2 + $NaNO_3$
Starting time			
Initial level			
Level after 1 min.			
Level after 5 min.			
Final level		_____	_____
Volume of O_2, 1 min.			
Volume of O_2, 5 min.			
Total vol. O_2		_____	_____
Per cent H_2O_2		_____	_____

2.

3.

Strength of the hydrogen peroxide solution prepared in part (A)

4.

Experiment XXIV

THE LAW OF MULTIPLE PROPORTIONS

Discussion. The law of multiple proportions states that *when two or more elements combine in more than one proportion, the quantities of one of the elements which unite with a given amount of the other element or elements, stand to each other in the ratio of small whole numbers.* Thus in water and in hydrogen peroxide the proportions by weight of the elements are:

H_2O . . . . . 2.016 : 16

H_2O_2 . . . . . 2.016 : 32

The ratio of the weights of oxygen combining with identical amounts of hydrogen in these two compounds is 16 to 32 or 1 to 2.

The above law may be illustrated with potassium chlorate ($KClO_3$) and potassium perchlorate ($KClO_4$). The weights of oxygen united with identical amounts of KCl will be found to be in the ratio of small whole numbers.

Materials: 1 g. of potassium chlorate; 1 g. of potassium perchlorate.

The Ratio of Oxygen in Potassium Chlorate and Potassium Perchlorate. Push a loose plug of glass wool a short distance into a Pyrex test tube. Weigh the test tube and wool to the nearest 0.01 g. Record all data for the experiment in the blank spaces provided on the report sheet.[1] Remove the glass wool and add about 1 g. of potassium chlorate. Replace the glass wool and obtain the combined weight of the test tube and its contents.[1]

Clamp the test tube to the ring stand with a burette clamp from which the rubber has been removed. The burette clamp should be near the top of the test tube and the test tube should be inclined at an angle of about 45 degrees to the horizontal. Insert into the mouth of the test tube a one-holed stopper carrying a glass tube with a 45-degree or a 60-degree bend. Use a rubber tube to attach a straight piece of glass tubing to the bend. The delivery tube should be long enough to permit the submersion of its end in a beaker of water.

Heat the test tube slowly with a small flame until the potassium chlorate melts and then decomposes. Place the end of the delivery tube under the surface of the water in the beaker and continue the heating as long as there is evidence for the escape of gas. As the residue in the test tube begins to solidify, heat the test tube more strongly, especially around the upper part where any solid material may have collected. When no more oxygen can be driven off, remove the rubber stopper from the test tube, and allow the tube to cool to room temperature. What would happen if the test tube were allowed to cool without removing the delivery tube from the water? [2] Weigh the test tube plus its contents.[1]

Repeat the same procedure but this time use about 1 g. of potassium perchlorate. Record all data in the spaces provided on the report sheet.[1] (Begin this part of the experiment while the test tube used in the first part of the experiment is cooling.)

Carry out the calculations indicated in the table on the report sheet.[1] What is the ratio between the two weights of oxygen combined with 74.5 g. of KCl? [3] Express this ratio in terms of small whole numbers.[4]

Calculate the weight of copper combined with 1 g. of chlorine in the following compounds: CuCl and $CuCl_2$. Show that the law of multiple proportions applies to these two compounds.[5]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIV

THE LAW OF MULTIPLE PROPORTIONS

The Ratio of Oxygen in Potassium Chlorate and Potassium Perchlorate

1.

	$KClO_3$	$KClO_4$
Weight of test tube + glass wool + compound.		
Weight of test tube + glass wool + residue (KCl)	_____	_____
Weight of oxygen		
Weight of test tube + glass wool + residue (KCl)		
Weight of test tube + glass wool	_____	_____
Weight of residue (KCl)		
Weight of oxygen combined with 1 g. of KCl		
Weight of oxygen combined with 74.5 g. of KCl		
Ratio of the weight of oxygen in $KClO_3$ and $KClO_4$		
Ratio expressed in whole numbers		

2.

3.

4.

5.

Experiment XXV

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

Discussion. The molecular weight of a gas or vapor is defined as the weight of a molecule of the gas relative to the weight of the oxygen molecule (O_2) taken as 32. One *gram-molecular weight* of oxygen at standard conditions (0° and 760 mm.) occupies 22.4 liters (Exp. XV). Avogadro's law states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules. Therefore, it follows that the weight in grams of 22.4 liters of a gas or a vapor measured at standard conditions is the gram-molecular weight.

The determination of the molecular weight of a gas requires the determination of the weight of a known volume of the gas at a given temperature and pressure. The volume is then reduced to standard conditions and the weight of 1 liter at these conditions is calculated. This weight multiplied by 22.4 is equal to the molecular weight of the gas.

Several different experimental methods are suitable for the determination of the weight and the volume of a gas (Exp. XV). In this experiment (XXV) the weight of a measured volume of a gas is obtained by direct weighing. The weight of an empty flask is equal to the combined weight of the flask and the air minus the calculated weight of the air contained in the flask. The weight of the gas alone is then equal to the difference between the weight of the flask plus the gas and the weight of the empty flask.

The above procedure is modified for *the determination of the molecular weight of a liquid* whose boiling point is below 100°. When the flask containing a small amount of the liquid is placed in boiling water, the liquid vaporizes, displaces the air from the flask, and finally the excess liquid escapes in the form of a gas. The flask is now filled with the vapor at the temperature of the boiling water and at atmospheric pressure. When the flask is cooled, the vapor condenses to a small volume of liquid (1 to 2 ml.) and air is drawn into the flask. The weight of the vapor that was contained in the flask is equal to the weight of the condensed liquid. No correction for air in the flask is required because both the initial and final weighings are made with the flask practically filled with air under the same conditions of temperature and pressure. If 2 ml. of liquid condense, what is the difference between the weight of the air originally contained in the flask and that of the air present when the final weighing is made? [1] The density of the air at the conditions of the weighings may be taken as 1.28 g. per liter.

The determination of the atomic weight of a metal involves the following steps: (1) The determination of the equivalent weight of the metal. This is the weight of the metal that combines with one atomic weight of a univalent element or its equivalent (35.46 g. of chlorine, 1.008 g. of hydrogen, or 8 g. of oxygen). (2) The determination of the specific heat and the calculation of the approximate atomic weight from Dulong and Petit's law (6.4 divided by the specific heat of the metal is approximately equal to the atomic weight). (3) Calculation of the valence (approximate atomic weight divided by the equivalent weight). (4) Calculation of the atomic weight by multiplying the equivalent weight by the valence.

The specific heat of a metal is determined by measuring the amount of heat lost to water when the metal cools from one temperature to another. The amount of heat transferred to the water is determined from the rise in temperature of a known weight of water when the metal is immersed in it. This method is known as the "method of mixtures."

Accurate measurements are carried out in a well insulated apparatus called a calorimeter (Fig. 69). The principal sources of error in the method described in this experiment are: (*a*) the loss of heat to the beaker and to the thermometer used to measure the rise in temperature; (*b*) the loss of heat from the water during the time that temperature equilibrium is being established between the water and the metal; and (*c*) the loss of heat from the metal as it is being transferred from the higher temperature to the water. Approximate corrections can be made for the first two sources of error, (*a*) and (*b*). The thermometer must be read as accurately as possible because the rise in temperature is not large. A small error in reading the temperature, therefore, causes a relatively large percentage error in the result.

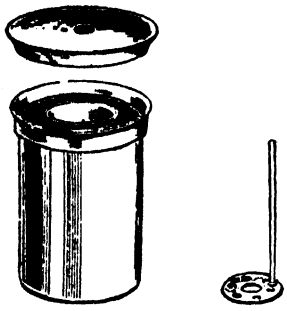


FIG. 69. A calorimeter

Apparatus and Materials: Carbon dioxide generator (each student may set up a generator if a tank or the sources shown in Figs. 70 and 71 are not available in the laboratory); unknown liquid (carbon tetrachloride, chloroform, acetone, or ethyl alcohol); beam balance; 4-mm. glass rod for a triangle; 250° thermometer; a 20-cm. length of string; a 100- to 150-g. piece of lead.*

(A) Molecular Weight of a Gas. Fit a dry 150-ml. Erlenmeyer or Florence flask with a stopper. Mark the flask at the lower level of the stopper with a wax pencil or by a label pasted at the proper position. Weigh the flask and the stopper to the nearest 0.01 g. This is the weight of the flask filled with air. Record this weight and all of the subsequent data and calculations in the form provided on the report sheet.[1]

Introduce the delivery tube from a source of supply of carbon dioxide (see the following paragraph) into the flask so that the end of the tube rests on the bottom of the flask. Pass the gas into the flask at the rate of several bubbles per second. The gas should flow until a lighted splinter held just above the flask is extinguished; this should occur in from 2 to 3 min. Replace the stopper and weigh the flask plus its contents.[1] Measure the volume of

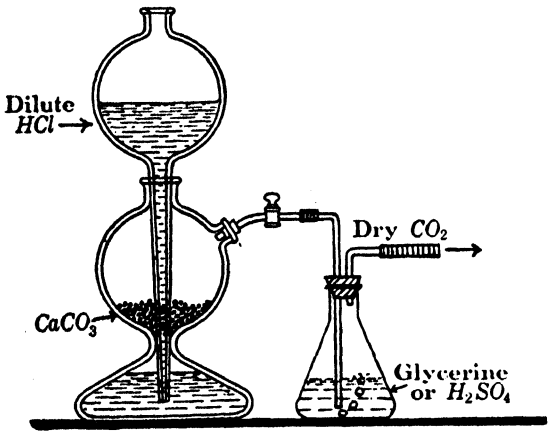


FIG. 70. Kipp generator

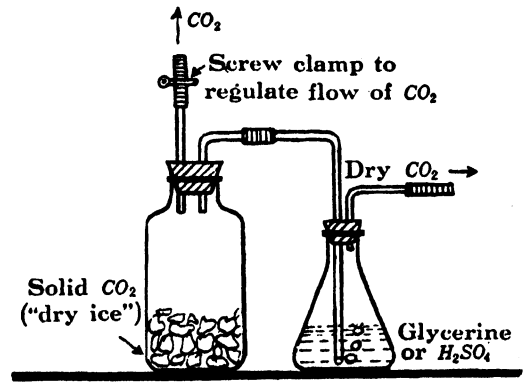


FIG. 71. Carbon dioxide from "dry ice"

the gas by filling the flask to the mark with water from a graduated cylinder. Record the temperature and the barometric pressure.[1] Calculate the molecular weight from these data as indicated on the report sheet.[1]

Carbon dioxide may be supplied in the laboratory from a Kipp generator (Fig. 70), a dry-ice generator (Fig. 71), or from a steel tank. In case a general laboratory supply is

* Lead pieces may be made by pouring molten lead into sand molds having holes 1½ in. deep and from ⅜ to ⅝ in. in diameter.

not available, each student should prepare carbon dioxide by the reaction of 4*N* hydrochloric acid on marble (calcium carbonate) in a generator similar to the one used for the preparation of hydrogen (Fig. 58). If the molecular weight of sulfur dioxide is determined, the flask must be filled under the hood to prevent the escape of sulfur dioxide into the laboratory.

(B) Molecular Weight of a Liquid. Bend a glass tube to an angle of 90 degrees and draw out one end of the tube to a capillary. Insert the other end of the tube in a one-holed rubber stopper selected to fit a 150-ml. flask. Obtain the combined weight of the flask, rubber stopper, and glass tube to the nearest 0.01 g. Record this weight and the subsequent data and calculations on the form provided on the report sheet.[1]

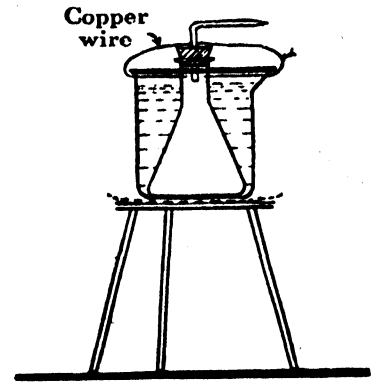


FIG. 72. Apparatus for determining the molecular weight of a liquid

Obtain from 2 to 3 ml. of an unknown liquid,* pour it into the flask, and immerse the flask in a 400-ml. beaker of water. Fasten down the flask with string or copper wire as illustrated in Fig. 72. Vaporize the liquid in the flask by boiling the water in the beaker. Continue to boil 10 min. after all of the liquid has evaporated. Read the barometric pressure and the temperature of the boiling water. Remove the flask from the beaker, wipe the water from the flask, and allow it to cool. Weigh the flask and its contents without removing the stopper.

Fill the flask and the glass tube with water; then measure the volume of the apparatus by pouring the water into a graduated cylinder. Calculate the molecular weight as indicated on the report sheet.[1]

(C) Determination of the Approximate Atomic Weight of Lead. An approximate value for the atomic weight is to be calculated, by means of Dulong and Petit's law, from the experimentally determined value for the specific heat of the metal. Two experimental procedures are offered; the first of these is used if the metal is in one piece, while the second is supplied in the event that the metal is available only in the granular form or as shot.

Procedure 1. Obtain a 100- to 150-g. piece of lead from the stockroom and clean the surface of the metal with sandpaper. Weigh the metal to the nearest 0.1 g. on the laboratory trip balance.[1] Tie a piece of string around the metal to facilitate handling it while it is hot. Fill a 400-ml. beaker half full of water. Place the metal in the water and hang the string over the side of the beaker. Heat the water until it boils. While the water is heating to its boiling point, cool some distilled water until its temperature is 4 or 5° below the room temperature. This is done by pouring about 100 ml. of distilled water into an Erlenmeyer flask and allowing cold tap water to run over the lower part of the flask. Measure 50 ml. of the cooled water and pour it into a 100-ml. beaker or a larger one, if necessary, to hold the piece of metal. If this amount of water does not cover the metal, a larger volume should be used. The exact volume, however, must be known and recorded.[1] Place the 100-ml. beaker in an empty 150-ml. beaker. It should hang freely, the only point of contact being at the rim (Fig. 73). This arrangement lowers the rate of heat transfer to and from the water in the 100-ml. beaker. If a 150-ml. beaker is necessary to hold the metal, partial insulation may be achieved by placing the 150-ml. beaker in a 250-ml. beaker, the bottom of which has been covered with cotton or several layers of paper.

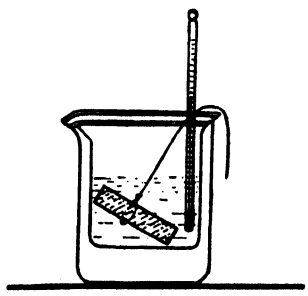


FIG. 73. An improvised calorimeter

* The following liquids are satisfactory as unknowns: Carbon tetrachloride, chloroform, acetone, or ethyl alcohol.

Allow the metal to remain in the boiling water about 5 min. Record the exact temperature of the boiling water as the temperature of the metal.[1] Cool the thermometer to room temperature, and observe the temperature of the water in the 100-ml. beaker.[1] Hold the improvised calorimeter near the beaker containing the heated metal, and transfer the metal to the 100-ml. beaker as rapidly and as carefully as possible. The metal should be completely immersed. Stir the water continually and observe the temperature every 10 sec. until it reaches a maximum and then falls a degree or two. The maximum temperature will be reached in 1 to 2 min. Record the maximum temperature reached.[1] Repeat the determination using 45 ml. of water in the 100-ml. beaker. Record the data on the form given on the report sheet.[1]

Calculate the specific heat of the metal from the following considerations. The number of calories of heat lost by the metal is equal to the number of calories of heat gained by the water. Therefore: (g. of metal) × (change in temperature) × (specific heat) = (vol. of water) × (rise in temperature). Solve this equation for the specific heat of the metal [2] and complete the calculations.

Make a correction for the heat absorbed by the 100-ml. beaker as follows: A 100-ml. beaker weighs about 30 g. Approximately two thirds of the glass in the beaker is in contact with water after the metal has been added. Therefore, approximately 20 g. of glass in the beaker and 2 g. of glass in the thermometer are heated from the temperature of the cold water to the maximum temperature reached. The specific heat of Pyrex glass is 0.185 cal./g./°C. Calculate the number of calories of heat taken up by the glass. Add this to the calories of heat taken up by the water, and recalculate the specific heat of the metal.[1] Calculate the approximate atomic weight of lead from the average value of the specific heat.[3] Use this value of the atomic weight in part (D) to calculate the valence of lead.

Procedure 2. If 150-g. pieces of lead are not available, the above procedure may be modified so as to allow the use of lead shot or granulated lead.

Weigh from 100 to 150 g. of the metal and place it in a large test tube. Immerse the bottom end of the test tube in boiling water and allow it to remain 15 min. The surface of the boiling water must be at least 2 cm. above the metal. Record the temperature of the boiling water as the temperature of the metal. Cool the thermometer and measure the temperature of the water in the 100-ml. beaker in the same way as previously described. Remove the test tube from the boiling water and pour the metal into the 100-ml. beaker as rapidly as possible. Stir the metal and the water vigorously. Note the temperature every 10 sec. until it starts to fall slowly. Record the maximum temperature and calculate the specific heat [1] and the approximate atomic weight,[3] as described in Procedure 1.

(D) Determination of the Equivalent Weight, Valence, and Exact Atomic Weight of Lead. Heat a clean evaporating dish and, after it has cooled to room temperature, weigh it on a small beam balance or an analytical balance. Record this weight as well as all subsequent weighings and calculations on the form provided on the report sheet.[1] Place about 0.5 g. of granulated lead in the dish and obtain their combined weight.[1]

Mix 5 ml. of 16*N* nitric acid with 5 ml. of water, add the solution to the lead, and cover the dish with a watch glass. Place the covered dish on a 250-ml. beaker containing about 150 ml. of water. Boil the water in the beaker until the lead has dissolved. Rinse the bottom of the watch glass with a stream of water from the wash bottle. Allow the washings to run into the dish.

Add 3 ml. of 12*N* hydrochloric acid to precipitate the lead as lead chloride. Use 4-mm. glass rod to prepare a triangle which will fit on the evaporating dish. Place the watch glass on the triangle. Set the dish on the 250-ml. beaker and boil the water until the solution has evaporated to dryness. Rinse into the dish any solids that have collected on the watch glass and glass triangle. Add 5 ml. of 12*N* hydrochloric acid and again evaporate the solution to dryness.

Remove the watch glass, place the dish on a clay triangle which is supported on a tripod, and then heat the dish with a small nonluminous flame (keep the flame in motion). Do not melt the lead chloride. Decrease the size of the flame if the residue begins to fuse. Continue to heat 5 min.

Weigh the dish and the lead chloride as soon as they have cooled to room temperature. Record the weight and carry out the following calculations as indicated on the form on the report sheet:[1] percentage of lead and chlorine in the lead chloride; and the equivalent weight of lead. Use this value of the equivalent weight, and the approximate atomic weight determined in part (C) to calculate the valence of lead. This is the whole number nearest the value obtained by dividing the approximate atomic weight by the equivalent weight. Now calculate the "exact" atomic weight from the valence and the equivalent weight determined above.[1] Calculate the percentage error of the result.[1]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXV

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

Discussion

1.

(A) Molecular Weight of a Gas

1. Weight of the flask + air + stopper . . . . . .
   Temperature . . . . . .
   Barometric pressure . . . . . .
   Volume of flask (volume of air) . . . . . .
   Volume of air reduced to 0° − 760 mm. . . . . .
   Weight of air (density at 0° − 760 mm. = 1.293 g.) . . . . . .
   Weight of empty flask . . . . . .

   Weight of flask + CO_2 . . . . . .
   Weight of empty flask . . . . . _____
   Weight of CO_2 . . . . . .

   Weight of 22.4 liters of CO_2 at 0° − 760 mm. . . . . .
   Accepted value of the molecular weight . . . . . .
   Percentage error . . . . . .

(B) Molecular Weight of a Liquid

1. Weight of flask + fittings + condensed vapor . . . . . .
   Weight of flask + fittings . . . . . _____
   Weight of condensed vapor . . . . . .

   Volume of apparatus (volume of hot vapor) . . . . . .
   Temperature of the boiling water . . . . . .
   Barometric pressure . . . . . .
   Volume of vapor reduced to 0° − 760 mm. . . . . .

   Weight of 22.4 *l.* at 0° − 760 mm. (molecular weight) . . . . . .

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXV (Cont'd)

(C) Determination of the Approximate Atomic Weight of Lead

1.

	Trial 1	Trial 2
Weight of metal	g.	g.
Temperature of the boiling water (temperature of the metal)		
Maximum temperature reached in calorimeter		
Change in temperature of metal		
Volume of cold water		
Maximum temperature reached in calorimeter		
Temperature of cold water in calorimeter		
Rise in temperature of water		
Calculated specific heat		
Corrected specific heat		
Average		

2.

3. Approximate atomic weight of lead =

(D) Determination of the Equivalent Weight, Valence, and Exact Atomic Weight of Lead

1.

Weight of evaporating dish + Pb	
Weight of evaporating dish	_____
Weight of Pb	
Weight of evaporating dish + $PbCl_2$	
Weight of evaporating dish	_____
Weight of $PbCl_2$	
Weight of chlorine (wt. of $PbCl_2$ − wt. of Pb)	
Percentage of lead in $PbCl_2$	
Percentage of chlorine in $PbCl_2$	
Weight of Pb uniting with 35.46 g. of Cl (equivalent wt.)	
Approximate atomic weight of Pb	
Valence of Pb	
Atomic weight (equivalent wt. × valence)	
Accepted atomic weight of Pb	
Percentage error	

Experiment XXVI

THE HALOGENS

Discussion. The halogens may be prepared from inorganic halides. In the latter, the oxidation state of the halogens is -1. Thus the removal of an electron from them by oxidizing agents or by electrolytic oxidation results in the liberation of the halogens.

Represent diagrammatically the electronic structure of F^-, Cl^-, Br^-, and I^-.[1]

Note: Inasmuch as the vapors of the halogens quickly attack the membranes of the nose, throat, and lungs, the inhalation of these vapors must be avoided. If the procedures and the specified amounts of materials are adhered to, dangerous concentrations of the halogens will not be encountered in the laboratory. All the experiments may be carried out in a ventilating hood if space is available for the class.

Apparatus and Materials: A 20-cm. length of 8-mm. glass tubing; potassium iodide-starch paper; 0.2 g. of NaBr or KBr; 0.2 g. of NaI or KI; 0.2 g. of iodine.

(A) Preparation of the Halogens. 1. Chlorine. Place the following in separate 10-cm. (4-in.) Pyrex test tubes: 4 small crystals of potassium permanganate, an equal number of crystals of potassium dichromate, and about the same quantity of silicon dioxide, lead dioxide, and manganese dioxide. Add 1 ml. of concentrated ($12N$) hydrochloric acid to each tube, and note any action that occurs. Gently warm each tube in turn by dipping it into hot water. Now hold each tube in front of a white background, for example, a sheet of paper or a card. Observe the color of the gas evolved.[1] Note the odor of the gas (CARE!) by wafting some of the gas toward the nose. Write an equation to express each reaction that takes place.[2]

Mix 0.1-g. portions of sodium chloride and manganese dioxide in a test tube. Add 1 ml. of concentrated ($36N$) sulfuric acid and warm gently. Test the issuing gas with wet potassium iodide-starch paper. Describe the result and tell what it proves.[3] Write equations for the reactions that have taken place.[4]

Determine whether or not chlorine is liberated by the action of concentrated sulfuric acid on sodium chloride. Result? [5]

Write equations for the reactions occurring at the electrodes during the electrolysis of: (*a*) fused sodium chloride and (*b*) an aqueous solution of sodium chloride.[6]

What oxidizing agent is employed in Deacon's process for the preparation of chlorine? [7]

2. Bromine. Mix in a 10-cm. test tube several crystals of sodium or potassium bromide with a small amount of manganese dioxide and 5 drops of $36N$ sulfuric acid. Warm gently and note the color of the evolved vapor.[8] What is the colored substance? Write an equation to express its formation.[9] Test the action of the vapor on wet potassium iodide-starch paper. Write an equation for the reaction.[10] Can this test be used to give any information regarding the relative oxidizing power of bromine as compared with that of chlorine? Explain.[11]

Add 5 drops of $36N$ sulfuric acid to several crystals of sodium or potassium bromide contained in a 10-cm. test tube. Result? [12] What is the oxidizing agent in this case? [13] Recall the action of sulfuric acid on a chloride, and make a statement regarding the relative ease of oxidation of Cl^- and Br^-.[14]

3. Preparation of Bromine from a Bromide. Set up the apparatus shown in Fig. 74. Place 10 ml. of a $4N$ solution of sodium hydroxide in the 50-ml. beaker. Measure out 25 ml.

of a 1*N* solution of potassium bromide into the 250-ml. Erlenmeyer flask, and then place 0.2 g. of manganese dioxide and 4 ml. of concentrated hydrochloric acid in the 15-cm. test tube. Fit the stoppers tightly into the test tube and the flask. Warm the test tube slightly to start the evolution of chlorine. Continue the passage of the gas for a period of 4 min. after the first appearance of a yellow color in the solution of potassium bromide. Now remove the test tube generator, quickly fill it with cold water from the tap, and then pour the contents of the tube down the drain.

Replace the sodium hydroxide solution in the beaker by 25 ml. of a solution containing 4 g. of sodium carbonate. The bromine liberated from the solution of potassium bromide is now to be blown out of that solution by steam into the carbonate solution. Measure out 25 ml. of water into a 50-ml. Erlenmeyer flask fitted with the one-holed rubber stopper

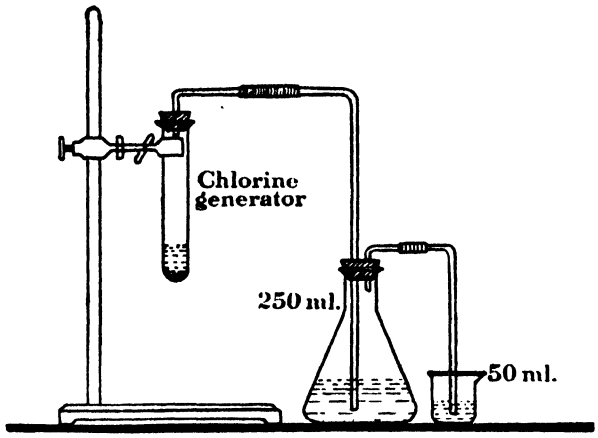


FIG. 74. Preparation of bromine from a bromide

and the right-angle delivery tube used in the chlorine generator. Attach the delivery tube to the 250-ml. Erlenmeyer flask and then boil the water vigorously in the smaller flask. Continue the passage of steam until the vapors of bromine are no longer observed in the larger flask.

Examine the solution in the beaker for droplets of free bromine. If these are present, warm the solution until they disappear. Now evaporate the solution to dryness, transfer the residue to a test tube, and then add dilute (4*N*) sulfuric acid, drop by drop, until a brown vapor is evolved. What is the colored substance? [15] Write equations to express all the reactions that have taken place in this series of operations.[16] With what commercial process of preparing bromine is this laboratory method comparable? [17]

4. Iodine. Mix several small crystals of sodium or potassium iodide with about the same amount of manganese dioxide in a 10-cm. test tube, and then add 5 drops of 36*N* sulfuric acid. Warm the mixture. Result? Write the equation for the reaction.[18]

Add 5 drops of 36*N* sulfuric acid to several crystals of sodium or potassium iodide in a 10-cm. test tube. Warm gently, and carefully note the odor of the gas evolved. Write equations to express the reactions that have taken place.[19] How could the iodine be separated from the mixture and obtained in a pure state? (Exp. VIII) [20]

To 1 ml. of a 0.1*N* solution of potassium or sodium iodide in a test tube add chlorine water drop by drop until a permanent precipitate is formed. What is the insoluble substance? [21] Verify the answer by heating the mixture to boiling and then noting the color of the vapor formed in the tube. Repeat with bromine water and 1 ml. of the iodide solution. Result? [22] Arrange the three ions (Cl^-, Br^-, and I^-) in the order of increasing ease of oxidation.[23] Write equations for the reactions involved.[24]

5. Fluorine. How is fluorine prepared?[25] Why is this preparation not carried out in the laboratory?[26]

(B) Properties of Chlorine. 1. Action with Metals and a Nonmetal. Set up the apparatus shown in Fig. 75. The horizontal tube, 20 cm. in length, contains a small wad of steel wool in its central portion, several small pieces of tin placed at a distance of 3 cm. from the end nearest the test-tube chlorine generator, and a small piece of roll sulfur 3 cm. from the end nearest the beaker.

Measure out 15 ml. of a 4*N* solution of sodium hydroxide into the 50-ml. beaker. Now generate chlorine in the test tube by the action of 4 ml. of 12*N* hydrochloric acid on 0.3 g. of manganese dioxide. Observe carefully what takes place in the 20-cm. tube. Tell which substance is the first to react, and describe the appearance of the product formed.[1] Now

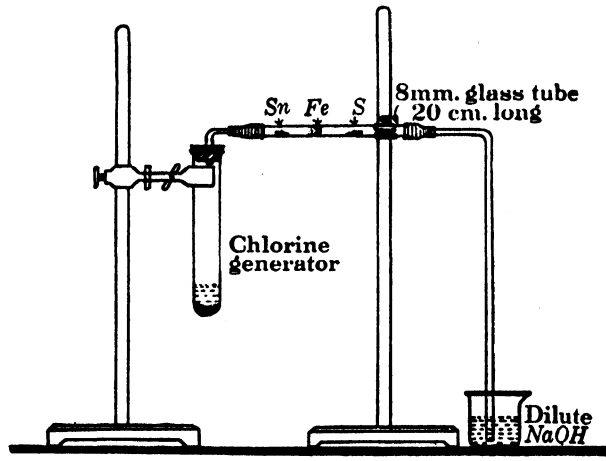


FIG. 75. Action of chlorine with certain elements

heat the tube under the steel wool. Result?[2] Discontinue the heating as soon as a reaction occurs. Describe the appearance of the product formed by the reaction of chlorine with sulfur.[3] Write equations to express the observed reactions of chlorine.[4]

2. Displacement Reactions of Chlorine. Cite two instances of this type of reaction shown by chlorine in this experiment.[5]

3. Reaction of Chlorine by Substitution. Write an equation to illustrate the action of chlorine in this type of chemical change (Text).[6]

(C) Properties of Bromine. 1. Solubility in Various Solvents. Pour 3 ml. of bromine water into each of three test tubes. Add 3 ml. of chloroform to the first tube, 3 ml. of carbon tetrachloride to the second, and 3 ml. of carbon disulfide to the third. Shake each tube 1 min. Compare the intensity of the color of the water layer with that observed in the other solvent present. Make a general statement regarding the relative solubility of bromine in water and in the three other solvents.[1]

2. Combination with Metals. Shake 0.1 g. of powdered zinc in a test tube with 5 ml. of bromine water. What evidence is there for a chemical change?[2] Allow unreacted zinc to settle, and then decant a few milliliters of the liquid into a test tube. Add 3 ml. of chlorine water, an equal volume of carbon tetrachloride, and then shake the tube. Result?[3] Write equations for the reactions that have taken place.[4]

Place a small wad of copper turnings and 3 ml. of bromine water in a test tube. Boil the liquid in the tube 2 min. Note the color of the solution. To what is it due?[5] Write an equation for the reaction responsible for its formation.[6]

(D) Properties of Iodine. 1. Solubility in Various Solvents. Obtain a sufficient quantity of iodine (7 or 8 small crystals) from the stockroom to test the solubility of the

element in 3-ml. portions of each of the following solvents: water, 0.1*N* potassium iodide solution, 95 per cent alcohol (ethyl), carbon disulfide, carbon tetrachloride, chloroform, and ether. Record the color of each solution.[1] Record the value for the solubility of iodine in that solvent in which the element appears to be the least soluble (Text).[2] In which of the above cases is a chemical compound formed? Write an equation for the reaction.[3]

2. A Test for Iodine. Dilute 1 ml. of iodine water to a volume of 15 ml. Pour this solution into a 50-ml. Erlenmeyer flask and then shake it to insure thorough mixing. Measure out 1 ml. of this solution and add to it 1 drop of starch solution. Result? [4] Use the solubility value recorded in (2) as a basis for the calculation of the number of grams of iodine present in the 1-ml. portion of the solution just tested.[5] How many parts of iodine per million parts of solution does this represent? [6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVI

THE HALOGENS

Discussion

1.

(A) Preparation of the Halogens. *Chlorine*

1.

2.

3.

4.

5.

6.

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVI (Cont'd)

(A) Cont'd

Bromine

8.

9.

10.

11.

12. **13.**

14.

Preparation of bromine from a bromide

15.

16.

17.

Iodine

18.

19.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVI (Cont'd)

(A) Cont'd

20.

21.

22.

23.

24.

Fluorin

25.

26.

(B) Properties of Chlorine. *Action with metals and a nonmetal*

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVI (Cont'd)

(B) Cont'd

4.

5.

6.

(C) Properties of Bromine. *Solubility in various solvents*

1.

Combination with metals

2.

3.

4.

5.

6.

(D) Properties of Iodine. *Solubility in various solvents*

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVI (Cont'd)

(D) Cont'd

3.

A test for iodine

4.

5.

Experiment XXVII

THE HYDROGEN HALIDES

Discussion. With the exception of hydrogen fluoride, which boils at 19°, the hydrogen halides are gases at ordinary temperatures and pressures. In the absence of water these substances consist of covalent molecules which do not show the ordinary reactions of solutions of acids. However, they react with water to form the hydronium ion (H_3O^+) present in the aqueous solution of every acid, and to which the characteristic properties of aqueous solutions of acids are due.

The hydrogen halides may be formed by the action of the metal halides with a concentrated nonvolatile acid such as sulfuric acid or phosphoric acid in which these gases are very insoluble. Recall the action of concentrated sulfuric acid on iodides and bromides (Exp. XXVI). What happens to a large part of each of the hydrogen halides formed in these reactions? [1]

Apparatus and Materials: Lead dish; 0.2 g. of NaBr or KBr; potassium iodide-starch paper; 0.2 g. of NaI or KI; hydrogen sulfide.

(A) Hydrogen Chloride. 1. Preparation and Properties. Place a 0.1-g. portion of sodium chloride in each of two test tubes. To one tube add a milliliter of 36*N* sulfuric acid and to the other add the same volume of concentrated (85%) phosphoric acid. Warm the tubes gently. In which case is the gas evolved more rapidly? [1] Write an equation for each reaction.[2] Blow over the mouth of each tube. Result? Explain.[3] Test the issuing gas in each case with both *wet* and *dry* pieces of blue litmus paper. Explain the results.[4] Now dip a *clean* glass rod into a concentrated (15*N*) solution of ammonia and then hold the rod at the mouth of each test tube in turn. Describe what takes place, and write an equation for the reaction.[5] What is the color of hydrogen chloride? [6]

Prepare to generate hydrogen chloride in a test tube by the action of 2 ml. of 36*N* sulfuric acid on 0.3 g. of sodium chloride. Clamp the generator tube onto a ring stand and fit it with a one-holed stopper carrying a delivery tube which extends to the bottom of a test tube resting on the top of the desk.

After the apparatus has been approved, place the above quantities of materials in the generator, stopper it tightly, and warm it to hasten the evolution of hydrogen chloride. Collect a test tube full of the gas. Hold a piece of moist blue litmus paper near the mouth of the tube in order to determine when the tube is filled with the gas. Quickly invert the filled tube in a 50-ml. beaker containing 25 ml. of water. What takes place? What does this show with regard to the solubility of the gas in water? [7] Test the reaction of the solution with 0.5 ml. of a 0.1*N* solution of silver nitrate. Describe the appearance of the product, write an equation for its formation, and test its solubility in 16*N* nitric acid by adding 2 ml. of the concentrated acid to the solution containing the precipitate.[8]

Collect another test tube full of hydrogen chloride and then plunge a lighted splint into it. What can be said about the ability of the gas to burn or to support combustion? [9]

2. Chemical Properties of Aqueous Solutions of Hydrochloric Acid. Test the action of 4*N* hydrochloric acid on litmus paper. Which ion is responsible for the result? Write an equation for its formation.[10]

Test the action of both hot and cold dilute hydrochloric acid (4*N*) on a small iron nail, on a small amount of powdered zinc, and on a short piece of copper wire or turnings. Write equations for the reactions that take place.[11]

Treat separately 0.1-g. portions of calcium oxide (CaO) and ferric oxide (Fe_2O_3) with 5-ml. portions of 4*N* hydrochloric acid. If no reaction occurs in the cold, heat the mixtures. Results? Write equations for the reactions.[12]

Add 4*N* hydrochloric acid to 5 ml. of 4*N* sodium hydroxide until the resulting solution is acid to litmus. Evaporate the solution until crystals begin to appear and then set it aside to cool. Examine the crystals. Describe their form, tell what they are, and write an equation for the reaction leading to their formation.[13]

To 5 ml. of a 0.1*N* solution of aluminum chloride contained in a test tube add a 4*N* solution of ammonia drop by drop until no more precipitate is formed. Shake the tube after the addition of each drop of ammonia solution. Now add concentrated hydrochloric acid a little at a time until the solution is strongly acid. How is this determined? [14] What happens to the precipitate? [15] Write equations for all the reactions that have been carried out.[16]

Add 3 ml. of 12*N* hydrochloric acid to a piece of calcium carbonate, $CaCO_3$ (marble, limestone). Quickly thrust a lighted splinter into the test tube. Result? What does this show with regard to the ability of the gas to burn or to support combustion? [17] Name the gas and write an equation to show its formation.[18]

3. Summary. Make a general statement regarding the action of aqueous solutions of hydrochloric acid with each of the following classes of substances: metals, oxides of metals, hydroxides, and carbonates.[19] Name the chlorides that could be obtained by the evaporation of the solutions formed by the action of hydrochloric acid on the substances tested in the preceding part of this experiment.[20] Write equations to show how each of the chlorides of the following metals might be prepared by three different methods (nine equations in all): K, Mg, Cu.[21] Could mercuric chloride be obtained by the action of hydrochloric acid on mercury? Give a reason for the answer.[22]

4. Reactions of the Chloride Ion, Cl^-. Place in separate test tubes 3-ml. portions of 0.1*N* solutions of silver nitrate, lead nitrate, and mercurous nitrate. Add to each an equal volume of 4*N* hydrochloric acid. Record the appearance of each precipitate.[23] Among the commonly occurring chlorides of the metals these three are the only ones found to be difficultly soluble. Heat the contents of each tube to the boiling point, and state the effect of raising the temperature on the solubility of each of the precipitates.[24]

What is the effect of oxidizing agents on chloride ion? Refer to Exp. XXVI and name two oxidizing agents capable of bringing about this change.[25]

(B) Hydrogen Bromide. 1. Preparation and Properties. Recall the action of concentrated sulfuric acid on a bromide (Exp. XXVI).[1]

Test the action of both cold and hot concentrated (85%) phosphoric acid (2 ml.) on a crystal of sodium or potassium bromide. What is the color of the gas evolved? [2] Test it for bromine by the use of moist potassium iodide-starch paper. Result? [3] What is the action of the gas on dry and on moist litmus paper? [4] Test the reaction of the gas with ammonia as in part (A). Result? Write an equation to show the formation of the observed product.[5] What disadvantage is there in making hydrogen bromide by the action of phosphoric acid on a bromide? [6] (Text)

Pass hydrogen sulfide into 5 ml. of bromine water.* *Do not inhale hydrogen sulfide—it is toxic!* What evidence is there for a chemical change? [7] Write an equation for the reaction.[8] Could all the hydrogen bromide be driven out of this solution by boiling? Give the reason for the answer.[9]

Write equations to illustrate two methods used to prepare gaseous hydrogen bromide in larger quantities.[10] (Text)

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* Consult the instructor regarding the laboratory supply of hydrogen sulfide. If the gas is not available from a tank it is to be generated in a test tube either by the action of a few milliliters of dilute sulfuric acid on 0.2 g. ferrous sulfide, or by warming the material sold commercially as "Aitch-tu-ess."

2. Chemical Properties of Aqueous Solutions of Hydrogen Bromide. Use the 1*N* solution of hydrobromic acid found on the reagent shelf in the laboratory. Determine whether or not its action is analogous to that of hydrochloric acid with the following substances (use 2-ml. portions of hydrobromic acid and 0.1 g. of each of the other materials): powdered zinc, copper turnings, ferric oxide, aluminum oxide, and calcium carbonate. Name and write the formulas of the compounds formed, and make a general statement regarding the similarity between the actions of this acid and those of hydrochloric acid with various classes of substances.[11]

Heat 1 ml. of 1*N* hydrobromic acid solution with an equal volume of 36*N* sulfuric acid. Tell what the result shows regarding the relative ease of oxidation of chloride ion and bromide ion, and write an equation to express the reaction.[12]

Warm 1 ml. of 1*N* hydrobromic acid with a small amount of manganese dioxide. Compare the result with that obtained by the action of this oxidizing agent on Cl^- and write an equation for the reaction.[13]

Add 3 ml. of chlorine water to an equal volume of 1*N* hydrobromic acid. Now shake with 2 ml. of carbon tetrachloride. What ion is thus shown to be present in the acid solution? Explain.[14]

3. Formation of Insoluble Bromides. Place in separate test tubes 2 ml. of 0.1*N* solutions containing the following ions: Zn^{++}, Ag^+, Cu^{++}, Hg^{++}, Pb^{++}, and Hg_2^{++}. Add several drops of 1*N* hydrobromic acid to each tube. Which bromides are soluble in water? [15] Note the form and color of the insoluble bromides and test their solubility in hot water.[16]

(C) Hydrogen Iodide. 1. Preparation and Properties. Test separately the action of 1-ml. portions of 36*N* sulfuric acid and 85 per cent phosphoric acid on 0.1-g. portions of sodium or potassium iodide. Record the differences observed.[1] Warm the tubes and test for the presence of hydrogen iodide by blowing the breath over the mouth of each tube, by means of moist litmus paper, and by holding at the mouth of each tube a rod which has been dipped into a 4*N* solution of ammonia. Results? [2] In what gas does sulfur appear as one of the constituents? [3] Test for this gas with a piece of filter paper moistened with a 0.1*N* solution of lead acetate. To what compound is the dark color on the paper due? [4] Write equations to account for all of the reactions observed above.[5]

Fit a test tube, in which a gas is to be generated, with a one-holed stopper and a delivery tube which reaches to the bottom of a test tube containing 6 ml. of iodine water. Place 0.5 g. of sodium bisulfite ($NaHSO_3$) in the generator tube and then quickly add to it 5 ml. of hydrochloric acid which has been prepared by adding 2.5 ml. of water to an equal volume of 4*N* hydrochloric acid. Pass the sulfur dioxide which is formed into the iodine water until the latter is decolorized. Boil the solution until it no longer has the odor of sulfur dioxide. The equations for the reactions are:

$$HSO_3^- + H_3O^+ \rightarrow H_2SO_3 + H_2O$$

$$\downarrow \rightarrow H_2O + SO_2\uparrow \qquad \text{(generator)}$$

$$SO_2 + H_2O \text{ (in the iodine water)} \rightleftharpoons H_2SO_3$$

$$H_2SO_3 + I_2 + 5H_2O \rightarrow 4H_3O^+ + SO_4^= + 2I^-$$

Divide the colorless solution into three equal portions. Test one for the presence of sulfate ion by the addition of a few drops of a 0.1*N* solution of barium chloride ($BaCl_2$). A white precipitate ($BaSO_4$) insoluble in 4*N* nitric acid proves the presence of the $SO_4^=$. Does the test show sulfate ion to be present? Write an equation for the reaction.[6]

Test another portion of the solution to determine whether or not it is acid in reaction. How is this done? [7] What ion is shown to be present by this test? [8]

To the remaining portion of the solution add *one drop* of chlorine water and 1 ml. of carbon tetrachloride. Shake. Result? [9] What ion was proved to be present? [10]

Add 5 ml. of hydrogen sulfide water (water saturated with H_2S) to an equal amount of iodine water (saturated). What immediate evidence is there for a chemical change? [11] Set the tube aside for 5 min. and then describe the appearance of the contents. Tell what the insoluble substance is, and write the equation for the reaction that has resulted in its formation.[12] Boil out the hydrogen sulfide and then test for the iodide ion. Result? [13]

2. Chemical Properties of Aqueous Solutions of Hydrogen Iodide. The reactions of these solutions, like those of hydrogen chloride and hydrogen bromide, are those of a strong acid. Make a general statement covering the actions of this acid with metals, their oxides, hydroxides, and carbonates.[14]

To 10 ml. of a 0.1*M* solution of ferric chloride add 1 ml. of a 0.1*N* solution of hydriodic acid and 2 ml. of carbon tetrachloride. Shake the tube vigorously and then note the color of the carbon tetrachloride layer. What substance is shown to be present? Write an equation for the reaction that has taken place.[15]

Add 1 ml. of 0.1*N* hydriodic acid to 10 ml. of a 0.1*N* solution of cupric sulfate. What is the precipitate? [16] Test the solution for iodine. Result? [17] Write an equation for the reaction between Cu^{++} and I^-.[18]

3. Formation of Insoluble Iodides. Add 2-ml. portions of 0.1*N* hydriodic acid to an equal amount of 0.1*N* solutions of each of the following: zinc sulfate, silver nitrate, mercuric chloride, magnesium chloride, mercurous nitrate, and lead nitrate. Which of these iodides are soluble in water? [19] Write the formula for, and record the color of, each of the insoluble iodides.[20]

(D) Hydrogen Fluoride. 1. Preparation and Action on Glass. Boil water in a beaker which is covered with a glass plate. When the latter is thoroughly warmed, remove it from the beaker, quickly dry it, and coat one side with a film of paraffin by rubbing a small lump of this substance over the surface of the glass. Scratch a design through the paraffin with the end of a file and then place the plate, coated side down, over a lead dish * containing about 3 g. of calcium fluoride and enough 36*N* sulfuric acid to cover the solid. Remove the plate after a half-hour, warm it to melt the paraffin and then wipe it off with a piece of filter paper. Note the etching on the glass. An aqueous solution of hydrogen fluoride reacts with glass but the surface that has been attacked does not exhibit the frosted appearance created by gaseous hydrogen fluoride.

Write equations to express the formation of hydrogen fluoride and its action on glass.[1] To what practical purpose is the latter action put? [2] What materials are used to make containers for aqueous solutions of hydrofluoric acid? [3] (Text)

2. Reactions of Fluoride Ion. Test the action of a 0.1*N* solution of sodium fluoride on 2-ml. portions of 0.1*N* solutions of each of the following ions: Ag^+, Pb^{++}, Mg^{++}, Zn^{++}, Hg_2^{++}, and Hg^{++}. Tell which of the fluorides of these substances are soluble, and which are insoluble.[4] What is the color of the insoluble fluorides? [5] Devise a table (on the report sheet) in which is shown the color and the solubility in water of all of the halides of the above ions.[6] Denote a soluble halide by "S" and an insoluble one by "I."

* A porcelain evaporating dish whose inner surface is coated with paraffin may be used if a lead dish is not available.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII

THE HYDROGEN HALIDES

Discussion

1.

(A) Hydrogen Chloride. *Preparation and properties*

1.

2.

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(A) Cont'd

9.

Chemical properties of aqueous solutions of hydrochloric acid

10.

11.

12.

13.

14.

15.

16.

17.

18.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(A) Cont'd

Summary

19.

20.

21.

22.

Reactions of the chloride ion, Cl^-

23.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(A) Cont'd

24.

25.

(B) Hydrogen Bromide. *Preparation and properties*

1.

2. **3.**

4.

5.

6.

7.

8.

9.

10.

Chemical properties of aqueous solutions of hydrogen bromide

11.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(B) Cont'd

12.

13.

14.

Formation of insoluble bromides

15.

16.

(C) Hydrogen Iodide. ***Preparation and properties***

1.

2.

3. **4.**

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(C) Cont'd

6.

7. **8.**

9. **10.**

11.

12.

13.

Chemical properties of aqueous solutions of hydrogen iodide

14.

15.

16. **17.**

18.

Formation of insoluble iodides

19.

20.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVII (Cont'd)

(D) Hydrogen Fluoride. *Preparation and action on glass*

1.

2.

3.

4.

5.

6.

Experiment XXVIII

OXYGEN COMPOUNDS OF THE HALOGENS

Discussion. Whereas the hydrogen halides decrease in stability from hydrogen fluoride to hydrogen iodide in the series HF—HCl—HBr—HI, the stability of the oxygen acids of the halogens increases with the atomic weight of the halogens from chlorine to iodine. No oxygen acid of fluorine or any salt of a hypothetical oxyacid of this element is known. Furthermore, the stability of the oxygen acids in each of the series of acids formed by the elements increases with the number of oxygen atoms in the molecule.

Construct a table, as indicated on the report sheet, giving the names, formulas, and oxidation states of the halogens in all of their oxygen acids.[1] (Text)

Materials: Potassium iodide-starch paper; 4 g. of potassium hydroxide; 1 g. of potassium perchlorate; solution of indigotin (soluble indigo); saturated aqueous solution of sulfur dioxide.

(A) Preparation of Bleaching Powder, Potassium Chlorate, and Sodium Hypochlorite. Set up the apparatus shown in Fig. 76. The *loose* plug of cotton in the bulb of the drying

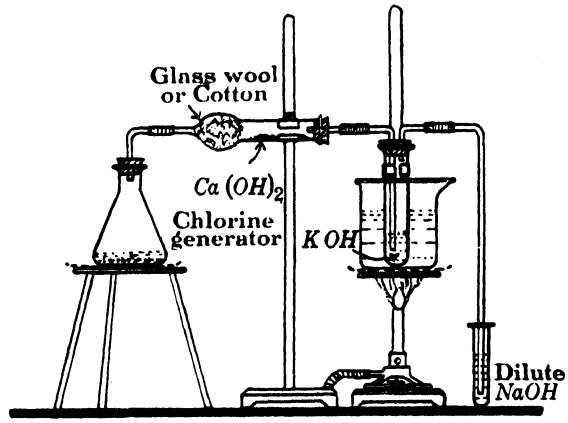


FIG. 76. Preparation of bleaching powder, potassium chlorate, and sodium hypochlorite

tube prevents the entrance of spray from the chlorine generator. If the cotton is packed in too tightly, the stopper will be blown out of the generator soon after the evolution of chlorine begins. Use a steel spatula to mix 1.5 g. of calcium hydroxide with 0.5 ml. of water in a mortar until a pasty mass is obtained. Spread the latter in a thin layer in the drying tube.

Place a solution of 4 g. of potassium hydroxide in 10 ml. of water in the 20-cm. test tube, measure out 175 ml. of water into the 400-ml. beaker and heat it to boiling. *The water must be kept at the boiling point throughout the experiment.* Now add 10 ml. of 4*N* sodium hydroxide to the small test tube.

Charge the chlorine generator with 9.5 g. of manganese dioxide, 40 ml. of water, 36 ml. of concentrated hydrochloric acid, and then quickly connect the generator to the drying tube. Warm the generator gently so that a *slow* stream of chlorine passes through the apparatus. Note the absorption of the gas in the solution of potassium hydroxide after the air has been driven out of the generator and the drying tube. Continue the passage of the gas until it ceases to be absorbed in the solution of *sodium* hydroxide.

Remove the small test tube and stopper it at once. Disconnect the large test tube, pour its contents into a small beaker, and then boil the solution for 1 min. Set the solution aside for use in part (C). Detach the drying tube containing the bleaching powder, stopper it at one end, and close the smaller end by attaching to it a short piece of rubber tubing closed by means of a pinch clamp. Now fit the generator flask with a delivery tube which dips down into 300 ml. of cold water contained in a beaker. This prevents the escape of chlorine into the laboratory. Do not dispose of the contents of the generator until almost the close of the laboratory period.

Write equations for the formation of the products obtained in this part of the experiment.[1] What would have formed in the solution of potassium hydroxide if the latter had not been heated? [2]

(B) Properties of Hypochlorites. 1. Bleaching Action. Test the solution of sodium hypochlorite prepared in part (A) with litmus paper. Result? Explain.[1] Add 4 ml. of 4*N* sodium hydroxide to the solution and again test it with litmus paper. What difference is observed? [2] (If the solution is not alkaline to litmus add 4*N* sodium hydroxide until this condition is brought about.)

Place a 2-ml. portion of a solution of "soluble indigo" * (indigotin) in each of two 4-in. test tubes. Add a drop of the solution of sodium hypochlorite to one of the tubes. Result? [3] To the other tube add 1 drop of sodium hypochlorite and 10 drops of 4*N* sulfuric acid. Warm both tubes about 2 min. and then record the results.[4] Compare these results with those obtained in the case of litmus, and make a general statement regarding the bleaching action of a hypochlorite in acid and in alkaline solution.[5]

2. Oxidation with Hypochlorite Ion, ClO^-; Detection of Br^- in the Presence of I^-. Place 0.5 ml. of a 0.1*N* solution of potassium iodide in a 10-cm. test tube containing 1 ml. of carbon tetrachloride. Measure out 1.5 ml. of the alkaline sodium hypochlorite solution into a 5-ml. graduate. Add 2 or 3 drops of this solution to the contents of the test tube. Shake the tube vigorously. Tell what substance is shown to be formed, and write an equation to show its formation.[6] Now add the remainder of the sodium hypochlorite solution, and again shake the test tube. Result? Write the equation for this reaction.[7]

Repeat the above procedure, but use a 0.1*N* solution of potassium bromide instead of potassium iodide. What can be said about the ability of the hypochlorite ion to oxidize bromide ion in alkaline solution? [8] Acidify the solution with 5 drops of 4*N* sulfuric acid. Shake the tube. Tell what substance is concentrated in the carbon tetrachloride layer, and write an equation to show how it is formed.[9]

The difference in the behavior of iodide ion and bromide ion toward hypochlorite ion in alkaline solution, and the ability of hypochlorite ion to oxidize free iodine is made the basis of the following procedure used to detect bromide ion in the presence of iodide ion. Mix in a 6-in. test tube 0.5 ml. of 0.1*N* potassium iodide solution with an equal volume of potassium bromide of the same normality. Add 2 ml. of carbon tetrachloride and several drops of the alkaline sodium hypochlorite solution. Result? [10] Now add an additional 2 ml. of the sodium hypochlorite and shake the tube until the color has disappeared. Acidify the solution with 10 drops of 4*N* sulfuric acid, and then shake the tube. What evidence is there for the presence of bromide ion in the original solution? [11]

3. Reactions of Bleaching Powder and Hypochlorous Acid. Treat a small amount of the bleaching powder prepared in this experiment with several drops of dilute sulfuric acid. Determine the nature of the gas evolved by testing it with potassium iodide-starch paper.[12] Write an equation to show what takes place.[13]

Shake the remainder of the bleaching powder with 25 ml. of water for a period of from 3 to 4 min. Filter the mixture into a 50-ml. Erlenmeyer flask. Now generate carbon dioxide from several chips of marble (or an equal amount of powdered calcium carbonate) and 5 ml.

* 1 g. of indigotin per liter of water.

of 4*N* hydrochloric acid contained in a test tube. Write the equation for this reaction.[14] Pass the gas through the solution of bleaching powder 15 min. At the end of this time filter the solution. If the filtrate is not clear, pour it once more through the same paper. Write the equation for the reaction of carbon dioxide with a solution of bleaching powder.[15]

Test the action of the solution of hypochlorous acid on litmus,[16] indigo,[17] and 0.1*N* solutions of potassium iodide [18] and potassium bromide.[19]

(C) Properties of Chlorates. 1. Recrystallization of Potassium Chlorate. Filter the solution containing the crystals of potassium chlorate prepared in part (A). Use the steel spatula to transfer to the filter paper those crystals remaining in the beaker. Wash the crystals on the filter paper with 3 ml. of cold water. After this liquid has drained, transfer the crystals to a small beaker containing 7 ml. of water, and dissolve the solid by bringing the solution to its boiling point. Cool the solution by holding the beaker containing it in a larger beaker partly filled with cold water. Stir the solution with a glass rod to hasten the process of cooling.

Which of the two salts contained in the solution is the more soluble one? (Text) [1] Which salt therefore can be expected to constitute the greater part of the crystals which have settled out from the cooled solution? [2] Filter off the crystals and wash them once on the filter paper with 5 ml. of a cold solution containing equal volumes of alcohol and water. Allow the liquid to drain thoroughly, and then transfer the crystals to a double thickness of filter paper placed on a watch glass. Press the crystals on the paper to dry them as much as possible, and then transfer them to another piece of filter paper to complete the drying process. Allow the crystals to remain exposed to the air for a period of 10 min. before proceeding with the next part of the experiment.

Test for a chlorate by heating about 0.5 g. of the crystals with a small amount of manganese dioxide contained in a 10-cm. test tube (Exp. XI). Is the test positive or negative? [3]

2. Oxidation with Chlorate Ion. Make a solution of 0.2 g. of the potassium chlorate crystals in 10 ml. of water. Divide the solution equally between two test tubes. To one tube add 1 ml. of indigo solution, and to the other add a piece of litmus paper. Result? [4] Now add 5 drops of 36*N* sulfuric acid to each tube. What do the results show in regard to the oxidizing power of a chlorate in acid solution as compared with that shown in a neutral solution? [5]

Test the action of 1 ml. of 12*N* hydrochloric acid on a few crystals of the chlorate. Identify the gas evolved by cautiously noting its odor, and write an equation to show how it is formed.[6]

3. Solubility of Chlorates. Treat separate 2-ml. portions of a 0.1*M* solution of potassium chlorate with equal volumes of 0.1*N* solutions of the following ions: Ag^+, Pb^{++}, Mg^{++}, Zn^{++}, Hg_2^{++}, and Hg^{++}. Contrast the solubility of each of the preceding chlorates with that of the corresponding chlorides (Exp. XXVII).[7]

(D) Properties of Perchlorates. 1. Thermal Decomposition of a Perchlorate. Heat 0.5 g. of potassium perchlorate strongly in a 10-cm. test tube. Use a glowing splint to test for oxygen. Write an equation for the reaction by which the gas is formed.[1] Show by an equation how a perchlorate can be prepared from a chlorate.[2]

2. Stability of Perchlorate Ion in Acid Solution. Add 1 ml. of 12*N* hydrochloric acid to 0.1 g. of potassium perchlorate contained in a test tube. Does a reaction take place? Compare with the action of a chlorate on the same reagent.[3]

Dissolve 0.4 g. of potassium perchlorate in 30 ml. of water to make an approximately 0.1*N* solution of the salt. Place 3 ml. of this solution together with 5 drops of 36*N* sulfuric acid in each of two test tubes. To one tube add 1 ml. of indigo solution, and to the other a piece of litmus paper. Compare the results with those noted in the reaction of chlorate ion with these same substances in acid solution.[4] Make a statement regarding the degree of

stability of perchlorate ion as compared with that of chlorate ion toward the oxidizable substances used above.[5]

3. Solubility of Perchlorates. Measure a 3-ml. portion of the potassium perchlorate solution into each of six test tubes, and then determine whether or not any of the following ions bring about the formation of insoluble perchlorates: Ag^+, Pb^{++}, Mg^{++}, Zn^{++}, Hg_2^{++} and Hg^{++} (use 1 ml. of 0.1*N* solutions). Results? [6] Compare with the solubility of the corresponding chlorates.[7]

(E) Properties of Bromates and Iodates. 1. Bromates. Shake 3 ml. of iodine water with 1 ml. of carbon tetrachloride in a test tube until most of the iodine has been extracted from the aqueous layer. Now add to the mixture 5 ml. of a 0.1*M* solution of potassium bromate and 10 drops of 4*N* sulfuric acid. Shake the tube vigorously. Note the color changes and write equations for the reactions that take place.[1]

Mix in a test tube 3 ml. of a 0.1*M* solution of potassium bromate with 3 ml. of 0.1*N* potassium iodide solution. Add to the mixture 1 ml. of carbon tetrachloride and 1 drop of 4*N* sulfuric acid. Shake the tube. What substance is extracted by the carbon tetrachloride? Write an equation to show its formation.[2]

Add 1 ml. of a 0.1*N* solution of silver nitrate to 1 ml. of potassium bromate solution. Shake the test tube vigorously until a precipitate forms. Note the color of the precipitate and tell what it is.[3] Now add 5 ml. of water and heat the mixture to its boiling point. What does the result show regarding the solubility of silver bromate? [4] How does the solubility of this salt compare with that of silver chlorate at ordinary temperatures? [5] Repeat the experiment with a bromide in place of the bromate. Compare the color and solubility of silver bromide with those of silver bromate.[6]

2. Iodates. Dilute 1 drop of a 0.1*M* solution of potassium iodate to a volume of 10 ml. To this solution add 1 ml. of carbon tetrachloride, 5 drops of 0.1*N* potassium iodide solution, and then 1 drop of 4*N* sulfuric acid. Shake the mixture thoroughly. Describe what takes place, and write an equation for the chemical reaction responsible for the observed change.[7]

Dilute 1 drop of 0.1*M* potassium iodate solution to a volume of 10 ml., and then add 1 drop of a 0.1*N* solution of silver nitrate. Heat the resulting mixture to boiling. Result? [8] Compare the solubility of silver iodate with that of silver bromate and silver chlorate.[9]

Place in a test tube 1 ml. of carbon tetrachloride and 10 ml. of a solution made by diluting 1 drop of 0.1*M* potassium iodate to a volume of 10 ml. Add 2 drops of a saturated aqueous solution of sulfurous acid, and then shake the tube. Write an equation to account for the formation of the substance found in the carbon tetrachloride layer.[10] Now add an additional 5 ml. of sulfurous acid. Result? [11] Write an equation for the reaction.[12]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVIII

OXYGEN COMPOUNDS OF THE HALOGENS

Discussion

1.

Oxygen Acids of the Halogens

Name	Chlorine	Bromine	Iodine	Oxidation state

(A) Preparation of Bleaching Powder, Potassium Chlorate, and Sodium Hypochlorite

1.

2.

(B) Properties of Hypochlorites. *Bleaching action*

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVIII (Cont'd)

(B) Cont'd

5.

Oxidation with hypochlorite ion, ClO^-; detection of Br^- in the presence of I^-

6.

7.

8.

9.

10. **11.**

Reactions of bleaching powder and hypochlorous acid

12.

13.

14.

15.

16. **17.**

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVIII (Cont'd)

(B) Cont'd

18.

19.

(C) Properties of Chlorates. *Recrystallization of potassium chlorate*

1.

2.

3.

Oxidation with chlorate ion

4.

5.

6.

Solubility of chlorates

7.

(D) Properties of Perchlorates. *Thermal decomposition of a perchlorate*

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVIII (Cont'd)

(D) Cont'd

Stability of perchlorate ion in acid solution

3.

4.

5.

Solubility of perchlorates

6.

7.

(E) Properties of Bromates and Iodates. *Bromates*

1.

2.

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXVIII (Cont'd)

(E) Cont'd

Iodates

7.

8.

9.

10.

11.

12.

Experiment XXIX

EFFECT OF TEMPERATURE ON SOLUBILITY

Discussion. The solubility of a substance at a given temperature is defined as the concentration of a saturated solution of a solute in a solvent. The concentration may be expressed in any units desired, as, for example, grams of solute dissolved in 100 g. of solvent; grams of solute dissolved in 100 ml. of solution; or moles of solute dissolved in 1 liter of solution (molar solubility).

A solution is saturated when it is in equilibrium with excess of the undissolved solute. Saturation is usually achieved by shaking the solution with an excess of the solute until there is no further change in concentration. A measured quantity of the saturated solution is then evaporated or analyzed by chemical means to determine the solubility.

In this experiment the solubility of potassium nitrate, expressed in grams of solute per 100 g. of water, is determined at a series of temperatures in the following manner. Measured amounts of potassium nitrate and water are heated together until the solute is completely dissolved. The solution is then cooled and the temperature at which the solute just begins to separate is noted. At this temperature the solution is saturated. A measured amount of water is added to the solution and the procedure is repeated. This time the solute will appear at a lower temperature. For what type of solute would the crystals appear at a higher temperature? [1] It is important that the solute does not readily form supersaturated solutions. Why? [2]

A curve drawn to represent the data of this experiment gives the solubility of the salt at any temperature within the temperature range studied.

Apparatus and Materials: Beam balance; 35 cm. of No. 14 B. & S. gauge copper wire for a stirrer; 5-ml. pipette; 10 g. of KNO_3.

(A) Solubility Curve for Potassium Nitrate. Equip an 8-in. test tube with a two-holed rubber stopper, a thermometer and a stirrer as illustrated in Fig. 77. The stirrer is made from glass rod or heavy copper wire. It should move freely through the stopper.

Weigh 10.00 g. of potassium nitrate to the nearest 0.05 g. and transfer it to the test tube. Note the temperature of the distilled water in the wash bottle.[1] Transfer 5 ml. of this water to the test tube with a 5-ml. pipette. What weight of water was added? [2] (Appendix E) Record all of the data for the experiment on the form provided on the report sheet.[2]

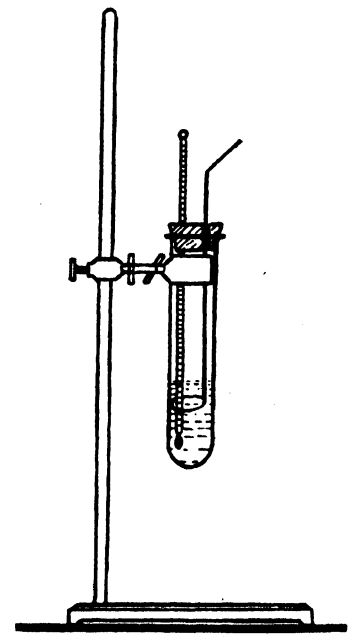


FIG. 77. Determination of the solubility of a salt at various temperatures

Stir the solution continuously and heat it with a small flame until the potassium nitrate has completely dissolved (about 95 to 100°). Allow the solution to cool. Note the approximate temperature at which crystallization begins. Now carefully heat the solution a few degrees above this temperature and determine accurately the temperature at which crystals begin to form.[2]

Add another 5 ml. of the distilled water, heat until the solid dissolves, and again note the temperature at which crystallization begins. Repeat after a third and finally a fourth addition of 5 ml. of distilled water. Calculate the solubility of potassium nitrate in grams of solute dissolved by 100 g. of water at each of the above temperatures.[2]

Place the test tube and its contents in a beaker of water at about 25° and stir the solution at intervals for 10 min. Weigh an evaporating dish to the nearest 0.01 g.[3] Note the temperature of the solution.[3] When the crystals have settled, rinse the 5-ml. pipette with 1 or 2 ml. of the solution, and then carefully transfer 5 ml. of the clear solution to the evaporating dish. Weigh the dish and the solution.[3] Evaporate the solution to dryness over a beaker of boiling water. Dry the bottom of the evaporating dish, allow the latter to cool, and finally weigh the evaporating dish plus the residue.[3] Calculate the solubility of potassium nitrate at the observed temperature in grams of solute per 100 g. of water.[3] Calculate its molar solubility at this temperature.[4]

The solubility of potassium nitrate at 0° is 13 g. per 100 g. of water and at 100° it is 242 g. per 100 g. of water. Plot a curve on the graph paper (provided with the report sheets) using these two values and the values determined experimentally. Plot the temperatures as abscissae and the solubilities as ordinates.[5]

Read from the curve the solubility of potassium nitrate at the following temperatures: 15.0°, 25.0°, 35.0° and 50.0°.[6]

(B) Solubility Curve for Sodium Chloride. Plot the following data for sodium chloride on the sheet of graph paper used for part A:

Temperature	Solubility (Grams of NaCl per 100 g. H_2O)
0°	35.7
25°	36.2
50°	37.0
75°	38.1
100°	39.8

Study the two curves and suggest a method of separating sodium chloride and potassium nitrate on the basis of their differences in solubility.[1] Compare the solubility curves of sodium nitrate and potassium chloride with the curves drawn in this experiment and explain why it is possible to prepare potassium nitrate from sodium nitrate and potassium chloride.[2] (Text) Suggest a procedure for this preparation.[3]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIX

EFFECT OF TEMPERATURE ON SOLUBILITY

Discussion

1.

2.

(A) Solubility Curve for Potassium Nitrate

1.

2.

Total Volume of Water Added	Total Weight of Water	Weight of KNO_3	Temperature at Crystallization	Solubility (Grams per 100 g. of H_2O)
5 ml.				
10 ml.				
15 ml.				
20 ml.				

3. Weight of evaporating dish + solution . . . . . .
Weight of evaporating dish . . . . . .
Weight of solution . . . . . .

Weight of evaporating dish + residue . . . . . .
Weight of residue . . . . . _____
Weight of KNO_3 . . . . . .

Weight of water . . . . . .
Solubility of KNO_3 at _____° C in g./100 g. H_2O . . . . . .

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXIX (Cont'd)

(A) Cont'd

5. Graph

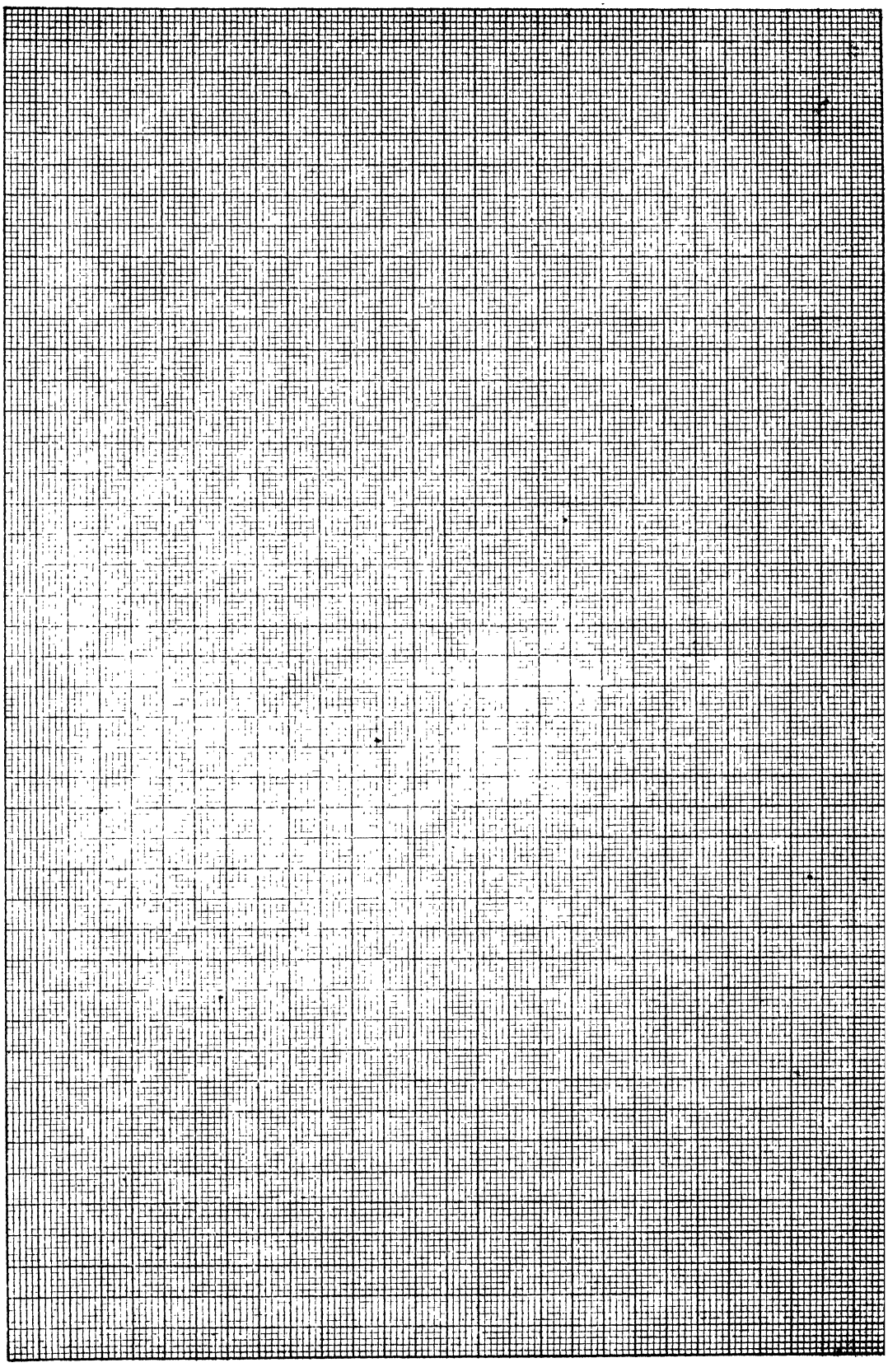
6.

(B) Solubility Curve for Sodium Chloride

1.

2.

3.



Experiment XXX

SOLUTIONS

Discussion. Certain general properties of solutions of solids, gases, and liquids are studied in this experiment.

Materials: 2 g. of $Na_2CO_3 \cdot 10H_2O$; 12 ml. of ethyl alcohol; 12 ml. of carbon tetrachloride; 0.05 g. of iodine; 2 g. of anhydrous sodium carbonate; 5 g. of sodium acetate; 0.05 g. of paraffin.

(A) Particle Size (Surface) and Rate of Solution. Select two crystals of cupric sulfate of about the same size (1 g.). Thoroughly grind one of them in a mortar. Place the powder in one test tube and the crystal in a second test tube. Add 15 ml. of water to each test tube, stopper them tightly, and shake both of them at the same time in the same hand. Note the time required to dissolve the cupric sulfate in each test tube.[1] Explain.[2]

(B) Effect of Convection Currents and Stirring. Fill two test tubes with water and into one of them drop a small crystal of potassium permanganate. Bend a narrow strip of paper into the shape of a U and place it in the other tube so that the bottom of the U is below the surface of the water. Place on this strip of paper a second crystal of about the same size. Note the convection currents set up in this test tube. Record the time required to dissolve each crystal.[1] Explain the difference in the rate at which the water in the two test tubes becomes colored.[2]

(C) Effect of Temperature on the Solubility of Solids. Place about 4 g. of finely pulverized potassium dichromate in a test tube and add about 10 ml. of water. Approximately how much of the solid dissolves? [1] Heat the solution slowly, stir it continually, and note the temperature at which all of the solid dissolves.[2] Divide the solution into two equal parts. Cool one of the test tubes rapidly by shaking it in a stream of cold water; allow the other to cool slowly in the test-tube rack. Describe the difference in the appearance of the crystals.[3]

To 10 ml. of 0.1*N* lead acetate solution add 1 ml. of 4*N* hydrochloric acid. Repeat the experiment, but this time heat the lead acetate solution to boiling before adding the hydrochloric acid. Explain the difference in behavior.[4] Observe the solution as it cools.[5]

(D) Effect of Temperature on the Solubility of Gases. Completely fill a 20-cm. (8-in.) test tube with tap water. Place a small square of paper over the top of the test tube and invert it in a 400-ml. beaker of water. If all air bubbles were not excluded, try again. Clamp the test tube in position with as much of the test tube above the clamp as is possible. Heat the test tube about 1 in. above the clamp until the level of the water begins to fall rapidly. Note the formation of gas bubbles during the heating. After the test tube has cooled make a mark at the boundary between the gas and the liquid, empty the water from the test tube, and then measure the volume that was occupied by the gas.[1] Measure the volume of the test tube and estimate the volume of air dissolved in 100 ml. of the water.[2] Compare gases and solids with respect to the influence of increased temperature on their solubility.[3]

(E) Thermal Effects Accompanying Solution. Shake 2 g. of ammonium chloride with 5 ml. of water. Is heat liberated or absorbed? Will ammonium chloride be more soluble or less soluble with increased temperature? [1]

Add 2 g. of anhydrous sodium carbonate to 5 ml. of water. What heat effect accompanies the solution of this substance? [2] Repeat the experiment but this time add 2 g. of

sodium carbonate decahydrate to 5 ml. of water. Explain the difference between the heat effects in these two cases.[3]

What relation exists between the sign of the thermal effect observed when a salt is dissolved in its nearly saturated solution and the change in solubility with temperature? [4] (Text) Heat is liberated when anhydrous sodium sulfate is dissolved in water at temperatures above 33°. Will the solubility increase or decrease with a rise in temperature? [5]

(F) Supersaturated Solutions. Place about 5 g. of sodium acetate in a test tube, add 2 ml. of water, and heat until the solid dissolves. Stopper the test tube and allow it to cool to room temperature. Remove the stopper and drop a small crystal of sodium acetate into the solution. What happens? [1] How can it be determined whether a given solution is unsaturated, saturated, or supersaturated? [2]

(G) Choice of Solvent. Test the solubility of each of the following substances in ethyl alcohol, carbon tetrachloride, and water: paraffin, sodium acetate, potassium chloride, iodine, and sugar. Use small samples of each solid (0.05 g., about the size of the head of a match) and about 3 ml. of each solvent. List after each solvent the solids that dissolve in it.[1] Arrange the three solvents in the order of their polarity.[2] What general rule may be stated with regard to the type of substance dissolved by nonpolar solvents; by polar solvents? [3] What procedure should be followed to remove a mixture of sugar and grease (or paraffin) from a piece of cloth? [4]

Add 5 ml. of alcohol to a solution of cupric sulfate made by dissolving 0.3 g. of the sulfate in 3 ml. of water. Explain the formation of the precipitate.[5]

(H) Miscibility of Liquids. Test the miscibility of the following pairs of liquids: alcohol-water, alcohol-carbon tetrachloride, carbon tetrachloride-water. Add the first liquid of the pair, drop by drop, to 1 ml. of the second liquid. In which pairs are the components completely miscible? [1] Describe and explain what takes place during the addition of an excess of alcohol (95%) to carbon tetrachloride.[2] What general rule may be stated with regard to the types of liquids that dissolve in each other? [3]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXX

SOLUTIONS

(A) Particle Size (Surface) and Rate of Solution

1.

2.

(B) Effect of Convection Currents and Stirring

1.

2.

(C) Effect of Temperature on the Solubility of Solids

1. **2.**

3.

4.

5.

(D) Effect of Temperature on the Solubility of Gases

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXX (Cont'd)

(E) Thermal Effects Accompanying Solution

1.

2.

3.

4.

5.

(F) Supersaturated Solutions

1.

2.

(G) Choice of Solvent

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXX (Cont'd)

(G) Cont'd

5.

(H) Miscibility of Liquids

1.

2.

3.

Experiment XXXI

DETERMINATION OF MOLECULAR WEIGHT IN SOLUTION

Discussion. One mole of any nonvolatile, nonionizing or nonassociating solute dissolved in 1000 g. of a solvent raises the boiling point and lowers the freezing point of the solvent a definite amount. Thus each mole of such a solute dissolved in 1000 g. of water raises the boiling point 0.52° at 760 mm. and lowers the freezing point 1.86°. These values are called the molecular boiling-point constant and the molecular freezing-point constant respectively for water.

The molecular boiling-point constant for carbon tetrachloride is 5.03°. Therefore, the rise in the boiling point of this liquid for a given solution is equal to the number of moles of the solute dissolved in 1000 g. (the molal concentration) times 5.03, that is,

$$\Delta T_b = m \times 5.03 = \frac{(g)\ (1000)}{(G)\ (M)} \times 5.03$$

where ΔT_b is the rise in boiling point, m is the molality, G is the weight of solvent, g is the weight of solute, and M is the molecular weight of the solute. If the rise in boiling point is measured, and if the weights of the solute and the solvent are known, the molecular weight of the solute can be calculated from the above expression.

The molecular freezing-point constant of diphenyl ($C_6H_5 \cdot C_6H_5$) is 8.0°. This means that each mole of solute dissolved in 1000 g. of diphenyl lowers the freezing point 8.0°, that is,

$$\Delta T_f = m \times 8.0 = \frac{(g)\ (1000)}{(G)\ (M)} \times 8.0$$

where ΔT_f is the freezing-point depression and the remaining symbols have the same meaning as in the previous equation.

What is the principal advantage of these two substances (carbon tetrachloride and diphenyl) over water as a solvent for the determination of molecular weight by these two methods? [1]

Apparatus and Materials: 50 cm. of 8-mm. glass tubing; 20 ml. of carbon tetrachloride; 6 g. of naphthalene; 15 g. of diphenyl.

(A) The Boiling-point Method.* Set up an apparatus as illustrated in Fig. 78. Use a 20-cm. (8-in.) test tube fitted with a two-holed cork stopper which has in one hole an 8-mm. glass tube about 50 cm. long and in the other hole a thermometer (preferably 110°). Adjust the thermometer until the bulb is 2 cm. above the bottom of the test tube. To prepare the capillary tubes, heat a piece of glass tubing in the flame until it is soft and then draw the heated portion of the tube to a length of about 2 ft. Cut 5-cm. sections from the capillary portion of the tube and seal them at one end. Place 6 or 8 capillary tubes in the test tube with the open ends down. These tubes facilitate boiling and prevent superheating of the liquid.

Add 20 ml. of carbon tetrachloride (density = 1.59 g./ml.) to the test tube. Heat the water in the beaker to about 80°. Turn off the gas until the flame is large enough to maintain the temperature of the water between 85 and 90°.

* This experiment is similar to that described by Rose and Billinger, J. Chem. Ed. 7, 2715 (1930).

After the temperature of the water has been adjusted and after the carbon tetrachloride begins to condense in the glass tube and drop back into the test tube, read the thermometer to tenths of a degree every minute until the readings do not vary more than 0.3° in 5 consecutive minutes. Record the temperature readings in the spaces provided on the report sheet.[1] The average of these values is the boiling point of the carbon tetrachloride under the existing barometric pressure. Remove the test tube from the bath and cool the carbon tetrachloride in a beaker of cold water or in a stream of running water. Weigh out 3 g. of naphthalene to the nearest 0.01 g. and add it to the carbon tetrachloride.[2] Place the test tube in the beaker of water and determine the boiling point of the solution in the same manner as described above. Record the temperature readings on the form provided on the report sheet.[1]

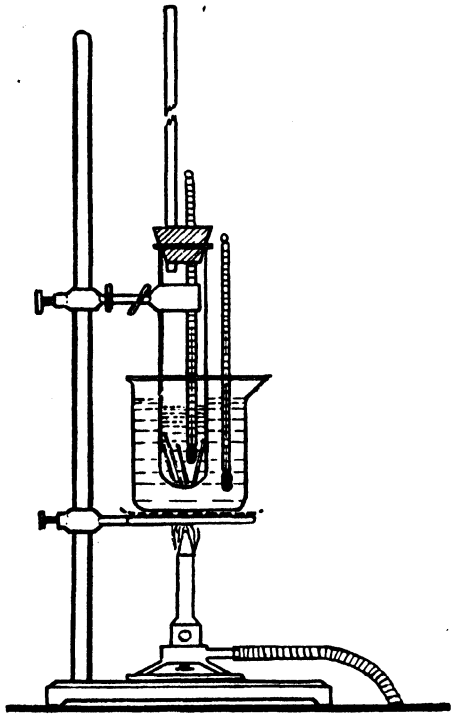


FIG. 78. Molecular weight by the boiling-point method

Calculate the molecular weight of naphthalene.[2] List several sources of error in the determination.[3]

(B) Freezing-point Method. Set up a melting-point apparatus similar to the arrangement shown in Fig. 77, except that a beaker two thirds full of water is supported on a ring under the 20-cm. test tube. The two-holed stopper holds the thermometer in place with its bulb about 1 cm. from the bottom of the test tube. A stirrer, prepared from No. 14 copper wire, passes loosely through the other hole.

Weigh out 15 g. of diphenyl to the nearest 0.1 g. and transfer it to the test tube. Heat the water in the beaker until all of the diphenyl has melted (about 75°). Remove the test tube from the water and stir the diphenyl while it cools. Record the temperature every minute until the diphenyl has solidified at about 65°.[1]

Weigh out 3 g. of naphthalene to the nearest 0.01 g. Record its weight.[2] Place the test tube in the beaker of water and heat the beaker until the diphenyl has melted. Transfer the naphthalene to the test tube and stir the mixture until the naphthalene has dissolved. Raise the test tube, stir the contents continually, and note the temperature every 30 sec. until solidification is complete (about 50°). Record these temperatures in the spaces provided on the report sheet.[1]

Plot the two sets of data on graph paper (Exp. VI, Fig. 44).[3] The temperature corresponding to the center of the section of the curve that is parallel, or nearly parallel, with the time axis is taken as the freezing point. Record the freezing point of the diphenyl and of the solution of naphthalene in diphenyl.[2] Calculate the molecular weight of naphthalene.[2] Compare it with the value obtained in part (A) by the boiling-point method.[4] The formula of naphthalene is $C_{10}H_8$. What is the molecular weight corresponding to this formula?[5] What is the percentage error of the two values determined in this experiment?[6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXI

DETERMINATION OF MOLECULAR WEIGHT IN SOLUTION

Discussion

1.

(A) The Boiling-point Method

1.

Readings	Boiling Point CCl_4	Boiling Point of Solution
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
Average of last 5		

2. Volume of CCl_4 . . . . . .
Weight of CCl_4 . . . . . .
Weight of naphthalene . . . . . .
Rise in boiling point . . . . . .
Calculated molecular weight . . . . . .

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXI (Cont'd)

(B) Freezing-point Method

1.

Diphenyl		Diphenyl + Naphthalene	
Time	Temperature	Time	Temperature

2. Weight of diphenyl . . . . . .
Weight of naphthalene . . . . . .
Freezing point of diphenyl . . . . . .
Freezing point of diphenyl + naphthalene . . . . . _____
Freezing point depression . . . . . .
Calculated molecular weight . . . . . .

3. Graph

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXI (Cont'd)

(B) Cont'd

5.

6.

Experiment XXXII

VELOCITY OF CHEMICAL REACTIONS. EQUILIBRIUM

Discussion. Many chemical reactions proceed so rapidly that their rate cannot be measured. Neutralizations and other ionic reactions are, in general, said to be instantaneous. On the other hand, certain chemical changes take place slowly enough to permit the measurement of their velocity. A number of factors influence the rate at which these "time reactions" occur; the effects of temperature and concentration are studied in this experiment. List the other factors which affect the rate of a chemical reaction (Text).[1]

Apparatus and Materials: Stop watch, or wrist or pocket watch with second hand; 12 cm. of 7-mm. rubber tubing; 30-cm. of 6-mm. glass tubing; 0.05*M* sodium thiosulfate; standard solutions of iodic acid and sulfurous acid [see part (B)]; 1 g. of $CoCl_2 \cdot 6H_2O$; ice.

(A) Rate of Reaction. The Effect of Temperature. Read this entire experiment carefully before carrying it out. Measure out a 10-ml. portion of a 0.05*M* solution of sodium thiosulfate ($Na_2S_2O_3$) into each of five test tubes. Place these tubes in a 400-ml. beaker and then add cold water until its level rises slightly above that of the solutions in the test tubes. The temperature of the water should be between 10 and 15°. If the water from the tap is not cold enough, add small pieces of ice to the water in the beaker until the temperature falls within the stated range.

Prepare 8 ml. of 0.5*N* sulfuric acid from the 4*N* desk reagent. Use a thermometer to stir the solution in one of the test tubes until the temperature remains constant over a period of 3 min. When this temperature equilibrium is reached between the solution of thiosulfate and the water in the beaker, quickly pour 1 ml. of the 0.5*N* acid into the tube containing the thermometer. Note and record on the report sheet the time to the second * at which the acid is added.[1] Now stir the contents of the tube with the thermometer to insure thorough mixing. Observe the solution carefully and, at the first appearance of a faint milky color, note and record the time in the designated column on the form provided on the report sheet.[1] Write equations for the reactions taking place.[2]

Remove from the beaker the test tube in which the reaction has occurred. Wash and dry the thermometer and place it in one of the four test tubes remaining in the beaker. Heat the beaker until the temperature of *the thiosulfate solution* rises from 8 to 10°, and then remove the gas burner. Stir the solution until temperature equilibrium is reached. Record the temperature, add 1 ml. of 0.5*N* sulfuric acid, and record the time of addition. Stir the contents of the tube thoroughly, and again note the time at which the first sign of cloudiness becomes visible.

Repeat the procedure at successive 10° rises in temperature until all five time-temperature readings have been made. It is not necessary to attempt to obtain a rise of exactly 10°; a difference of from 8 to 13° between successive trials serves the purpose equally well.

Determine the elapsed time for each run, and then plot these values (as ordinates) against the temperature readings on one of the sheets of graph paper supplied with this

* A stop watch is preferred for this purpose. If this is not available, use a wrist or pocket watch which has a second hand. In this event the time at which the acid is to be added is selected in advance and recorded on the report sheet. The movement of the second hand is then observed, and when the hand reaches the selected position (preferably the 60-sec. mark) the acid is added.

experiment. Let each millimeter division on the paper represent 1 sec. and also 1°. Draw a smooth curve joining the points. Read from the curve the number of minutes required for the reaction at 20° and at 30°. What effect does a rise of 10° have upon the time required for the reaction to take place? [3] Determine whether or not the effect is the same for other 10° intervals. Make a general statement covering the influence of a 10° change of temperature upon the time required for this reaction to take place.[4]

Since the time is inversely proportional to the rate at which a chemical reaction takes place, then the reciprocal of the time ($1/t$) is proportional to the rate of the reaction. Thus, if $1/t$ is plotted against the temperature, the effect of temperature on the rate of the reaction can be read directly. Calculate $1/t$ for each period of elapsed time measured in this experiment.[1] Plot these values as ordinates and the temperatures as abscissae on the same sheet of graph paper used for the first curve. Let each millimeter division on the horizontal axis be equivalent to 0.002 unit, and each division on the vertical axis represent 1°. Draw a smooth curve joining the points. What does this curve show with regard to the effect of temperature on the rate of a reaction? [5] From this curve read and record three sets of data which show that a 10° rise in temperature approximately doubles the rate of a chemical reaction.[6]

(B) Rate of Reaction. The Effect of Concentration. Obtain about 20 ml. of a solution which contains 4.86 g. of potassium iodate and 9 ml. of 4*N* sulfuric acid per liter of solution. Measure out into a small flask 30 ml. of a solution containing 3.33 g. of sodium sulfite and 30 ml. of 4*N* sulfuric acid in 5 liters of solution. Stopper this flask immediately and do not remove the stopper except when pouring out the portions of the solution required in this experiment. Lastly, measure out 5 ml. of starch solution and pour it into a small beaker.

Read the remainder of this experiment before carrying it out. Measure 16 ml. of distilled water into a 20-cm. test tube and then add to it 5 ml. of the sulfite solution and 2 drops of starch solution. Add the latter from a medicine dropper. Now pour into the test tube exactly 1 ml. of the iodate solution and record the time to the second.[1] Quickly shake the tube to insure thorough mixing and then place it in an empty 400-ml. beaker. Record also the number of milliliters of water and iodate solution used.[1] Watch the solution in the tube carefully and record the exact time at which a blue color appears.[1] The color change occurs suddenly, and the color reaches its full intensity almost immediately. In order to facilitate the reading of the time, place the watch on the desk immediately in front of the beaker. This arrangement permits the simultaneous observation of the solution and the watch.

The acidified solutions of potassium iodate and sodium sulfite used in this experiment may be regarded as solutions of iodic acid and sulfurous acid respectively. These two acids react in several steps:

$$IO_3^- + 3H_2SO_3 + 6H_2O \rightarrow I^- + 3SO_4^= + 6H_3O^+ \quad (1)$$

$$IO_3^- + 5I^- + 6H_3O^+ \rightarrow 3I_2 + 9H_2O \quad (2)$$

$$H_2SO_3 + I_2 + 5H_2O \rightarrow 2I^- + SO_4^= + 4H_3O^+ \quad (3)$$

Free iodine in a concentration sufficient to give the blue color with starch exists only after the sulfurous acid has been used up in reactions (1) and (3). In order to study the effect of concentration alone on the rate of reaction, the temperature of the water and the solutions used must remain constant (room temperature) throughout the succeeding parts of the experiment.

In each of the following series of measurements the concentration of the iodic acid is increased while the total volume of the solution remains the same as that used in the first

trial (22 ml.). In accordance with this plan, repeat the experiment with the following volumes of each solution:

ml. H_2O	ml. HIO_3	ml. H_2SO_3	Drops of Starch Solution
15	2	5	2
14	3	5	2
13	4	5	2
12	5	5	2

Calculate the elapsed time for each trial.[1] Plot these values as abscissae, and the volumes of iodic acid used as ordinates on the second sheet of graph paper furnished with this experiment. Let each millimeter division on the time axis equal 2 sec., and let 2 cm. on the volume axis equal 1 ml. Draw a smooth curve joining the points.

Now calculate the reciprocal of the elapsed time ($1/t$) and the molar concentration of the iodic acid for each of the trials, and record the values on the report sheet.[1] Draw on the same sheet of graph paper just used, a curve whose points are located by plotting $1/t$ against the molar concentrations of the iodic acid. Plot the values for $1/t$ as abscissae; let each millimeter division on this axis equal 0.001 unit. Plot the molar concentrations as ordinates with 2 cm. equal to 0.001 unit.

What is shown by these curves regarding the effect of concentration on the rate of a reaction? [2] Why must the temperature remain the same for each trial throughout the series? [3]

(C) Homogeneous Equilibrium in Solution. Hydrated cobaltous chloride of the formula $CoCl_2 \cdot 6H_2O$ crystallizes in ruby-red crystals. When these crystals are dissolved in water a pink hydrated ion, probably $[Co(H_2O)_6]^{++}$, is present.

At temperatures above 50° a blue ion is formed from $[Co(H_2O)_6]^{++}$ with the following equilibrium being set up:

$$[Co(H_2O)_6]^{++} \text{ (pink)} + 4Cl^- \rightleftharpoons [CoCl_4]^{=} \text{ (blue)} + 6H_2O$$

Dissolve 1 g. of cobaltous chloride, $CoCl_2 \cdot 6H_2O$, in 4 ml. of water. Divide the solution equally between two test tubes. Note the color of the solution.[1] Heat one of the tubes until the solution boils and then hold it beside the other tube in order to note the color contrast. What is the color of the hot solution? [2] Allow the tube to cool, and observe the change taking place in the color. Does the change to the original color take place sharply and at a definite temperature? [3] Show on the basis of this answer that an equilibrium such as is indicated actually exists.[4] Which one of the reactions in the equilibrium is endothermic and which is exothermic? [5]

(D) Equilibrium in the Gas Phase. Le Chatelier's Law. Fit a 6-cm. length of 7-mm. rubber tubing onto each end of a piece of 6-mm. glass tubing which is about 30 cm. long. Place a screw clamp in the center of one of the rubber tubes, but do not tighten the clamp enough to restrict materially the flow of a gas through the tube. Support the glass tube in a horizontal position on a ring stand by means of a clamp. Since the jaws of the latter will not close sufficiently to hold the tube rigidly, the clamp must be held by a split cork (*cf.* Fig. 42, Exp. VI). Now connect the end of the tube carrying the screw clamp with a 50-ml. Erlenmeyer flask fitted with a one-holed rubber stopper and a right-angle delivery tube, and supported on a wire gauze over a tripod.

Remove the stopper and its delivery tube from the Erlenmeyer flask and place in the latter 0.5 g. of copper (wire or turnings) and a solution of nitric acid made by diluting 2 ml. of the 16*N* acid with 1 ml. of water. Stopper the flask quickly and then warm it, if necessary, to cause the evolution of nitrogen dioxide (NO_2). As soon as the 30-cm. tube is filled with the brown fumes, disconnect it from the generator flask, tighten the screw clamp, and quickly close the other end of the tube by means of a pinch clamp. This creates a closed system.

Now stand the closed tube in a 400-ml. beaker filled with cold water. Heat the central part of the tube gently, and then remove the tube and hold it up before a white background. What difference in depth of color is shown by the gas in the hot and the cold parts of the tube? [1] Nitrogen tetroxide (N_2O_4) is a pale-yellow gas formed from the brown nitrogen dioxide (NO_2). These two gases form an equilibrium mixture at ordinary temperatures. Express the equilibrium by means of equations.[2] On the basis of the experimental observation, tell which substance predominates at lower temperatures.[3] Which reaction is endothermic and which is exothermic? [4] State Le Chatelier's law and show that, in accordance with the experimental facts, it applies to this system.[5]

(E) Heterogeneous Equilibrium. The Distribution Law. Place 5 ml. of iodine water and 1.5 ml. of carbon tetrachloride in a test tube. Shake it until most of the iodine appears to be concentrated in the carbon tetrachloride layer. Allow the latter to settle and then decant as much of the aqueous layer as possible into another test tube. Extract the aqueous layer with another 1.5-ml. portion of carbon tetrachloride and again decant the upper layer. Repeat the extraction and decantation once more. What conclusion could be drawn from the color of the water as regards the presence of dissolved iodine? [1] State the distribution law.[2] What conclusion must be drawn from this law regarding the presence of iodine in the water? [3] Test the correctness of the answer to the preceding question by adding 2 drops of starch solution to the water from which iodine has been extracted. Is the conclusion drawn in ([3]) verified or must it be discarded on the basis of the result observed after the addition of starch solution? Explain.[4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXII

VELOCITY OF CHEMICAL REACTIONS. EQUILIBRIUM

Discussion

1.

(A) Rate of Reaction. *The effect of temperature*

1.

Temp.	t (Time in Seconds)			$1/t$
	Start	Finish	Elapsed	

2.

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXII (Cont'd)

(B) Rate of Reaction. *The effect of concentration*

1.

ml. H_2O	ml. HIO_3	t (Time in Seconds)			$1/t$	Molar Concn. of HIO_3
		Start	Finish	Elapsed		

2.

3.

(C) Homogeneous Equilibrium in Solution

1. **2.**

3.

4.

5.

(D) Equilibrium in the Gas Phase. Le Chatelier's Law

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXII (Cont'd)

(D) Cont'd

2.

3.

4.

5.

(E) Heterogeneous Equilibrium. The Distribution Law

1.

2.

3.

4.

Experiment XXXIII

CONDUCTANCE AND ELECTROLYSIS

Discussion. The classification of a substance as a nonelectrolyte or as an electrolyte is based on the conductance of its aqueous solution. Aqueous solutions of nonelectrolytes do not conduct an electric current to any greater extent than pure water does, whereas aqueous solutions of electrolytes conduct an electric current and undergo electrolysis. Weak electrolytes give solutions which are relatively poor conductors because of a limited degree of ionization. On the other hand, aqueous solutions of strong electrolytes readily conduct an electric current.

If a strong electrolyte is formed as a result of a chemical reaction involving two weak electrolytes, the conductance of the resulting solution increases. If the ions of a strong electrolyte are removed from solution as an insoluble precipitate, or form a weak electrolyte with the ions of another reactant, the conductance of a mixture of the reactants is less than that of the strong electrolyte. After the reaction is complete, the conductance will increase upon further addition of the second reactant, provided the latter is a strong electrolyte. Examples of the above types of reactions are included in this experiment.

Electrolysis always accompanies the passage of a direct current through an aqueous solution. Cations are reduced to a lower oxidation state, some of them to the free state, at the cathode; anions are oxidized to ions with a higher oxidation state, or to the free state, at the anode.

(A) Conductance. 1. Nonelectrolytes, Weak Electrolytes, and Strong Electrolytes. Test the conductance of each of the solutions listed (p. 268) by placing 10 ml. of the solution

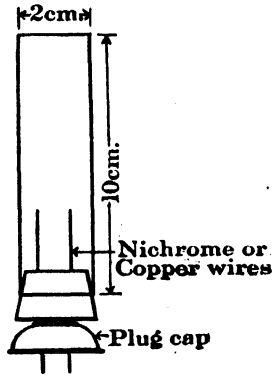


FIG. 79. Conductivity cell

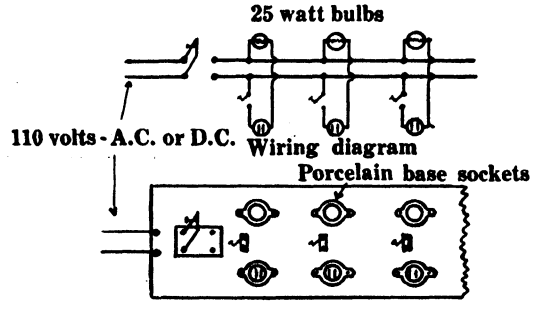


FIG. 80. Arrangement for testing the conductivity of solutions

in the conductivity cell shown in Fig. 79, and then plugging the cell into the cell bank illustrated in Fig. 80. The brightness of the light indicates the relative conductance of the solution. Wash and dry the cell thoroughly before testing the conductance of the next solution. **(CAUTION!** Make certain that the cell is easily removable from the receptacle, otherwise the solution may be spilled. The prongs of the plug may be bent or lightly greased if they fit too tightly. In order not to spill the test solution, stopper the cell before it is pulled out of the receptacle. Always pull out the cell by grasping its base—not the glass tube.)

The solutions to be tested are: (1) water, (2) 4*N* HCl (3) 4*N* CH_3COOH, (4) 95 per cent ethyl alcohol, (5) 1*M* sugar, (6) 4*N* ammonia, (7) 4*N* NaOH, (8) 0.1*N* NaCl, (9) 0.1*N* $Pb(CH_3COO)_2$, and (10) HCl in toluene.

Describe the conductance of each of these solutions as poor, slight, medium, or good.[1] State in each case whether the solute is an electrolyte or a nonelectrolyte; a weak or a strong electrolyte.[1] Explain the difference between the conductance of solutions of HCl in water and in toluene.[2]

2. Effect of Concentration. Add 2 ml. of glacial (anhydrous) acetic acid to the dry conductivity cell (Fig. 79) and note the brightness of the lamp. Now add slowly 10 drops of water. Stir the solution during the addition of the water, and then add more water in 1-ml. portions until the level of the solution reaches the top of the electrodes. Explain the change in brightness of the lamp.[3]

Wash and dry the conductivity cell and then place in it 1 g. of dry powdered sodium chloride. Add water as instructed above. Compare the results of this experiment with those noted in the case of acetic acid. Explain.[4]

3. Effect of Chemical Reaction. Place 3 ml. of 4*N* CH_3COOH in the cell and note the brightness of the lamp. Now add an equal volume of 4*N* NH_4OH, 1 ml. at a time. Stir after the addition of each portion of the base. Describe and explain the change in the brightness of the lamp.[5]

Repeat the above experiment with 10 ml. of a saturated solution of $Ba(OH)_2$ to which is added slowly from 6 to 7 drops of 4*N* H_2SO_4. Describe and explain the change in the brightness of the lamp.[6]

To 5 ml. of 0.1*N* $Ba(CH_3COO)_2$ add 2 or 3 drops of 4*N* H_2SO_4. Stir after the addition of each drop. Note the change in the brightness of the lamp.[7] Now repeat the experiment but use 0.1*N* $Ba(NO_3)_2$ in place of barium acetate. Compare and explain the results of these two reactions.[8]

(B) Electrolysis. 1. Mechanism. To 1 ml. of 0.1*N* KI in the conductivity cell add 9 ml. of water, 2 drops of phenolphthalein solution, and 1 ml. of starch solution. Turn on the switch * and note carefully the appearance of the solution at each electrode. Turn off the current after 1 min. in order to prevent corrosion of the electrodes. Explain the color changes that take place.[1] Write the equations for the electrode reactions.[2]

2. Faraday's Law. A Coulometer. Set up an apparatus as illustrated in Fig. 81. If the polarity of the 110-volt D. C. line is not known,* it must be determined in the following

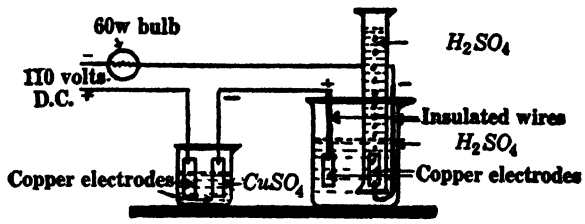


FIG. 81. A coulometer

manner. Touch a piece of filter paper moistened with a solution of sodium chloride and 1 drop of phenolphthalein solution with the wires held (**CAUTION!**) about an inch apart. The paper turns red at the point of contact with the *negative* wire. Why?[3]

Clean, dry, and weigh carefully the piece of copper used as the cathode in the 50-ml. beaker. Record the weight.[4] Now place 25 ml. of 1*N* $CuSO_4$ in the 50-ml. beaker and 300 ml. of distilled water in the 400-ml. beaker. To the solution of cupric sulfate add 3 drops of 36*N* H_2SO_4 and 1 drop of 16*N* HNO_3 which has been boiled to remove oxides of nitrogen.

* If 110-volt D.C. current is not available use a 6-volt storage battery and eliminate the 60-watt lamp.

Cover with a small square of paper the mouth of a 100-ml. graduate which is completely filled with distilled water, and then invert the graduate in the water over the negative electrode in the 400-ml. beaker. Support the graduate with a burette clamp fastened to a ring stand, add 5 ml. of 36*N* H_2SO_4 to the water in this beaker, and then stir the solution thoroughly. Now turn on the current.

Watch the level of the water in the graduate and, when it approaches the 50-ml. mark, adjust the height of the graduate so that the water level inside coincides with the level outside. Turn off the current when the inside level reaches the 50-ml. mark. Record the room temperature and the barometric pressure.[4]

Rinse the weighed copper electrode with distilled water and then dry it by holding it high over the flame of a burner. *Do not wipe the electrode with a cloth.* Weigh the dry electrode and determine the weight of copper deposited during the electrolysis. Record the data on the form provided on the report sheet.[4]

On the basis of the weight of copper deposited, calculate the number of coulombs that passed through the solution.[4] This quantity of electricity liberated 50 ml. of hydrogen at the then prevailing temperature and pressure. Reduce this volume to that which would be occupied by dry hydrogen at 0° and 760 mm., and then calculate the number of coulombs required to liberate an equivalent weight (11.2 liters) of hydrogen.[4] Calculate the percentage error in this determination of the faraday.[5] How could the accuracy of the determination be increased? [6]

3. Electroplating. Equip a 50-ml. beaker with a carbon or a nickel anode and a strip of copper as a cathode. The copper strip should be cleaned with sandpaper or by immersion in 50 ml. of water to which has been added 5 ml. of 4*N* HNO_3.

Pour from 30 to 35 ml. of a special nickel-plating solution (Appendix H, IV, 5) into the beaker and allow the current * to pass through the solution from 3 to 5 min. Now turn off the current, wash the nickel-plated copper electrode, and then rub it briskly with a towel or a piece of filter paper. Describe the result and write equations for the electrode reactions.[7]

If permission is granted by the instructor, plate the brass wing top burner or the forceps supplied as desk equipment.

* Use current from a 110-volt D.C. line and connect a 60-watt lamp in series with the cell.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIII

CONDUCTANCE AND ELECTROLYSIS

(A) Conductance. *Nonelectrolytes, weak electrolytes, and strong electrolytes*

1.

Solution	Conductivity: Poor, Slight, Medium, Good	Electrolyte or Nonelectrolyte	Weak or Strong Electrolyte
1. Water			
2. 4*N* HCl			
3. 4*N* CH_3COOH			
4. Alcohol (95%)			
5. 1*M* sugar			
6. 4*N* ammonia			
7. 4*N* NaCl			
8. 0.1*N* NaCl			
9. 0.1*N* $Pb(CH_3COO)_2$			
10. HCl in toluene			

2.

Effect of concentration

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIII (Cont'd)

(A) Cont'd

4.

Effect of chemical reaction

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIII (Cont'd)

(B) Electrolysis

Mechanism

1.

2.

Faraday's Law. A coulometer

3.

4.

Data for the coulometer:

Final weight of copper cathode . . . . . .
Initial weight of copper cathode . . . . . _____
Weight of copper deposited . . . . . .
Number of coulombs. . . . . .

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIII (Cont'd)

(B) Cont'd

Data for Faraday's law:

Volume of gas liberated . . . . . .
Temperature . . . . . .
Barometric pressure . . . . . .
Volume of dry gas at S.T.P. . . . . .
Coulombs to liberate 11.2 liters . . . . . .
Percentage error . . . . . .

5.

6.

Electroplating

7.

Experiment XXXIV

IONIC REACTIONS AND EQUILIBRIA

Discussion. Dilute solutions of ionic salts and of the alkali hydroxides are completely ionized. Strong acids are also practically completely ionized in dilute solution. Therefore when dilute solutions of strong electrolytes are mixed the reactions that occur are between ions and not between molecules. Thus, the reaction between solutions of strontium chloride ($Sr^{++} + 2Cl^-$) and sodium sulfate ($2Na^+ + SO_4^=$) is written as follows:

$$Sr^{++} + SO_4^= \rightleftharpoons SrSO_4 \downarrow$$

Weak acids, bases, and salts, however, are not completely ionized in solution, and a comparatively large percentage of their molecules remain as such. Accordingly the convention adopted uses the molecular formula of a weak electrolyte in equations for its reactions. This procedure is followed even though the reaction involves only the small percentage of ions formed from the weak electrolyte. Thus, the reaction between aqueous solutions of acetic acid and sodium bicarbonate is written

$$CH_3COOH + HCO_3^- \rightleftharpoons CH_3COO^- + H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow$$

while the same reaction with hydrochloric acid is written

$$H_3O^+ + HCO_3^- \rightleftharpoons H_2O + H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow$$

In the same way slightly soluble substances and solids are represented in an equation by their molecular or empirical formulas. Thus:

$$FeS + 2H_3O^+ \rightleftharpoons Fe^{++} + 2H_2O + H_2S \uparrow$$

An appreciable reaction between ions in solution takes place only when there exists the possibility for the formation of a slightly soluble substance (solid or gas), a slightly ionized substance, or a complex ion. Oxidation and reduction reactions also occur between ions in solution, but these reactions are not considered in this experiment.

Ionic equilibria are affected by changes in such factors as the concentration of the reacting substances, the temperature, and the nature of the solvent medium. The influence of the concentration of the reacting substance is studied in this experiment. Since the ions of a slightly soluble salt are in equilibrium with the solid, the lowering of the concentration of one or both of the ions by one of the methods described in the last paragraph causes the solid to dissolve. The equilibrium is displaced until the solid is completely dissolved or until the product of the molecular concentrations of the ions raised to the appropriate power is again equal to the solubility product constant.

Apparatus and Materials: Indicators in dropping bottles: methyl violet, sodium indigodisulfonate, phenol red, phenolphthalein, and methyl orange; saturated solutions of potassium chlorate, potassium chloride, sodium chlorate, and sodium chloride; medicine droppers.

(A) Formation of Slightly Soluble Substances. 1. Insoluble Solids. Add 1 ml. of 4*N* sulfuric acid to 5 ml. of 0.1*N* barium chloride solution; 5 ml. of 0.05*M* potassium chromate solution to 5 ml. of 0.1*N* lead acetate solution; and 5 ml. of 0.1*N* ammonium sulfide solution to 5 ml. of 0.1*N* nickel sulfate solution. Write the *ionic equations* for the reactions, describe the precipitates, and state what ions would remain in the filtrates from these precipitates.[1] What substances would be obtained by evaporating the filtrates to dryness?[2]

2. Insoluble Gases. Carry out reactions between 1-ml. portions of the following solutions: 0.1*N* sodium carbonate and 4*N* acetic acid; 0.1*N* sodium hydrogen sulfide and 4*N* sulfuric acid; sodium sulfite (prepare the solution from the solid salt) and 4*N* hydrochloric acid. Waft some of the gas evolved in each test tube past the nose and cautiously note the odor of each gas.[3] Immediately pour the solutions into the sink. Write the ionic equation for each reaction.[4] Why do these reactions proceed almost to completion?[5] Are there any requirements with respect to the acid used in the above reactions?[6]

(B) Formation of Slightly Ionized Substances. 1. Slightly Ionized Acid. Prepare 1*N* HCl by diluting 6 ml. of the 4*N* acid to 24 ml. with distilled water. Pour 5 ml. of this solution into each of three test tubes. Add 10 ml. of water to the first; 5 ml. of water and 5 ml. of 1*N* sodium acetate solution to the second; and 10 ml. of 1*N* sodium acetate to the third. The total volume of each solution is now 15 ml. Add 6 drops of methyl violet solution to each tube. Describe and explain the differences in the color of the indicator in the three test tubes.[1]

2. Slightly Ionized Base. Place 3 ml. of dilute sodium hydroxide (4*N*) and 6 drops of sodium indigodisulfonate indicator in each of three test tubes. To one add 12 ml. of water; to the second add 6 ml. of 1*N* ammonium chloride and 6 ml. of water; and to the third add 12 ml. of 1*N* ammonium chloride solution. Describe and explain the color changes.[2] Use an equation to facilitate the explanation.

3. Formation of Water. Neutralization. When an equivalent quantity of an acid is added to an aqueous solution containing a hydroxide base, neutralization occurs. Write the equation for this reaction.[3] Add 4 drops of phenolphthalein to 5 ml. of 4*N* sodium hydroxide solution and slowly pour 4*N* hydrochloric acid from a small graduate into the solution until the indicator changes color. Describe and explain the change in color.[4] Note the volume of acid used and calculate the normality of the base.[5] Assume the concentration of the hydrochloric acid solution to be exactly 4*N*.

4. Slightly Ionized Salt. Add 2 or 3 drops * of 4*N* hydrochloric acid to 2 ml. of 0.1*N* lead nitrate solution. Now pour into the test tube 5 ml. of 0.1*N* ammonium acetate solution. Write the equations for the reactions and explain why the precipitate dissolves.[6] Add two or three drops of 0.1*N* ammonium sulfide solution. Which is the more insoluble, lead chloride or lead sulfide? Give the reason for the answer.[7]

(C) Formation of Complex Ions. To 5-ml. portions of 0.1*N* solutions of cupric nitrate and silver nitrate in separate test tubes add 4*N* ammonium hydroxide solution, drop by drop, until an excess has been added and no further change occurs. Describe the changes that take place and write the equations for the reactions.[1]

(D) Hydrolysis. When a salt is dissolved in water the ions are hydrated and the forces between them are reduced to such an extent that the ions separate and are free to move about in the solution. Many of the hydrated cations are acidic with respect to the water molecule:

$$[Al(H_2O)_6]^{+++} + H_2O \rightleftharpoons H_3O^+ + [Al(OH)(H_2O)_5]^{++}$$

* Use a medicine dropper. Do not dip the medicine dropper in the reagent bottle. Pour a small quantity of the reagent into a small beaker or test tube. Rinse the medicine dropper well before using it for another solution. Small bottles with medicine droppers to fit may be labelled and filled with a few of the frequently used reagents, for example, dilute solutions of sodium hydroxide, hydrochloric acid, and ammonium hydroxide.

On the other hand, certain anions are basic with respect to the water molecule:

$$H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^-$$

Whether a solution of a given salt is acidic or basic depends upon the relative extent to which the cation and anion react with water:

1. *Salts whose cations are stronger as acids than their anions are as bases.* Solutions of aluminum chloride are acidic because the hydrated aluminum ion is stronger as an acid than the chloride ion is as a base.

2. *Salts whose anions are stronger as bases than their cations are as acids.* Sodium acetate dissolved in water gives a basic solution because the acetate ion is stronger as a base than the hydrated sodium ion is as an acid.

3. *Salts whose cations are about the same strength as acids as their anions are as bases.* A solution of a salt such as sodium chloride is nearly neutral because the hydrated sodium ion is a weak acid and the chloride ion is equally weak as a base. On the other hand, ammonium acetate solutions are nearly neutral because the ammonium ion is as strong as an acid as the acetate ion is as a base:

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^-$$

The extent of the hydrolysis is greater if one of the products separates from the solution as a slightly soluble precipitate or is removed from the system as a gas.

Add 5 ml. of distilled water to 5 ml. of a 0.1*N* solution of antimony trichloride. Write the equation for the formation of the precipitate.[1] Add 4*N* hydrochloric acid. Explain the result.[2]

Boil 5 ml. of 0.1*M* ferric chloride solution in a test tube. Explain the formation of the precipitate.[3] Use the equation for the reaction as a basis for the explanation.

Add 2 drops of a solution of phenol red (or pieces of blue and red litmus paper) to 5 ml. of solutions of the following: 1*M* sodium carbonate, 1*N* ammonium chloride, 1*N* sodium acetate, 0.1*N* aluminum chloride, 1*N* sodium chloride, 1*N* ammonium acetate, and 1*M* trisodium phosphate.

Classify these solutions into three groups: acidic, neutral, and basic.[4] Write the equation which accounts for the acidity or basicity in each case.[5]

(E) Displacement of Ionic Equilibrium. The following equilibrium exists in a solution of a chromate or a dichromate:

$$2CrO_4^= + 2H_3O^+ \rightleftharpoons Cr_2O_7^= + 3H_2O$$

To 5 ml. of 0.05*M* potassium chromate add about 0.5 ml. of 4*N* hydrochloric acid. Now slowly add about 1 ml. of 4*N* sodium hydroxide. Describe[1] and explain the color changes observed.[2]

(F) The Solution of Slightly Soluble Substances. In a saturated solution of a slightly soluble substance, for example, calcium oxalate, the following equilibrium exists:

$$CaC_2O_4 \rightleftharpoons Ca^{++} + C_2O_4^=$$

A reduction in the concentration of either the calcium ion or the oxalate ion shifts the equilibrium to the right and causes the solid calcium oxalate to dissolve. The addition of a strong acid results in the formation of a relatively weak acid ($HC_2O_4^-$) thereby reducing the concentration of $C_2O_4^=$.

Add 4 ml. of 0.1*N* oxalic acid solution to 4 ml. of 0.1*N* calcium chloride solution. Filter half of the mixture. Add 5 ml. of 12*N* hydrochloric acid to the precipitate remaining in the test tube and add 2 ml. of 4*N* ammonium hydroxide to the filtrate. Explain the results.[1]

Add 2 ml. of 0.1*N* ammonium sulfide solution to 3 ml. of 0.1*N* ferrous sulfate solution. Determine the solubility of the precipitate in 4*N* hydrochloric acid. Formulate the reaction involved and explain the result.[2]

Mercuric iodide with excess potassium iodide forms a complex ion [$HgI_4^{=}$]. To 3 ml. of 0.1*N* mercuric chloride solution add a 0.1*N* solution of potassium iodide drop by drop until an excess is present. Describe the results and write equations to explain them.[3]

(G) Common-Ion Effect. 1. Ionization. Add two drops of methyl orange to 5 ml. of distilled water. Now add 3 drops of acetic acid and then 5 ml. of a 1*N* solution of sodium acetate. Note and explain the change in color of the indicator.[1] Use equations to facilitate the explanation.

Add 5 ml. of a 1*N* solution of ammonium chloride to 5 ml. of a solution containing 3 drops of 4*N* ammonium hydroxide and 4 drops of phenolphthalein. Explain the change in color.[2] Repeat with a 1*N* solution of sodium chloride in place of the ammonium chloride solution. Explain why there is no marked change in the color.[3]

2. Solubility. Place 5 ml. of a saturated solution of potassium chlorate in each of three test tubes, and add 2 ml. of a saturated solution of potassium chloride to one test tube, 2 ml. of a saturated solution of sodium chlorate to another, and 2 ml. of a saturated solution of sodium chloride to the third. What takes place in each test tube? Explain.[4] [**Note:** The solutions must be saturated otherwise correct results will not be obtained.]

(H) Reactions of Amphiprotic Substances. An amphiprotic (amphoteric) substance is one which may act either as an acid or a base. Thus the ion HCO_3^- is amphiprotic because it may lose a proton to become $CO_3^{=}$ or gain a proton to become H_2CO_3. When the aluminum ion, $[Al(H_2O)_6]^{+++}$, loses three protons to hydroxide ions, a precipitate of aluminum hydroxide, $[Al(H_2O)_3(OH)_3]$, is formed. In the presence of an excess of hydroxide ion this precipitate dissolves with the formation of the aluminate ion, $[Al(H_2O)_2(OH)_4]^-$, or simply $[Al(OH)_4]^-$. By gaining three protons from an acid, the aluminum hydroxide dissolves with the formation of the aluminum ion, $[Al(H_2O)_6]^{+++}$.

Obtain about 2 ml. of each of the following 0.1*N* solutions in separate test tubes: aluminum chloride, stannous chloride (0.1*M*), magnesium chloride, ferric chloride (0.1*M*), and zinc chloride. Add 4*N* sodium hydroxide, drop by drop, to excess. To those test tubes in which the precipitates dissolved, add 4*N* hydrochloric acid drop by drop to excess. List those substances which are amphiprotic.[1] Formulate the reactions for two of them and explain why the precipitate reforms and then dissolves when the acid is added.[2]

To 2 ml. of 0.1*N* aluminum chloride solution and 0.1*N* zinc chloride solution in separate test tubes, add 4*N* ammonium hydroxide, drop by drop, to excess. Compare the results with those obtained in the experiments described in the last paragraph.[3] Explain why the zinc hydroxide redissolves in excess ammonia.[4] [See parts (C) and (F)].

(I) Displacement Reactions. Look up the activity or electromotive force (e.m.f.) series of the metals and list them in the order of their decreasing activity.[1]

Add 0.5 g. of mossy zinc to 5 ml. of 0.1*N* cupric sulfate solution, and 0.5 g. of copper turnings to 5 ml. of 0.1*N* mercuric chloride solution. Write the equations for these reactions and list the three metals concerned in the order of their activity.[2]

Recall the reactions of chlorine with bromide and iodide ions; the reaction of bromine with iodide ions (Exp. XXVI); the reaction of iodine with hydrogen sulfide (Exp. XXVII); the reaction of oxygen with a solution of hydrogen iodide to give water and free iodine; and the reaction of oxygen with a solution of hydrogen sulfide to give water and free sulfur. Arrange these nonmetals in the order of their decreasing activity.[3] Write the equations for the reactions referred to in this paragraph.[4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIV

IONIC REACTIONS AND EQUILIBRIA

(A) Formation of Slightly Soluble Substances

1.

2.

3.

4.

5.

6.

(B) Formation of Slightly Ionized Substances

1.

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIV (Cont'd)

(B) Cont'd

6.

7.

(C) Formation of Complex Ions

1.

(D) Hydrolysis

1.

2.

3.

4.

5.

(E) Displacement of Ionic Equilibrium

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIV (Cont'd)

(E) Cont'd

2.

(F) The Solution of Slightly Soluble Substances

1.

2.

3.

(G) Common-Ion Effect

1.

2.

3.

4.

(H) Reactions of Amphiprotic Substances

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIV (Cont'd)

(H) Cont'd

2.

3.

4.

(I) Displacement Reactions

1.

2.

3.

4.

Experiment XXXV

USE OF INDICATORS. TITRATION AND THE DETERMINATION OF pH

Discussion. In pure water at 25° the concentration of both the hydronium ion $[H_3O^+]$* and hydroxide ion $[OH^-]$ is 1×10^{-7} moles per liter. The product of their molecular concentrations is

$$[H_3O^+]\,[OH^-] = 1 \times 10^{-14}$$

This relation exists in every aqueous solution. Thus if $[H_3O^+]$ is 1×10^{-2} (0.01 moles per liter), the concentration of the hydroxide ion OH^- must be 1×10^{-12} in order that the product of the two concentrations remain equal to 1×10^{-14}.

The concentration of the hydronium ion is often expressed in terms of pH values. The pH is defined as the logarithm of the reciprocal of the hydronium ion concentration:

$$pH = \log \frac{1}{[H_3O^+]} \quad \text{or} \quad pH = -\log [H_3O^+]$$

It is the negative power to which 10 must be raised to equal the concentration of the hydronium ion. Thus the pH of a 0.01*N* HCl solution with a concentration of hydronium ion $[H_3O^+] = 1 \times 10^{-2}$ is 2. The pH of a neutral solution is 7 while the pH of a 0.01*N* solution of NaOH with $[OH^-] = 1 \times 10^{-2}$, and $[H_3O^+] = 1 \times 10^{-12}$ is 12. These relations are illustrated in the following table:

$[H_3O^+]$ Moles/Liter	$[H_3O^+]$ as a Power of 10	$[OH^-]$ as a Power of 10	pH	Solution
				strongly
1	10^0	10^{-14}	0	acid
0.1	10^{-1}	10^{-13}	1	↑
0.01	10^{-2}	10^{-12}	2	
0.001	10^{-3}	10^{-11}	3	
0.0001	10^{-4}	10^{-10}	4	
0.0_41	10^{-5}	10^{-9}	5	
0.0_51	10^{-6}	10^{-8}	6	
0.0_61	10^{-7}	10^{-7}	7	neutral
0.0_71	10^{-8}	10^{-6}	8	
0.0_81	10^{-9}	10^{-5}	9	
0.0_91	10^{-10}	10^{-4}	10	
$0.0_{10}1$	10^{-11}	10^{-3}	11	↓
$0.0_{11}1$	10^{-12}	10^{-2}	12	strongly
$0.0_{12}1$	10^{-13}	10^{-1}	13	basic

The indicators commonly used in the determination of the concentration of the hydronium ion and in acid-base titrations are either weak organic acids or weak organic bases.

* Brackets [ ] are used to denote molar concentrations.

Their color depends upon the hydronium or hydroxide ion concentration, that is, upon the pH of the solution. The ionization of methyl orange as a weak acid is represented as follows:

$$\underset{\text{red}}{HIn} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{yellow}}{In^-}$$

The ionized and un-ionized forms differ in color. An increase in the concentration of H_3O^+ displaces the equilibrium to the left. At a pH of 3.1 about 90 per cent of the indicator is in the red un-ionized form. Further increase in the concentration of H_3O^+ does not result in easily noticeable color changes.

A decrease in the concentration of H_3O^+ displaces the equilibrium to the right. At a pH of 4.4 about 90 per cent of the indicator is in the form of the yellow ion. A further decrease in the concentration of H_3O^+ or an increase in the concentration of OH^- does not produce noticeable changes in the color. Within the color-change interval, that is, within the pH range 3.1 to 4.4, there are varying proportions of the two forms of the indicator present, and the shade of color therefore varies with the pH.

The pH of an unknown solution is determined by comparing the color that the indicator exhibits in the solution with the color it shows in solutions of known pH. The pH of the solution must be within the pH range of the indicator.

The following table lists the pH range of a number of indicators, the color of the indicator at pH values above and below this range, and the color changes commonly selected when the indicator is used for acid-base titrations.

Indicator	Colors	pH Range	pH and Color Change Selected for Titrations
Methyl violet	y–v	0–2	yellow (0.4), blue (1.0)
Orange IV	r–oy	1.3–3.0	orange (2.0), yellow (3.0)
Thymol blue	r–y	1.2–2.8	pink (2.0), yellow (2.8)
Brom-phenol blue	y–b	3.0–4.7	yellow (3.2), violet (4.0)
Methyl orange	r–oy	3.1–4.4	pink (4.4), yellow (4.6)
Brom-cresol green	y–b	3.8–5.4	yellow (4.0), green (4.7)
Methyl red	r–y	4.4–6.0	pink (4.8), yellow (5.4)
Brom-cresol purple	y–p	5.2–6.8	drab (5.8), purple (6.2)
Litmus	r–b	4.7–8.2	red (5.0), blue (6.0)
Neutral red	r–o	6.8–8.0	red (6.8), orange (7.2)
Phenol red	y–r	6.4–8.4	yellow (7.0), red (7.4)
Cresol red	yp–r	7.2–8.8	yellow (7.6), lilac (8.2)
Phenolphthalein	c–r	8.3–10.0	colorless (7.8), pink (8.3)
Thymolphthalein	c–b	9.3–10.5	colorless (8.0), blue (9.3)
Alizarin yellow G	c–y	10.1–12.1	colorless (10.1), yellow (12.1)
Trinitrobenzene	c–o	12.0–14.3	colorless (13.0), orange (14.3)

c = colorless y = yellow v = violet b = blue p = purple r = red o = orange

(A) Color Change of Indicators. Determine the color of the following indicators at pH values above, below, and within their pH range: methyl violet, methyl orange, phenol red, and phenolphthalein. Add 3 drops of the indicator solution to 5 ml. of the solutions suggested below for each indicator. The approximate pH of each solution is given in the parentheses. The 0.1*N* HCl and 0.1*N* CH_3COOH required below may be prepared from the 1*N* reagents.

Methyl violet (0–2): 12*N* HCl, 0.1*N* HCl (1), 0.1*N* CH_3COOH (2.9)
Methyl orange (3.1 – 4.4): 0.1*N* CH_3COOH (2.9), 0.5*M* NaH_2PO_4 (4.0), 1*N* NH_4Cl (4.9)
Phenol red (6.4 – 8.4): 1*N* NH_4Cl (4.9), 1*N* CH_3COONH_4 (7.0), 1*M* Na_2HPO_4 (9.2)
Phenolphthalein (8.3 – 10.0): 1*N* CH_3COONH_4 (7.0), 1*N* CH_3COONa (9.6), 1*M* Na_3PO_4 (13.8)

List the colors obtained for each indicator.[1]

(B) Choice of an Indicator for Titration. The indicator chosen for a titration should have an easily distinguishable color change when the amount of acid added is equivalent to the amount of base originally present, that is, the color change should occur at the equivalence point. This means that the color change must occur at about the pH prevailing at the equivalence point. The solution is not necessarily neutral at this point.

1. The Titration of a Strong Base with a Strong Acid. This titration results in the formation of a salt whose solution is nearly neutral at the equivalence point. Therefore, the ideal indicator should have a sharp color change at about pH 7. However, if the concentrations of the acid and the base are 0.1*N* or greater, any indicator that has a color change between pH 4 and 10 is suitable. This rather wide range exists because the addition of a small amount of the strong acid or the strong base to the neutral solution of their salt produces rather large changes in the pH of the solution.

Study the table given in the **Discussion** and list a number of indicators that are suitable for use in the titration of a strong base with a strong acid.[1] In view of the fact that it is easier to notice the *appearance* of a color rather than the *disappearance* of one, suggest the proper procedure for the titration when the following indicators are used: neutral red, phenolphthalein.[2]

2. Titration of a Weak Base with a Strong Acid. A solution of ammonium chloride (ammonium ions and chloride ions) results from the addition of an equivalent amount of hydrochloric acid to a given volume of a solution of ammonia. Assume that the concentration of the ammonium chloride at the equivalence point is 0.5*N* with a pH of 4.8. Select two indicators from the table that would be suitable for this titration.[3] If phenolphthalein had been used as an indicator, would too much or too little acid have been added when the color change occurred?[4] Write the equation that accounts for the acidity of a solution of anmonium chloride.[5]

3. Titration of a Weak Acid with a Strong Base. The pH of a 0.5*N* solution of sodium acetate resulting from the titration of 1*N* acetic acid with 1*N* sodium hydroxide is about 9.2. Select two indicators suitable for this titration.[6] Would too much or too little alkali be added if methyl orange were used as an indicator for the titration?[7]

Test the answer to the last question as follows: Prepare approximately 1*N* acetic acid by diluting 10 ml. of 4*N* acetic acid to 40 ml., and 1*N* sodium hydroxide by diluting 10 ml. of 4*N* solution to 40 ml. To 10 ml. of the 1*N* acetic acid add 4 drops of phenolphthalein. Measure from a small graduated cylinder or a burette the volume of the 1*N* sodium hydroxide required to change the color of the indicator. Repeat the experiment but this time add 2 drops of methyl orange in place of the phenolphthalein. Record the volume of sodium hydroxide required in each case to bring about the color change selected for titrations.[8]

(C) Titration. 1. Standardization of an Acid. Prepare approximately 1*N* hydrochloric acid by diluting 25 ml. of 4*N* hydrochloric acid to 100 ml. with distilled water.

Weigh out two 0.6- to 0.7-g. portions of *anhydrous* sodium carbonate to the nearest 0.01 g. on a beam balance, or preferably to the nearest 0.001 g. on an analytical balance. Record these weights and all subsequent data in the spaces provided on the report sheet.[1] Transfer the sodium carbonate to a 250-ml. Erlenmeyer flask or a beaker. Add about 50 ml. of water and 5 drops of methyl orange.

Read the instructions for the use of a burette and pipette given in Exp. IV. Clean the burette if necessary, and rinse it well with distilled water and finally with two separate 5-ml. portions of the hydrochloric acid. Fill the burette and allow enough of the solution to flow out of the tip so that it is completely filled, and the level of the liquid is at or slightly below the zero mark. Record the initial reading of the burette to the nearest 0.02 ml.[1]

Allow the acid to run slowly into the sodium carbonate solution. Stir the solution continually during the addition of the acid. The flow of the acid should be reduced to a drop at a time near the end point, where the color of the methyl orange changes from yellow to pink. Record the final reading of the burette to the nearest 0.02 ml.[1]

Repeat the procedure with the other sample of sodium carbonate. Calculate the normality of the standardized acid from the following considerations.[1]

At the equivalence point the number of milligram equivalents of the acid is just equal to the number of milligram equivalents of the sodium carbonate, that is,

$$\frac{\text{g. of } Na_2CO_3 \times 1000}{\text{Formula wt. } Na_2CO_3 \div 2} = (\text{ml. of acid}) \times (\text{normality of the acid})$$

or

$$\frac{\text{mg.}}{\text{Equiv. wt.}} = (\text{ml.})\ (N)_{\text{acid}}$$

Calculate the weight of HCl in 1 ml. of this standard hydrochloric acid solution.[1]

2. Determination of the Normality of a Base of Unknown Concentration. Obtain 25 ml. of sodium hydroxide of unknown concentration * and pipette 10 ml. of it into the 250-ml. Erlenmeyer flask or a beaker. Add from 30 to 40 ml. of water and 5 drops of methyl orange as an indicator. Measure the volume of the standard hydrochloric acid required to change the color of the indicator from yellow to pink.[2] Add the acid slowly and stir the solution constantly. Allow the acid to flow into the flask drop by drop near the end point of the titration.

Titrate a second 10-ml. portion of the sodium hydroxide solution in the same way. Calculate the normality of the sodium hydroxide.[2]

The above calculation is carried out as follows. At the equivalence point the number of milligram equivalents of the acid added is equal to the number of milligram equivalents of the base originally present, that is,

$$(\text{ml.})\ (N)_{\text{acid}} = (\text{ml.})\ (N)_{\text{base}}$$

The normality of the acid, the milliliters of acid, and the milliliters of base are known. The normality of the base is then calculated by substitution in the above expression.

Why is it unnecessary to take into consideration the 30 to 40 ml. of water added to the solution of the base? [3]

(D) Determination of pH. 1. Preparation of Standards. Prepare solutions containing the following concentrations of hydrochloric acid: 0.1*N*, 0.01*N*, 0.001*N*, and 0.0001*N*.

If standard 1*N* hydrochloric acid is not available, prepare it from a 4*N* solution by carefully diluting 20 ml. of the acid to 80 ml. with distilled water. To prepare the 0.1*N* solution, withdraw 10 ml. of the 1*N* solution with a pipette and transfer it to a 100-ml. graduated cylinder. Fill the graduate to the 100-ml. mark with distilled water and mix the solution by pouring it into a dry beaker and then back into the graduated cylinder. In the manner just described prepare the 0.01*N* solution by diluting 10 ml. of the 0.1*N* solution to 100 ml. The remaining solutions are prepared in a similar way. The following pre-

* The concentration of the unknown solutions should not exceed 2*N*. If unknowns are not available, dilute the NaOH solution supplied as a reagent with an equal volume of water and determine the normality of this solution.

cautions should be observed: Rinse the pipette twice with distilled water and twice with small quantities of the solution to be withdrawn; rinse the graduated cylinder with distilled water; and clean and dry the beaker before making the next dilution.

Pour 5 ml. of each solution into separate, properly labelled test tubes. What is the pH of each of the hydrochloric acid solutions? [1] Write the value of the pH of the solution in each test tube on its label. Add 2 drops of Orange IV to each solution. Reserve these standards for use in the determination of the pH of acetic acid as described in the next paragraph.

2. Determination of the pH and Degree of Ionization of Acetic Acid Solutions. Prepare 0.1*N* acetic acid solution. To 5 ml. of this solution add 2 drops of Orange IV. Compare the color of the solution with the color of the standards and estimate the pH of the solution.[2] Calculate the concentration of the hydronium ion in the acetic acid solution from the relation: [2]

$$\text{pH} = \log \frac{1}{[H_3O^+]} \quad \text{or} \quad \frac{1}{[H_3O^+]} = \text{antilog pH}, \quad \text{and} \quad [H_3O^+] = \frac{1}{\text{antilog pH}}$$

The fraction of the acid ionized is calculated by dividing the concentration of the hydronium ion by the concentration of the acid. The percentage ionized is 100 times the fraction ionized. Calculate the percentage ionization of the 0.1*N* acetic acid solution.

The ionization constant of acetic acid is given by the expression

$$\frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = K_{\text{ionization}}$$

In a solution of pure acetic acid the concentration of the acetate ion is the same as the concentration of the hydronium ion, and the concentration of the acetic acid molecules is equal to the analytical concentration of the acid minus the concentration of hydronium ion.

Substitute the values for 0.1*N* acetic acid in the above equation and calculate the ionization constant.[1]

(E) Extent of Hydrolysis. To 5 ml. of each of the following solutions add 2 drops of a universal indicator: * 1*N* NH_4Cl, 1*N* CH_3COONa, and 1*N* NaCl. Compare the color of each solution with the color of the standards * in the laboratory and estimate the pH of each solution.[1] Calculate the concentration of the hydronium and hydroxide ions in the sodium acetate solution and in the ammonium chloride solution.[1]

The fraction of the acetate ions hydrolyzed is equal to the concentration of the hydroxide ion divided by the concentration of the sodium acetate (acetate ion). The percentage hydrolysis is equal to the fraction hydrolyzed multiplied by 100. In a similar way the percentage hydrolysis of ammonium chloride is given by the expression $([H_3O^+] \div [NH_4^+]) \times 100$.

Calculate the percentage hydrolysis of the sodium acetate and the ammonium chloride solutions.[1]

(F) Common-Ion Effect. To 5 ml. of 1*N* acetic acid (prepared from the 4*N* reagent) add 4 drops of the universal indicator solution and then 5 ml. of 1*N* sodium acetate solution. Compare the color of the solution with the color of the standards. Estimate the pH of the solution.[1]

The concentration of the hydronium ion in this solution is given by the expression

$$\frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = K_{\text{ionization}} \quad \text{or} \quad H_3O^+ = \frac{[CH_3COOH]}{[CH_3COO^-]} \times K_{\text{ionization}}$$

* See the Appendix for the composition of a universal indicator and for the preparation of standard buffer solutions.

The concentration of the acetic acid and of the sodium acetate (acetate ion) in the solution after mixing equal volumes of 1*N* solutions is 0.5*N*. Then

$$[H_3O^+] = \frac{0.5}{0.5} \times K_{\text{ionization}} = K_{\text{ionisation}} = 1.8 \times 10^{-5}$$

Therefore the concentration of the hydronium ion in a solution containing equal concentrations of a weak acid and its highly ionized salt is equal to the ionization constant of the weak acid. This is the case whenever a weak acid is half neutralized by an alkali. The pH of such a solution is called the pK value of the weak acid and is numerically equal to the negative logarithm of the ionization constant.

From the results of the present experiment, what is the pK value of acetic acid? [2] Calculate the ionization constant of acetic acid.[3] How does it compare with the value determined in part (D)? [4]

(G) Buffers. Pour 5 ml. of water into each of two test tubes and add 2 drops of the universal indicator to each tube. Add 1 drop of 4*N* hydrochloric acid to one of the test tubes, and 1 drop of 4*N* sodium hydroxide to the other. Note the changes in color.[1] Repeat the experiment, but this time use two test tubes containing 5 ml. of an acetic acid-sodium acetate buffer solution prepared by mixing equal volumes of 1*N* solutions of the two substances. Compare the results of the two experiments.[2] Explain why buffer solutions (solutions of a weak acid and its salt, or a weak base and its salt) resist small changes in the concentration of the hydronium or hydroxide ion.[3]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXV

USE OF INDICATORS. TITRATION AND THE DETERMINATION OF pH

A) Color Change of Indicators

1.

B) Choice of an Indicator for Titration

1.

2.

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXV (Cont'd)

(C) Titration

1.

	I	II
Weight of watch glass or weighing bottle + Na_2CO_3 . .		
Weight of watch glass	_____	_____
Weight of Na_2CO_3		
Final reading of burette		
Initial reading of burette	_____	_____
Volume of HCl solution		
Calculated normality of HCl		
Average value		
Weight of HCl in 1 ml.		

2.

	I	II
Volume of NaOH (volume of pipette).		
Final reading of burette		
Initial reading of burette	_____	_____
Volume of HCl solution		
Normality of HCl solution		
Calculated normality of NaOH		

3.

(D) Determination of pH

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXV (Cont'd)

(D) Cont'd

2.

Concn. of CH_3COOH	pH	$[H_3O^+]$	% ionization	$K_{ion.}$
0.1*N*				

(E) Extent of Hydrolysis

1.

Solution	Normality	pH	$[H_3O^+]$	$[OH^-]$	% hydrolysis
NH_4Cl CH_3COONa NaCl			_____	_____	_____

(F) Common-Ion Effect

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXV (Cont'd)

(G) Buffers

1.

2.

3.

Experiment XXXVI

OXIDATION-REDUCTION. ELECTROCHEMICAL CELLS

Discussion. Changes in the oxidation state of one or more elements always occur in an oxidation-reduction reaction. Those substances that have a relatively great tendency to take electrons from other substances are good oxidizing agents, while substances that lose electrons readily are good reducing agents.

Active metals, for example, sodium and magnesium, readily lose electrons to the ions of less active metals. Electrons are transferred from an active metal (reducing agent) to an ion of a less active metal (oxidizing agent). An arrangement of the metals in a series in the order of their decreasing tendency to lose electrons is also an arrangement in the order of decreasing chemical activity. In addition, this same series is in the order of the increasing oxidizing power of the *ions* of the metals. The first part of this experiment is concerned with the determination of the order of a few of the metals in the *activity* or *e.m.f.* (electromotive force) series.

Metals capable of existing in more than one oxidation state are often good oxidizing agents in their higher oxidation states. Thus, ferric iron, Fe^{+++}, and stannic tin, Sn^{+4}, have a relatively strong tendency to take electrons from other substances and become reduced to Fe^{++} and Sn^{++} respectively. Certain oxygen-containing ions and oxygen acids as MnO_4^-, ClO^-, $Cr_2O_7^=$, ClO_3^-, and HNO_3 are stronger oxidizing agents than are Fe^{+++} and Sn^{+4}. Consequently they will take electrons from Fe^{++} and Sn^{++} to oxidize these ions to Fe^{+++} and Sn^{+4}, respectively. The halogens are strong oxidizing agents because of their pronounced tendency to become reduced to the halide ions F^-, Cl^-, Br^-, and I^-. Tables have been compiled (Text) in which substances are listed in the order of their oxidizing power. Thus, it is possible to predict whether one substance will oxidize another. In this experiment the reactions of a few of the common oxidizing agents are studied.

A number of important analytical procedures are based on oxidation-reduction reactions. Titrations may be carried out with oxidizing agents and reducing agents in a manner similar to those with acids and bases. An indicator must be present to show the point at which the quantity of the titrating agent used is equivalent to the amount of the oxidizing or reducing substance originally present in the solution being titrated. Sometimes the color of the oxidizing or reducing agent itself may serve as the indicator; in other cases a substance is added that is colored in the presence of an excess of either the oxidizing or the reducing agent.

The equivalent weight of an oxidizing or a reducing agent is that weight of it associated with a change of a single unit in its oxidation state. As an instance, the equivalent weight of $KMnO_4$ is one fifth of the formula weight whenever the substance acts as an oxidizing agent in a reaction in which Mn^{+7} is reduced to Mn^{++}; when Mn^{+7} becomes Mn^{+4}, the equivalent weight of the permanganate is one third of the formula weight. Thus, the normality of an oxidizing agent or a reducing agent is equal to the number of gram-equivalent weights of the agent in 1 liter of solution. At the end point of the titration

$$(\text{ml.}) \times N_{\text{oxidizing agent}} = (\text{ml.}) \times N_{\text{reducing agent}}$$

In the above expression, ml. = volume in milliliters, and N = normality. When the weight

of a reducing agent in a solution is to be determined, it is found by substituting the proper values in the following expression:

$$\frac{\text{Weight of reducing agent} \times 1000}{\text{Equivalent weight of reducing agent}} = (\text{ml.}) \times N_{\text{oxidizing agent}}$$

The actual transfer of electrons in an oxidation-reduction reaction is demonstrated in part (D) of this experiment. Several electrochemical cells used for the production of electric current are described. In the operation of these cells, oxidation occurs at one electrode while reduction takes place at the other.

(A) Displacement Reactions. 1. Activity Series of the Metals. Add separate 0.5-g. portions of mossy zinc to 5 ml. of each of the following solutions: 0.1*N* cupric sulfate and 0.1*N* mercuric chloride. Now add separate 0.5-g. portions of copper (wire or turnings) to 5 ml. of 0.1*N* mercuric chloride and to 5 ml. of 0.1*N* zinc chloride. Describe the results in each case, and write equations for the reactions that take place.[1] On the basis of the results, list these three metals in the order of their decreasing activity.[2] Look up the activity series of the metals (Text) to verify the order.

2. Activity Series of the Nonmetals. Recall the action of chlorine with bromide ions and with iodide ions (Exp. XXVI); the reaction of bromine with iodide ions (Exp. XXVI); the reaction of iodine with hydrogen sulfide (Exp. XXVII); the reaction of oxygen with an aqueous solution of hydrogen sulfide to give water and free sulfur. Write equations for these reactions, and arrange these nonmetals in the order of their decreasing activity.[3]

3. Couples and the Corrosion of Metals. Small amounts of a less active metal increase the rate at which a metal such as zinc liberates hydrogen from an acid. Dilute 1 ml. of 4*N* HCl to 10 ml., and divide this solution equally between two test tubes. To one of the tubes add 1 ml. of 0.1*N* $CuSO_4$ and 0.2 g. of powdered zinc; place 0.2 g. of powdered zinc in the other tube. Describe and explain the results.[4] Recall the use of a couple in Exp. XVII. Write the equations for the above reactions.[5]

Wrap tightly small pieces of zinc wire or strips around each of two small iron nails; wrap two others with small pieces of tin foil. Then place one of the nails wrapped with zinc and one wrapped with tin in separate test tubes partially filled with tap water. Set these tubes aside until the next laboratory period. Observe and explain the results, and correlate them with the relative positions of the three metals in the activity series.[6]

The following procedure shows the effect of couples on the corrosion of iron in acid solutions. Place the two remaining wrapped nails in separate test tubes, each of which contains 10 ml. of distilled water, 5 drops of 4*N* H_2SO_4, and 5 drops of 0.1*N* potassium ferricyanide. In which tube does the solution turn blue? Explain.[7] Tell why galvanized (zinc-covered) iron resists corrosion.[8] Tinned iron resists corrosion only when it is completely covered by the tin. Why?[9]

(B) Oxidation-Reduction Reactions. 1. With Ferrous and Ferric Ions. Dissolve about 0.1 g. of solid ferrous ammonium sulfate in 10 ml. of distilled water, and then divide the solution equally between two test tubes. To one tube add 3 ml. of chlorine water and, in addition, 1 ml. of 0.1*N* potassium ferricyanide to each tube. Explain the results, and write the equations for the reactions.[1]

Place 3 ml. of 0.1*M* ferric nitrate in each of two test tubes. To one add 5 ml. of 0.1*M* $SnCl_2$, and then 1 ml. of 0.1*N* $K_4Fe(CN)_6$ to each tube. Explain the results, and write the equations for the reactions.[2]

Dilute 1 ml. of 0.1*N* KI to 5 ml. and add to it 1 ml. of 0.1*M* $Fe(NO_3)_3$ and then 1 ml. of starch solution. Explain the result and write the equation for the reaction.[3]

2. With Permanganate Ions. To 10 ml. of water add 1 ml. of 0.1*M* $KMnO_4$ and 4 ml. of 4*N* H_2SO_4. Divide this solution equally between three test tubes. To one tube add 3 ml. of 0.1*M* Na_2SO_3, to another, 3 ml. of 0.1*M* $NaNO_2$, and to the third, 2 ml. of 3 per cent H_2O_2.

Describe the results with reference to change in color and evolution of a gas.[4] Write the equation for each reaction, and indicate the changes in oxidation state of the oxidizing agents and the reducing agents.[5]

To 10 ml. of water add 1 ml. of 0.1*M* $KMnO_4$ and 4 ml. of 4*N* NaOH. Divide this solution equally between three test tubes. To one tube add 3 ml. of 0.1*M* Na_2SO_3, to another, 3 ml. of 0.1*M* $NaNO_2$, and to the third, 3 ml. of 3 per cent H_2O_2. Describe the results with reference to color changes, formation of precipitates, and evolution of a gas.[6] Write the equation for each reaction, and indicate the changes in oxidation state of the oxidizing agents and the reducing agents.[7]

3. With Chromate and Dichromate Ions. To 1 ml. of 0.1*M* $Cr(NO_3)_3$ in 5 ml. of water add 1 ml. of 4*N* NaOH and 1 ml. of 3 per cent H_2O_2. Describe all the changes, and write equations for the reactions.[8] Now add 5 ml. of 4*N* H_2SO_4. Describe the color change, and write an equation to show the effect of hydronium ions on a solution of a chromate.[9]

To 10 ml. of water add 1 ml. of 0.1*M* $K_2Cr_2O_7$ and 1 ml. of 4*N* H_2SO_4. Divide the solution equally between three test tubes. Add 2 ml. of 0.1*M* Na_2S to one tube, 2 ml. of 0.1*M* Na_2SO_3 to another, and 2 ml. of 0.1*M* ferrous ammonium sulfate to the third. Describe the observed changes, write an equation for each reaction, and indicate the changes in the oxidation states of the oxidizing and the reducing agents.[10]

Add 1 ml. of 0.1*M* K_2CrO_4 to 4 ml. of water, and then make the solution alkaline by the addition of 1 ml. of 4*N* NaOH. Add to this solution 1 ml. of 0.1*M* Na_2SO_3. Does a change occur? [11] Draw a conclusion as to whether chromate ion or dichromate ion is the stronger oxidizing agent.[12]

(C) Oxidation-Reduction Titrations. 1. Standardization of Potassium Permanganate with Sodium Oxalate. Prepare a solution of potassium permanganate for use in titrations by diluting 20 ml. of 0.1*M* $KMnO_4$ with 180 ml. of water. Obtain a 50-ml. burette, a 10-ml. pipette, and from 25 to 30 ml. of a standard solution of sodium oxalate. (Ask the instructor or the stockroom attendant for the exact value of the normality of the solution.*) Clean the burette in the approved manner (Exp. IV) and fill it to the zero mark with the permanganate solution. Now use the pipette to transfer 10 ml. of the standard oxalate solution into a 250-ml. beaker containing 100 ml. of water and 25 ml. of 4*N* H_2SO_4. Heat the contents of the beaker to about 90°, and slowly drop in the permanganate solution from the burette. Stir the solution constantly, and continue to add permanganate until a slight pink color persists throughout the entire volume of the liquid. Record the required data on the form provided on the report sheet for this determination, and calculate the normality of the potassium permanganate solution.[1] Repeat the titration, using another 10-ml. portion of the sodium oxalate solution. Record the data.[1]

2. Determination of Iron in a Sample of an Unknown.† Special provisions must be made in the event the unknown contains chloride ion or ferric ion. Therefore, tests for these ions must be made before the analysis is undertaken. Test for chloride ion [Exp. XXVII, part (A) **1**] on a solution containing about 0.1 g. of the unknown in 10 ml. of water; ferric ion is indicated if the unknown is reddish brown in color, or if it dissolves in 12*N* HCl to give a reddish yellow or yellow solution. If these two ions are absent, make the determination according to ***P. 1*** given below. If they are present, use ***P. 2.*** In the event the sample is an iron ore it will be insoluble in water, it will contain ferric iron, and it must be dissolved in hydrochloric acid. Therefore, Procedure 2 is called for in this case.

Procedure 1. Weigh accurately about 0.500 g. of the sample, and then transfer it to a 250-ml. beaker. Record this weight and all subsequent data and calculations on the forms provided on the report sheets.[2] Dissolve the sample in 25 ml. of 1*N* H_2SO_4 (prepared from

* The concentration of this solution of $Na_2C_2O_4$ should be about 0.05*M*.

† Suitable as unknowns are such salts as $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, and hematite ore (Fe_2O_3). Do not use $FeCl_2 \cdot 4H_2O$.

the 4*N* desk reagent), and add to the solution from 2 to 3 ml. of 85 per cent H_3PO_4. Now titrate this solution with standard permanganate until the first *permanent* pink color is obtained. Stir the solution vigorously throughout the titration. Calculate the percentage of iron in the sample.[2]

Phosphoric acid is added for the purpose of obtaining a sharper end point than is possible in its absence. Ferric ion forms a colorless complex with phosphoric acid, so the color change at the end point is from colorless to pink. This contrast is sharper than the change from a yellow to a pinkish tint observed in the absence of phosphoric acid.

Procedure 2. Weigh accurately about 0.500 g. of the sample, and transfer it to a 400-ml. beaker. Record this weight and all subsequent data and calculations on the forms provided on the report sheets.[2] Add 5 ml. of 12*N* HCl to the sample, cover the beaker with a watch glass, and then warm the mixture to bring about complete solution. Now drop in from a pipette a solution of 1*M* $SnCl_2$ (in 3*N* HCl) until the yellow color is discharged, then add 2 more drops. The stannous chloride brings about the necessary reduction of Fe^{+++} to Fe^{++}. Equation?[3] Cool the solution, add to it 50 ml. of *cold* distilled water and then 10 ml. of 0.1*N* $HgCl_2$ all at once. The mercuric ion oxidizes the excess of stannous ion. Equation?[4]

Before the permanganate titration can be carried out, it is necessary to prevent the oxidation of hydrochloric acid to hypochlorous acid or chlorine because these substances give reactions that interfere with the accuracy of the determination. A manganous salt added in the form of the Zimmerman-Reinhardt solution* prevents this interference.

After the treatment with mercuric chloride, as described above, add 200 ml. of water and 10 ml. of Zimmerman-Reinhardt solution. Now titrate with standard permanganate until a pink color persists (30 sec.) throughout the solution. Despite the presence of Mn^{++} the pink color may be fleeting, that is, it may fade out in a short time. Calculate the percentage of iron in the sample.[2]

3. Determination of Copper in a Soluble Copper Salt.† Cupric ion reacts with iodide ion in the following manner:

$$2Cu^{++} + 4I^- \rightarrow 2CuI\downarrow + I_2$$

If the quantity of iodine thus liberated is determined by titration with standard sodium thiosulfate solution,

$$I_2 + 2S_2O_3^{=} \rightarrow 2I^- + S_4O_6^{=}$$

the amount of copper equivalent to the thiosulfate used may be calculated. Since two cupric ions liberate 1 molecule of iodine, which then reacts with 2 thiosulfate ions, it is seen that 1 cupric ion is equivalent to 1 thiosulfate ion. Hence,

$$\text{milli-equivalents of } Cu^{++} = \text{milli-equivalents of } S_2O_3^{=}$$

or

$$\frac{(\text{Wt. of } Cu^{++})\ (1000)}{\frac{63.57}{2}} = (N)\ (\text{ml. of } S_2O_3^{=})$$

From the latter expression the following is obtained:

$$\text{Wt. of } Cu^{++} = \frac{(N)\ (\text{ml. of } S_2O_3^{=})\ (31.785)}{(1000)}$$

* This solution is to be made up by the stockroom. Dissolve 70 g. of $MnSO_4 \cdot 4H_2O$ in 500 ml. of water, stir in 125 ml. of 36*N* H_2SO_4 and 125 ml. of 85 per cent H_3PO_4, and then dilute the mixture to a volume of 1 liter.

† Suitable unknowns are: $CuSO_4 \cdot 5H_2O$; $CuCl_2 \cdot 2H_2O$; $Cu(CH_3COO)_2 \cdot H_2O$; $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$; $Cu(NH_3)_4SO_4 \cdot H_2O$.

Weigh out from 0.300 to 0.500 g. of an unknown cupric salt,[5] transfer it to a 250-ml. beaker, and dissolve it in a solution containing 10 ml. of 4*N* CH_3COOH in 25 ml. of water. Now stir in 15 ml. of 1*N* KI, and then titrate with 0.1*M* $Na_2S_2O_3$ * until the brown color has changed to a light yellow. Add 3 ml. of 1 per cent starch solution as an indicator, and continue the titration until the blue color disappears. Record the data on the report sheet, and calculate the percentage of copper in the sample.[5]

(D) Electrochemical Cells. 1. An Oxidation-Reduction Cell. The Mechanism of Oxidation-Reduction Reactions. Arrange the apparatus illustrated in Fig. 82, but do not

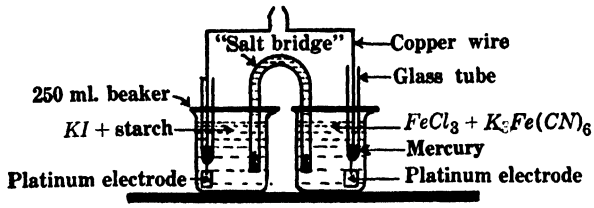


FIG. 82. An oxidation-reduction cell

connect the copper wires leading from the platinum electrodes.† In one beaker place 200 ml. of water, 10 ml. of 0.1*N* KI, and 1 ml. of 1 per cent starch solution; to the other add 200 ml. of water, 10 ml. of 0.1*M* $FeCl_3$, and 1 ml. of 0.1*N* $K_3Fe(CN)_6$. Prepare the salt bridge (see Fig. 82) from 7-mm. glass tubing. Fill the bridge with 1*N* KCl, and then plug the ends with cotton.

After the apparatus is assembled, connect the two wires leading from the electrodes, and, after a few minutes, observe the solutions near the electrodes. Describe and explain the results.[1] Write the equations for the electrode reactions.[2] Add the electrode reactions in the proper manner, and point out the similarity and the difference between the cell reaction and the action that takes place when solutions of potassium iodide and ferric chloride are allowed to interact.[3]

2. Primary Cells. The Daniell Cell. Place 50 ml. of 1*M* $CuSO_4$ in one 100-ml. beaker, and an equal volume of 1*M* $ZnSO_4$ in another beaker of the same capacity. Connect the two beakers with a salt bridge [part (D) **1**]. Suspend a copper electrode (a strip $\frac{1}{2} \times 2''$) in the cupric sulfate solution and a zinc electrode of the same dimensions in the solution of zinc sulfate (Fig. 83). Measure the e.m.f. of the cell with a voltmeter, and compare the reading

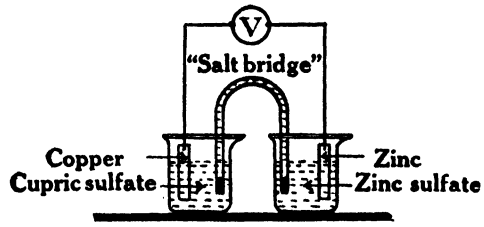


FIG. 83. The Daniell cell

with the theoretical value (Text).[4] Touch the copper wires from the electrodes to a piece of litmus paper moistened with 0.1*N* NaCl. Explain the appearance of the blue color at the point of contact with the negative wire, and the red color at the positive wire.[5] Write the equations for the reactions taking place at the copper and zinc electrodes while the cell is in operation.[6]

* Obtain the exact normality of this solution from the instructor.

† Graphite may be substituted for platinum.

3. The Lead Storage Cell. Clean two lead strips ($\frac{1}{2} \times 2''$) with sandpaper, and hang them in a 100-ml. beaker which contains an approximately 20 per cent solution of sulfuric acid (10 ml. of 36*N* H_2SO_4 and 75 ml. of distilled water). Connect the wires from the electrodes with the terminals of an automobile storage battery, or with a 110-volt D.C. line with a 60-watt lamp in series as shown in Fig. 84. (**CAUTION!** Do not touch the wires while current is flowing through them.) Allow current to flow through the cell from 10 to 15 min.

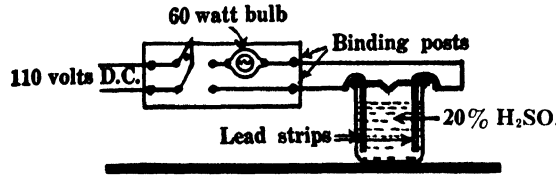


FIG. 84. Laboratory preparation of a lead storage cell

Describe the changes in the appearance of the electrodes.[7] Write the equations for the reactions that take place (Text).[8]

Disconnect the cell, and measure its voltage with a voltmeter.[9] Determine the polarity of the electrodes (of the storage cell just prepared) by touching the lead wires to a piece of litmus paper moistened with 0.1 *N* NaCl. Give the composition of each of the electrodes in a storage cell.[10] Write the equations for the electrode reactions taking place while the cell is being used as a source of current (Text).[11]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI

OXIDATION-REDUCTION. ELECTROCHEMICAL CELLS

(A) Displacement Reactions

Activity series of the metals

1.

2.

Activity series of the nonmetals

3.

Couples and the corrosion of metals

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(A) Cont'd

6.

8.

9.

(B) Oxidation-Reduction Reactions

With ferrous and ferric ions

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(B) Cont'd

2.

3.

4.

5

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(B) Cont'd

7.

8.

9.

10.

11.

12.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(C) Oxidation-Reduction Titrations

Standardization of potassium permanganate with sodium oxalate

1.

	I	II
Normality of the sodium oxalate		
Volume of sodium oxalate used		
Final reading of the burette		
Initial reading of the burette	_____	_____
Volume of potassium permanganate		
Normality of $KMnO_4$		

Determination of iron in a sample of an unknown

2.

Unknown number = Weight of sample =

Final reading of the burette		
Initial reading of the burette	_____	_____
Volume of potassium permanganate		
Normality of $KMnO_4$		
Weight of iron in sample		
Percentage of iron in sample		

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(C) Cont'd

Determination of copper in a soluble copper salt

5. Unknown number = Weight of sample =

Final reading of the burette . . . . . .
Initial reading of the burette . . . . . _____
Volume of sodium thiosulfate . . . . . .
Normality of $Na_2S_2O_3$ . . . . . .

Weight of copper in the sample . . . . . .
Percentage of copper in the sample . . . . . .

(D) Electrochemical Cells

An oxidation-reduction cell. The mechanism of oxidation-reduction reactions

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVI (Cont'd)

(D) Cont'd

Primary cells

4.

5.

6.

The lead storage cell

7.

8.

9.

10.

11.

Experiment XXXVII

SULFUR AND ITS COMPOUNDS

Discussion. The physical properties of sulfur have been studied in a previous experiment (Exp. VII). A study of the different forms of sulfur and of its chemical properties is made in this experiment. The preparation and properties of a few of the common compounds of sulfur are also studied.

(A) Forms of Sulfur. 1. Rhombic Sulfur. Shake 0.5 g. of sulfur with 3 to 4 ml. of carbon disulfide in a test tube. Filter the solution through a dry filter paper onto a watch glass. Allow the solution to evaporate slowly. Watch the formation of crystals; note their color, hardness, and transparency; and make a drawing of the form of the crystals.[1]

2. Monoclinic Sulfur. Fold a dry filter paper and place it in a funnel. Slowly heat from 8 to 10 g. of sulfur in a test tube until the solid melts to form a light-yellow mobile liquid. The appearance of brown patches indicates overheating. Pour part of the melted sulfur into the filter paper. Watch the formation of crystals on the surface. Break the crust and pour the remaining liquid sulfur into a beaker about half full of water. Examine the crystals formed in the filter paper. Describe their color, hardness, brittleness, and transparency; also make a drawing of their form.[2] What would happen to the crystals if they were allowed to remain for a week at ordinary temperatures (Text)?[3] Test the solubility of the crystals in carbon disulfide. Filter the carbon disulfide solution onto a watch glass. Allow the carbon disulfide to evaporate, and compare the crystals with those obtained in the experiment described in the preceding paragraph.[4]

3. Amorphous (Plastic) Sulfur. Heat the sulfur remaining in the test tube until it begins to boil. Describe and explain all of the changes in color and fluidity.[5] Pour the molten sulfur into a beaker containing cold water. Describe the product and test its solubility in carbon disulfide.[6] Illustrate, by means of equations, the equilibria existing between the different solid and liquid forms of sulfur (Text).[7]

4. Colloidal Sulfur. Sulfur precipitated in a finely divided state appears to be different from ordinary sulfur, but it is not a distinct form. Add from 2 to 3 ml. of $4N$ hydrochloric acid to 5 ml. of a $0.1M$ solution of sodium thiosulfate ($Na_2S_2O_3$). Compare the color of this precipitated sulfur with the color of ordinary sulfur.[8]

(B) Reactions of Sulfur. Place a small wad of copper wool half-way down the test tube in which the sulfur was heated for the experiments in part (A). Heat the sulfur remaining in the test tube until the liquid boils and the vapors are driven up to the copper turnings. Describe the result and write the equation for the reaction.[1]

Recall the reaction of sulfur with iron (Exp. IX) and with chlorine (Exp. XXVI). Write the equations for these reactions.[2]

(C) Hydrogen Sulfide. 1. Preparation. Set up the apparatus illustrated in Fig. 85, and place a few pieces (5 g.) of ferrous sulfide in the bottle. Dilute 7 ml. of $4N$ sulfuric acid to 50 ml. and pour enough of this solution into the bottle to cover the end of the thistle tube. Allow the hydrogen sulfide to flow through the water in the 8-in. test

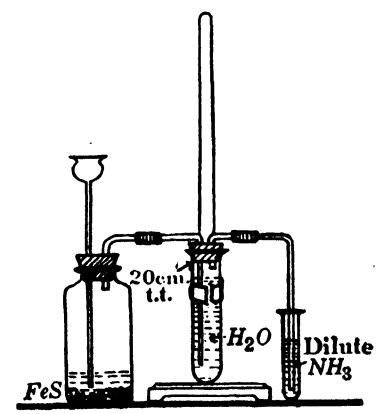


FIG. 85. Preparation of hydrogen sulfide

tube at the rate of about one bubble per second. The excess hydrogen sulfide reacts with the ammonia to form ammonium sulfide. If the reaction proceeds too rapidly, pour water into the thistle tube to dilute the acid. Stop the reaction after 8 to 10 min. by pouring from 10 to 15 ml. of 4*N* sodium hydroxide solution into the generator. *Disconnect* the test tubes but do not dismantle the generator until the hydrogen sulfide that remains in it has been absorbed by the sodium hydroxide solution. Write equations for all the chemical reactions that take place in this preparation.[1]

2. Reaction with Cations. Add 4 or 5 drops of 4*N* hydrochloric acid to 3 ml. of 0.1*N* solutions of each of the following substances: $CaCl_2$, $NiSO_4$, $MnCl_2$, $Cu(NO_3)_2$ and $SbCl_3$. To each solution add 3 ml. of the hydrogen sulfide solution just prepared. Describe the precipitates that are formed and write the equations for their formation.[2] Add 1 ml. of 4*N* ammonia and an additional 3 ml. of the hydrogen sulfide solution to those test tubes in which a precipitate did not form. Describe the precipitates and write equations for their formation.[3] Classify these sulfides into the following three groups: (1) Precipitated in acid solution (insoluble in dilute acid); (2) precipitated in alkaline solution (soluble in dilute acid, insoluble in water); (3) not precipitated in either acid or alkaline solution (soluble in water or decomposed by water).[4]

3. Oxidation of Hydrogen Sulfide. Add 5 ml. of the hydrogen sulfide solution to 2 ml. of a solution of each of the following substances: 0.1*M* $FeCl_3$, $KMnO_4$ (very dilute; faint purple color); 0.1*M* $K_2Cr_2O_7$ (to which has been added a few drops of 4*N* hydrochloric acid); 16*N* HNO_3. Describe the change in color of the solutions and note those in which a finely divided precipitate of sulfur is formed.[5] Write the equations for the above reactions.[6]

Pour 10 ml. of the hydrogen sulfide solution into a 50-ml. beaker and allow it to stand until the next laboratory period. Write the equation that accounts for the formation of the small amount of white precipitate.[7]

(D) Preparation of Sulfur Dioxide. 1. Direct Union of the Elements. Recall the reaction of sulfur with oxygen (Exp. XIII). Write the equation for this reaction.[1]

2. Oxidation of a Sulfide. Heat a small piece (0.5 g.) of iron pyrites (FeS_2) in a crucible. Note the odor of the gas evolved and the change in the appearance of the solid.[2] Write the equation for the reaction.[3]

3. Action of an Acid on a Sulfite. Add 1 ml. of 4*N* sulfuric acid to a solution of 0.5 g. of sodium sulfite dissolved in 5 ml. of water. Note the odor of the gas evolved and write the equation for its formation.[4]

4. Reduction of Sulfuric Acid. Place a short length (1 cm.) of copper wire or several copper turnings in a Pyrex test tube and add 3 ml. of 36*N* sulfuric acid. Carefully heat the test tube. (**CAUTION:** Make certain that the test tube is Pyrex. The green label found near the top of the test tube identifies the glass as Pyrex.) Note the evolution of sulfur dioxide when the temperature has been sufficiently increased. Write the equation for this reaction.[5] Cool the sulfuric acid and carefully pour it into a beaker of water before flushing it down the sink. Is sulfur dioxide formed when copper is heated with dilute sulfuric acid? Explain.[6]

(E) Preparation and Properties of Sulfurous Acid. 1. Preparation. Set up an apparatus for generating sulfur dioxide by (**a**) the reaction of copper with 36*N* sulfuric acid, or (**b**) the reaction of 4*N* sulfuric acid with sodium hydrogen sulfite.

a. Place 3 or 4 cm. of copper wire in a Pyrex test tube equipped with a one-holed rubber stopper as illustrated in Fig. 86. Pour 5 ml. of 36*N* sulfuric acid into the test tube through a funnel. Carefully heat the test tube until a steady stream of sulfur dioxide passes through the water in the large test tube. What is the purpose of the sodium hydroxide solution?[1] Write the equation for the reaction that occurs in this solution.[2] Discontinue the heating after from 8 to 10 min. and immediately disconnect the large test tube. Retain the generator for use in part (F).

b. If the second method is preferred, replace the test tube generator with the bottle and thistle tube as shown in Fig. 55. Place 5 g. of sodium hydrogen sulfite or sodium sulfite in the bottle and add sufficient water to cover the end of the thistle tube (the end should be near the bottom of the flask). Add 4*N* sulfuric acid at intervals to maintain the flow of sulfur dioxide through the water. Discontinue the addition of acid after from 8 to 10 min. Retain the generator for use in part (F). Answer the same questions asked in the preceding paragraph.

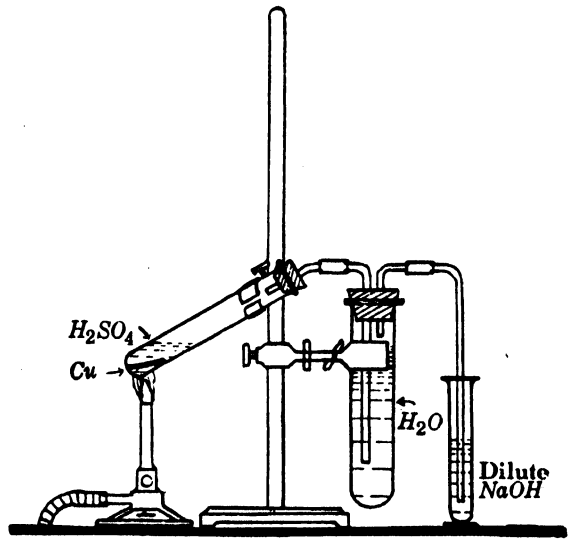


FIG. 86. Preparation of sulfur dioxide

2. Reaction as an Acid. Test the sulfurous acid solution prepared above for its acid properties as follows: Place a drop of the solution on a piece of blue litmus; add a small piece of magnesium metal to 3 ml. of the solution; to 1 drop of 4*N* sodium hydroxide in 5 ml. of water add 2 drops of phenolphthalein and then add sulfurous acid solution until the color is discharged. Describe the results and write equations for the reactions involved.[3]

3. Formation of Slightly Soluble Sulfites. Sulfurous acid contains $SO_3^=$ and therefore undergoes reactions characteristic of this ion. Place in separate test tubes 5 ml. of the sulfurous acid and 5 ml. of 4*N* sulfuric acid. To each of these add 2 ml. of 0.1*N* barium acetate solution. Equations.[4] Add 4*N* hydrochloric acid to each test tube. What happens?[5] Write a set of directions for an experiment that would determine whether a given solution contained the sulfite ion, the sulfate ion, or both.[6]

4. Oxidation by Oxygen of the Air. Pour 10 ml. of the sulfurous acid into a 50-ml. beaker and allow it to stand exposed to the air until the next laboratory period. Add 2 ml. of 0.1*N* barium acetate solution. Determine whether the precipitate is barium sulfite or barium sulfate.[7] Write the equation for the oxidation of sulfurous acid by the oxygen of the air.[8]

5. Reducing Properties. Sulfurous acid acts as a reducing agent toward a number of compounds, that is, it is easily oxidized. Add 5 ml. of the sulfurous acid solution to 2 ml. of a very dilute (faint purple) solution of potassium permanganate, and 5 ml. to 2 ml. of a 0.1*M* potassium dichromate solution. Explain the changes in color.[9] Test the solutions for $SO_4^=$. Prove that the precipitate obtained in each of the tests is not barium sulfite. Describe the procedure used.[10]

6. Bleaching Properties. Sulfurous acid is a bleaching agent for many colored materials, such as cloth, dyes, and vegetable colors. Test its bleaching action by adding 2 ml. of

the sulfurous acid solution to 5 ml. of sodium indigodisulfonate solution. Describe the result.[11]

7. Oxidizing Properties. Sulfurous acid oxidizes hydrogen sulfide to free sulfur. Add 5 ml. of sulfurous acid to 10 ml. of a saturated solution of hydrogen sulfide or bubble hydrogen sulfide through the sulfurous acid (Hood). Result? [12] Write the equation for the reaction.[13]

(F) Preparation of Sulfuric Acid. Place 2 or 3 drops of 16*N* nitric acid in a dry 250-ml. Erlenmeyer flask fitted with a two-holed rubber stopper and glass tubes as illustrated in Fig. 87. Heat the flask carefully until the fumes from the nitric acid fill the flask. Pass a rapid stream of sulfur dioxide into the flask from the generator used in part (E). Note the increase in the concentration of the brown gases. Continue to pass in sulfur dioxide until

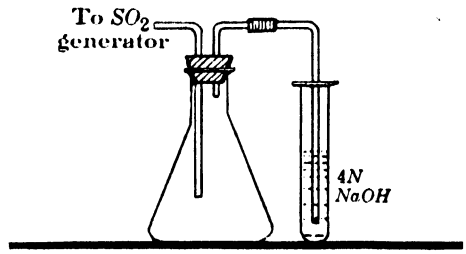


FIG. 87. Preparation of sulfuric acid

the brown color disappears and the gases begin to bubble through the 4*N* solution of sodium hydroxide. Note the formation of a frostlike deposit of nitrosylsulfuric acid on the walls of the flask. Equations.[1]

Add a few drops of water and shake the flask. Note the formation of brown fumes again. To what stage of the lead chamber process (Text) does this reaction correspond? [2] Pass in more sulfur dioxide until the brown fumes are again decolorized. Add 10 ml. of water and test for the sulfate ion.[3] Describe the test used.[4]

(G) Properties of Sulfuric Acid. 1. Stability. Place 1 drop (*not more*) of 36*N* sulfuric acid in a crucible. Heat the crucible slowly until dense white fumes are formed and then *discontinue* the heating. Use equations to explain the formation of the fumes.[1]

2. Dehydrating Action. Place 1 drop of 36*N* sulfuric acid on a small amount (0.05 g.) of sugar and on a small piece of filter paper, both in an evaporating dish. Warm the dish slightly. Describe and explain the result.[2] The formula of cane sugar (sucrose) is $C_{12}H_{22}O_{11}$. Write an equation to illustrate the reaction.[3]

Grind a few crystals of cupric sulfate pentahydrate in a mortar and place them in a Pyrex test tube. Add 5 ml. of 36*N* sulfuric acid and warm the test tube. Result? [4] Allow the acid to cool, then pour it into a beaker of water before disposing of it in the sink and flushing it down with water. Always discard concentrated acids in this manner.

Draw a diagram of an apparatus in which concentrated sulfuric acid might be used as a drying agent for (1) a gas and (2) a solid.[5]

3. Oxidizing Properties. Add 2 ml. of 36*N* sulfuric acid to a small piece (0.1 g.) of zinc or an equal amount of powdered zinc. Warm the test tube if necessary to produce a reaction. After the reaction has proceeded 1 or 2 min., note the odor and hold a piece of lead acetate paper (filter paper moistened with 0.1*N* lead acetate solution) over the mouth of the tube. What is the gaseous product? [6] Write the equation for the reaction.[7] Compare this with the reaction of concentrated sulfuric acid with hydriodic acid or iodide ion. Equation.[8]

Recall the reaction of concentrated sulfuric acid with copper and with bromide ion. Equations.[9]

4. Properties of Dilute Solutions of Sulfuric Acid. The acid properties of this substance are the same as those of any strong acid (Exp. XXVII, p. 222). Enumerate these properties.[10]

Solutions of sulfuric acid also show the properties of the sulfate ion, $SO_4^{=}$. Add 1 ml. of 4*N* sulfuric acid to 3 ml. of 0.1*N* solutions of each of the following substances: $Pb(NO_3)_2$, $BaCl_2$, $SrCl_2$. Test the solubility of the precipitates in 4*N* hydrochloric acid. Why is it necessary to make this test to prove the presence of $SO_4^{=}$? [11] Write the equations for the reactions.[12]

(H) Reduction of Sulfates. Mix 0.2 g. of barium sulfate or calcium sulfate with 0.2 g. of powdered charcoal in a crucible. Cover the crucible and heat it as strongly as possible from 4 to 5 min. Cool the crucible, add 1 ml. of water, and then break up the mass with a stirring rod. Add 1 ml. of 4*N* hydrochloric acid. Identify the gas by its odor. Equation? [1]

(I) Thiosulfates. 1. Preparation. In a 100-ml. beaker dissolve 3 g. of sodium sulfite in 15 ml. of water, add 1 g. of sulfur, and then boil the mixture gently from 10 to 15 min. Equation? [1] Filter the solution and use the filtrate in the following tests.

2. Reaction with an Acid. Add 1 ml. of 4*N* hydrochloric acid to 3 ml. of the sodium thiosulfate solution. Note the formation of a precipitate and the odor of the gas evolved. Equation? [2]

3. Reaction with Iodine. To 5 ml. of iodine water add 0.5 ml. of starch solution. Now add the sodium thiosulfate solution, drop by drop, until the color is discharged. Equation? [3] How could this reaction be used to determine the amount of iodine in a given solution? [4]

4. Reaction with Silver Chloride. When excess sodium thiosulfate is added to silver chloride (AgCl) the latter dissolves because a stable complex ion $[Ag_2(S_2O_3)_3]^{=}$ is formed. To 1 ml. of 0.1*N* silver nitrate solution add 1 ml. of a 0.1*N* solution of sodium chloride. How many ml. of the sodium thiosulfate solution are required to dissolve the precipitate? [5] Equation? [6]

5. Reaction with Silver Ions. Describe the changes in color that occur when 5 ml. of 0.1*N* silver nitrate solution is added to 1 ml. of the sodium thiosulfate solution. [7] The silver thiosulfate formed is unstable in water:

$$Ag_2S_2O_3 + 2H_2O \rightarrow Ag_2S + H_3O^+ + HSO_4^-$$

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII

SULFUR AND ITS COMPOUNDS

(A) Forms of Sulfur

1.

2.

3.

4.

5.

6.

7.

8.

(B) Reactions of Sulfur

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII (Cont'd)

(B) Cont'd

2.

(C) Hydrogen Sulfide

1.

2.

3.

4.

5.

6.

7.

(D) Preparation of Sulfur Dioxide

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII (Cont'd)

(D) Cont'd

3.

4.

5.

6.

(E) Preparation and Properties of Sulfurous Acid

1.

2.

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII (Cont'd)

(E) Cont'd

9.

10.

11.

12.

13.

(F) Preparation of Sulfuric Acid

1.

2.

3.

4.

(G) Properties of Sulfuric Acid

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII (Cont'd)

(G) Cont'd

4.

5.

6.

7.

8.

9.

10.

11.

12.

(H) Reduction of Sulfates

1.

(I) Thiosulfates

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVII (Cont'd)

(I) **Cont'd**

2.

3.

4.

5.

7.

Experiment XXXVIII

NITROGEN AND AMMONIA

Discussion. The great abundance of free nitrogen in the atmosphere shows that the molecule N_2 is fairly stable and also inactive at ordinary atmospheric conditions. However, if nitrogen is activated by means of high temperatures, catalysts, or electrical discharges, it will react with hydrogen to give ammonia, with active metals to give nitrides, and with oxygen to give oxides.

Nitrogen is prepared from its compounds by oxidation, by reduction, by thermal decomposition, or by catalytic decomposition. Nitrogen is obtained from the air commercially by first liquefying the air and then subjecting it to fractional distillation. In the laboratory, oxygen and carbon dioxide are removed from the air by chemical means. This leaves nitrogen mixed with about 1 per cent of argon and with other inert gases.

There are three compounds composed only of nitrogen and hydrogen: ammonia (NH_3), hydrazine (N_2H_4), and hydrazoic acid (HN_3). Of these ammonia is the most important. It is very soluble in water and reacts with it to give a weakly basic solution:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The addition of an alkali or other nonvolatile substance yielding a sufficiently high concentration of hydroxide ion liberates ammonia from ammonium salts. Gaseous ammonia is recognized by its reaction with moist red litmus, by its odor, or by its formation of a cloud of solid particles of ammonium chloride with hydrogen chloride. The preparation of ammonia in a variety of ways is studied in this experiment.

Ammonia reduces the oxides of heavy metals to give nitrogen and water; reacts with certain metals to form nitrides or amides; forms ammonium salts with acids; yields complex ions (ammines) with certain cations; and reacts with certain substances by ammonolysis in a manner analogous to those protolytic reactions of water classified as hydrolysis reactions. A number of the above reactions are studied in this experiment.

Ammonium salts are decomposed by heating them to a sufficiently high temperature. Ammonium chloride dissociates into ammonia and hydrogen chloride; ammonium nitrite yields water and nitrogen; ammonium nitrate decomposes into nitrous oxide and water; ammonium sulfate and ammonium phosphate form ammonia and comparatively nonvolatile acids; while ammonium dichromate decomposes into chromic oxide, water, and nitrogen.

Apparatus and Materials: 15 ml. of diamminecuprous chloride solution; sodium hypochlorite solution; pneumatic trough; 4 cm. of magnesium ribbon; 1 g. of soft coal; calcium cyanamide; 10-ml. pipette; burette.

(A) Preparation of Nitrogen. 1. From the Air. Set up an apparatus as shown in Fig. 88. The 20-cm. (8-in.) test tube is fitted with a two-holed rubber stopper. A short section of glass tubing drawn out in the form of a nozzle is placed in one hole of the stopper and a short piece of glass rod in the other. The tip of the glass tube and the lower end of the glass rod should be level with the bottom of the stopper. Connect the upper end of the glass tube to the stem of the funnel with a piece of rubber tubing about 20 cm. long.

Remove the test tube, pour 15 ml. of a solution of diamminecuprous chloride,* $[Cu(NH_3)_2Cl]$, into the funnel, and then open the pinch clamp until the solution completely fills both the rubber tube and the glass tube. Remove the glass rod from the stopper and fit the stopper into the test tube. This allows the escape of the air displaced by the stopper. Now replace the glass rod. With the apparatus in position *A* (Fig. 88), open the pinch clamp and allow the solution to flow into the test tube. As oxygen is absorbed more of the solution is drawn into the test tube. Close the clamp periodically and shake the test tube. Reopen the clamp to allow more solution to flow in. Continue these operations until no more solution flows into the test tube (about 5 min.).

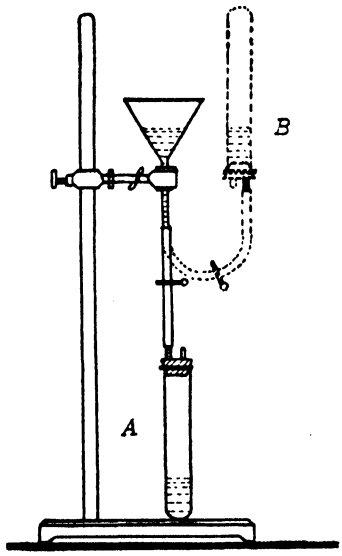


FIG. 88. Gas analysis apparatus

Invert the test tube (position *B*, Fig. 88), open the clamp, equalize the levels of the liquids, and finally close the clamp. Restore the test tube to position *A* (Fig. 88). Mark with labels the level of the liquid in the test tube and the position of the bottom edge of the stopper. Remove the stopper from the test tube, pour out the liquid and measure by means of a graduated cylinder or a burette the volumes of water required to fill the test tube to the two marks.[1] The volume occupied by the liquid in the test tube is equal to the volume of oxygen absorbed, whereas the larger volume is equal to the volume of air originally present.

Calculate the approximate percentage by volume of nitrogen and of oxygen in the air.[1] What gases are present with the nitrogen after the removal of the oxygen?[2] Point out a few errors inherent in this method.[3]

2. From Ammonia by the Action of a Hypochlorite. Hypochlorites and hypobromites react with ammonia and ammonium salts to form nitrogen. To 3 ml. of a 4*N* solution of ammonia, add 3 ml. of a 5 per cent sodium hypochlorite solution. Describe the nature of the reaction. Equation?[4]

3. From Ammonium Nitrite by Thermal Decomposition. Ammonium nitrite decomposes into nitrogen and water. Equation?[5] The rate of this decomposition increases with rise in temperature. If the concentration of ammonium nitrite is high, the rate of the reaction may increase spontaneously until an explosion results. The danger of an explosion is reduced to a minimum if the apparatus is arranged and operated in a manner that allows the presence of only a small quantity of ammonium nitrite at any one time. A solution of sodium nitrite is dropped at a very slow rate into a fairly concentrated solution of ammonium chloride heated to a temperature which causes the rapid decomposition of any nitrite present. This prevents the building up of a high concentration of the potentially explosive ammonium nitrite. The same general experimental method is applied to the preparation of other substances which are formed from reaction mixtures in which explosive substances are present.

Set up the apparatus shown in Fig. 89. Place in the 250-ml. Erlenmeyer flask 5 g. of ammonium chloride, 3 g. of sodium chloride, and 20 ml. of water. Close the clamp on the rubber tube and pour into the funnel † a solution containing 4 g. of sodium nitrite dissolved

* An alkaline solution of potassium pyrogallate may be substituted for the solution of diamminecuprous chloride. The latter is prepared as follows: Dissolve 10 g. of cupric chloride in 75 ml. of water, add 25 ml. of 12*N* hydrochloric acid, and then 10 g. of copper powder or turnings. Warm the solution or allow it to stand until the green color has disappeared. Now add a concentrated solution of ammonia until the solution is strongly ammoniacal. Keep excess copper in contact with the solution and protect it from the air in a tightly stoppered bottle.

† If separatory funnels are available they may be substituted for this arrangement.

in 15 ml. of water. Obtain a pneumatic trough, connect a delivery tube to the outlet tube of the generator, and arrange for the collection of a bottle of nitrogen by displacement of water. Heat the ammonium chloride solution until it begins to boil gently. Decrease the size of the flame so that the solution is barely maintained at its boiling point. Allow a drop of the sodium nitrite solution to fall into the hot solution. Note that decomposition takes place immediately. Regulate the screw clamp so that *not more than 1 drop falls into the solution every 5 sec.* This should maintain the rate of evolution of nitrogen at about 1 or 2 bubbles per second.

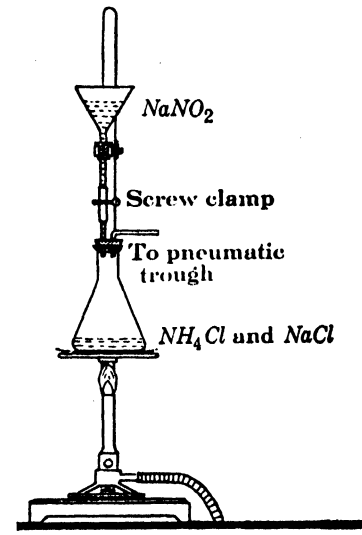


FIG. 89. Nitrogen generator

After nitrogen has been generated from 2 to 3 min., place the delivery tube under the bottle in the pneumatic trough and collect a bottle of nitrogen. Close the clamp to stop the flow of sodium nitrite, turn off the flame, *and remove the delivery tube from the water.* Why? [6]

Remove the bottle from the trough and thrust a burning splinter into it. Explain the result.[7]

(B) Chemical Properties of Nitrogen. Connect to the nitrogen generator, as shown in Fig. 90, a steam trap, a calcium chloride drying tube, and a combustion tube containing a porcelain boat in which 4 cm. of magnesium ribbon has been placed. Heat the ammonium chloride solution to its boiling point in the Erlenmeyer flask. Allow the sodium nitrite solution to drop into the hot solution at a rate which does not exceed *1 drop in 5 sec.* After the gas has passed through the tube from 3 to 4 min., begin to heat the combustion tube under the porcelain boat. Continue to heat the magnesium as strongly as possible for a period

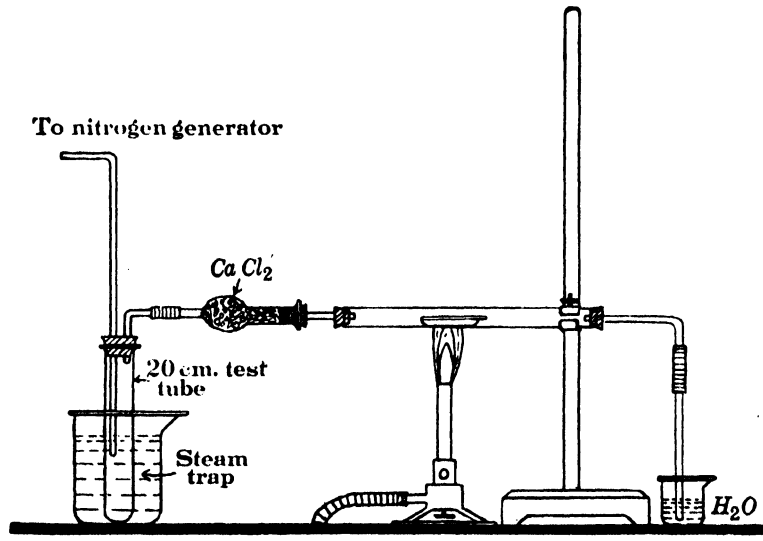


FIG. 90. Reaction of nitrogen with magnesium

of about 10 min. Finally stop the flow of sodium nitrite, remove the flames and *immediately remove the delivery tube from the water in the beaker.*

Remove the porcelain boat after the tube has cooled and place the product in a 50-ml. beaker. Wet a piece of red litmus paper and place it on the under side of a watch glass. Add a few drops of water to the product and immediately place the watch glass with the

litmus paper over the beaker. If magnesium nitride is present in the product, the litmus will slowly turn blue. Explain what happens to the litmus in this experiment.[1] Write equations for the formation of the magnesium nitride and for the formation of ammonia.[2]

Molecular nitrogen (N_2) is usually rather inactive. State at least two methods of activating nitrogen.[3] (**Discussion**)

(C) Preparation of Ammonia. 1. From the Elements (Haber Process). Under special conditions nitrogen and hydrogen react to form ammonia:

$$N_2 + 3H_2 \leftrightharpoons 2NH_3 + 21{,}880 \text{ cal.}$$

List the special conditions under which this reaction occurs.[1] State Le Chatelier's law and predict the influence of increased temperature and increased pressure upon the equilibrium.[2]

2. By-product Ammonia. Large quantities of ammonia are obtained as a by-product from the coking of coal. Place a small piece (1 g.) of soft (bituminous) coal in a test tube equipped with a one-holed rubber stopper and a delivery tube. Immerse the end of the delivery tube in 5 ml. of water containing a few drops of 4*N* sulfuric acid. Heat the test tube strongly until gases cease to be evolved. Transfer the sulfuric acid solution to a small beaker and add 4*N* sodium hydroxide until the solution is distinctly alkaline (test). Place a piece of wet red litmus on the under side of a watch glass. Now cover the beaker with this glass. What happens to the litmus? [1] Note the odor of the gases evolved and then hold over the beaker a rod that has been immersed in 12*N* hydrochloric acid. Explain.[2] Describe the method used to recover ammonia from the gases liberated during the coking of coal. Write equations for the reactions that take place in each part of the process.[3]

3. The Cyanamide Process. Place a few small pieces (0.5 g.) of calcium cyanamide in a 50-ml. beaker. Place over the beaker a watch glass with a piece of wet litmus paper (red) adhering to the under side. How rapidly does the litmus change color? [4] Warm the solution if necessary. Write equations to express the formation of calcium cyanamide and its reaction with water (Text).[5]

4. From Nitrides. Recall the reaction of magnesium nitride with water (part B). Write the equations for the reaction of two other metallic nitrides with water (Text).[6]

5. From Ammonium Salts. To 3 ml. of 0.1*N* solutions of ammonium nitrate, sodium nitrate, and ammonium sulfate in separate test tubes add 4*N* sodium hydroxide and test the gases for ammonia by means of moist litmus paper, odor, and 12*N* hydrochloric acid on a rod.[7] Write equations for the reactions that occur.[8] Do all compounds containing nitrogen give ammonia when heated with sodium hydroxide? [9]

6. From an Aqueous Solution of Ammonia. Waft the gases from a bottle of ammonia past the nose. Hold dry and wet litmus paper (red) over the bottle. Explain why the litmus must be wet.[10] How could a quantity of ammonia gas be obtained from the aqueous solution? [11] What weight of ammonia is contained in 25 ml. of an aqueous solution which has a density of 0.892 g./ml. and contains 30 per cent NH_3? [12] Calculate the volume occupied by this weight of ammonia at standard conditions, and at 740 mm. and 25°.[13] (**Hint:** First calculate the density of ammonia at standard conditions by use of the gram-molecular volume.)

(D) Properties and Determination of Ammonia. 1. Physical Properties and Tests. Grind together in a mortar 10 g. of ammonium chloride and 10 g. of calcium hydroxide (slaked lime). Note the odor.[1] Transfer the mixture to a 50-ml. Erlenmeyer flask arranged as shown in Fig. 91. Place a loose wad of cotton in the mouth of the test tube in order to prevent convection currents. Now heat the flask slowly until the test tube is filled with gaseous ammonia. The tube is filled if a piece of moist red litmus paper rapidly turns blue when placed near the mouth of the test tube.

Remove the cotton and transfer the test tube in an inverted position to a 50-ml. beaker

about two thirds full of water. Immerse the mouth of the tube in the water. Explain the result.[2] Test the solution with litmus paper.[3]

Fill a second test tube with the gas and, while the tube is in an inverted position, insert a burning splinter. Does the ammonia ignite or support combustion?[4] Under what conditions does ammonia react with oxygen (Text)?[5]

While a third test tube of ammonia is being collected, warm another test tube and drop into it 1 drop of 12*N* hydrochloric acid. Place the two test tubes mouth to mouth. Explain the results.[6]

2. Reducing Action. Replace the vertical glass tube in the generator flask by a glass tube with a right-angle bend. Place a piece of cupric oxide wire in the horizontal section of

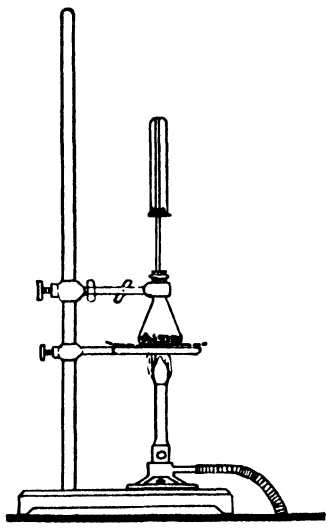


FIG. 91. Preparation and collection of ammonia

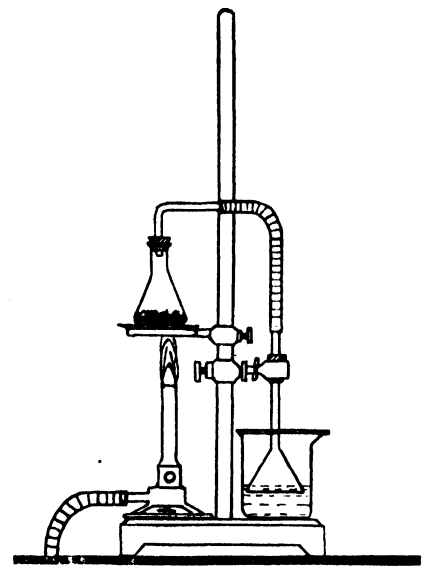


FIG. 92. Preparation of a solution of ammonia

the glass tube. Heat the generator flask until a stream of ammonia gas issues from the tube as shown by a test with moist litmus. Now heat the glass tube under the cupric oxide. What happens to the cupric oxide? Write an equation for the reaction.[7]

3. Reaction with Water. Set up the apparatus shown in Fig. 92. Place 100 ml. of distilled water in the beaker and adjust the height of the funnel so that it is not more than 0.5 cm. below the surface of the water.

This arrangement illustrates the essential features of an apparatus designed to absorb a very soluble gas in a solvent. If a small glass tube were immersed in the water, the ammonia gas would dissolve so rapidly that the liquid would be drawn into the generator flask. The arrangement shown in Fig. 92 obviates this danger because air is automatically admitted to the system whenever liquid is drawn up into the space provided by the funnel. It is necessary to make certain that the funnel is not immersed too far down into the liquid, otherwise the arrangement would have no advantages over an ordinary delivery tube.

Heat the generator about 5 min. Note that the water rises in the funnel after the air has been displaced from the apparatus. Explain.[8] Remove the funnel from the beaker and stir the solution thoroughly. Note the odor of the solution, test it with litmus, and hold near the beaker a glass rod which has been dipped into 12*N* hydrochloric acid. Result?[9]

4. Volumetric Determination of Ammonia. Now determine the concentration of the solution of ammonia and the total weight of ammonium chloride that can be prepared from

it as follows: Measure the total volume of the solution in a graduated cylinder.[10] Withdraw 10 ml. with a pipette and transfer this solution to an Erlenmeyer flask or a 250-ml. beaker. Refer to Exp. XXXV and select from the indicators available in the laboratory the one best suited for the titration of a weak base with a strong acid. Obtain a burette and titrate the solution with 0.1*N* hydrochloric acid.[10] (If a standard solution of hydrochloric acid is not supplied in the laboratory, prepare it by diluting 10 ml. of the 4*N* acid to 50 ml.; then dilute 10 ml. of this solution to 100 ml.) Calculate the concentration of the solution of ammonia.[10] Determine from this value the weight of ammonia in the total volume of solution, and the weight of ammonium chloride that would be formed by complete neutralization with hydrochloric acid.[10]

5. Gravimetric Determination of Ammonia. Measure out 75 ml. of the remaining solution of ammonia. Transfer it to a beaker and add 12*N* hydrochloric acid to it until the solution is acid to litmus. Weigh an evaporating dish to the nearest 0.01 g.[11] Pour the solution into the evaporating dish until it is about two thirds full. Cover the dish with a watch glass supported above the dish by means of a glass triangle. Now evaporate the solution over a small flame. Replace the liquid that evaporates with more of the neutralized solution. When the solution has been evaporated to about 10 ml., complete the evaporation by placing the dish on a beaker of boiling water. (**Note:** Continue with the remaining parts of the experiment while the evaporation is proceeding.) Finally scrape the residue from the watch glass and the triangle into the dish and obtain the combined weight of the dish and the ammonium chloride.[11] What weight of ammonium chloride is obtained?[11] Calculate the weight of ammonium chloride present in each milliliter of the solution that was evaporated.[11] Now calculate the weight of ammonium chloride that would have been obtained if all of the original ammonia solution had been neutralized with hydrochloric acid.[11] How does this weight compare with the weight calculated in the preceding paragraph?[12]

6. Action on Metals. Draw a diagram of an apparatus which could be used to carry out the reaction between magnesium and dry ammonia at high temperatures to give magnesium nitride (Mg_3N_2).[13] What difficulty would be encountered if calcium chloride were used as a drying agent?[14] Name a suitable drying agent.[15]

7. Formation of Complex Ions. To 5 ml. of 0.1*N* cupric sulfate solution add a 4*N* solution of ammonia, drop by drop, until an excess has been added. Describe the changes that take place and write equations for the reactions.[16]

To 5 ml. of 0.1*N* silver nitrate solution add 0.5 ml. of a 1*N* solution of sodium chloride (equivalent amounts of the two substances). Shake the test tube to coagulate the precipitate, allow it to settle, decant (pour off) the liquid, add 5 ml. of water to the precipitate, and then decant the liquid again. Add 4*N* ammonia solution. Explain why the precipitate dissolves. Equations?[17]

8. Ammonolysis. When ammonia is added to a solution of mercuric chloride, the reaction which occurs is analogous to the hydrolysis of salts:

$$Hg^{++} + 2Cl^- + 2H_2O \rightleftharpoons Hg(OH)Cl + H_3O^+ + Cl^-$$

$$Hg^{++} + 2Cl^- + 2NH_3 \longrightarrow Hg(NH_2)Cl\downarrow + NH_4^+ + Cl^-$$

Add 4*N* ammonia to 0.1*N* mercuric chloride solution. Result?[18] The precipitate, amidomercuric chloride, is often called "ammoniated mercuric chloride" or "infusible white precipitate."

Add 4*N* ammonia to 0.1*N* mercurous nitrate solution. Compare the result with that obtained in the last paragraph.[19] The reaction is a rather complicated one resulting in the formation of mercury and amidomercuric nitrate:

$$Hg_2^{++} + 2NO_3^- + 2NH_3 \rightarrow Hg(NH_2)NO_3\downarrow + Hg\downarrow + NH_4^+ + NO_3^-$$

Write on a piece of paper with 0.1*N* mercurous nitrate solution. After part of the water has evaporated, hold the paper over a bottle containing 15*N* ammonia solution. Explain the result.[20]

(E) Ammonium Salts. 1. Preparation from Ammonia. Ammonium chloride was prepared in part (D) of this experiment. Suggest a method for preparing ammonium sulfate; ammonium nitrate; and ammonium acetate. Equations.[1]

Ammonium salts may also be formed by the reduction of nitrates in acid solution. These reactions are studied in Exp. XXXIX.

2. Thermal Decomposition. Place about 0.2 g. of ammonium chloride in a test tube clamped in a nearly horizontal position. The mouth of the test tube should be slightly lower than the bottom of the tube in order to minimize interference from convection currents. Place over the mouth of the test tube pieces of wet litmus paper (red and blue). Heat the ammonium chloride with a medium-sized flame. Note and explain the changes that occur in the color of the litmus.[2] State Graham's law of diffusion and explain on the basis of this law which of the dissociation products of ammonium chloride should be the first to emerge from the mouth of the test tube.[3]

Repeat the experiment with ammonium sulfate. Explain the difference in behavior of this salt and ammonium chloride when they are heated, and why only one color change of the litmus is observed during the thermal decomposition of the sulfate.[4] (**Hint:** Consider the volatility of the acids.) Predict the results that would be obtained when an ammonium phosphate is heated.[5]

Write equations for the thermal decomposition of the following ammonium salts (**Discussion**): NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, NH_4NO_2, $(NH_4)_2CrO_4$.[6]

3. Test for Ammonium Salts. Obtain a solution of any ammonium salt. Pour about 1 ml. of it into a 50-ml. beaker and add an excess of 4*N* sodium hydroxide (4 ml.). Immediately cover the beaker with a watch glass which has a piece of wet red litmus paper on the under side. Warm the beaker. A change in the color of the litmus from red to blue after the solution is warmed shows the presence of ammonium ion. *The solution must not be boiled.* Why not?[7]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII

NITROGEN AND AMMONIA

(A) Preparation of Nitrogen. *From the air*

1. Volume of air . . . . . .
Volume of oxygen absorbed . . . . . .
Percentage of oxygen . . . . . .
Percentage of nitrogen . . . . . .

2.

3.

From ammonia by the action of a hypochlorite

4.

From ammonium nitrite by thermal decomposition

5.

6.

7.

(B) Chemical Properties of Nitrogen

1.

2.

3.

(C) Preparation of Ammonia. *From the elements (Haber process)*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII (Cont'd)

(C) Cont'd

2.

By-product ammonia

1.

2.

3.

The cyanamide process

4.

5.

From nitrides

6.

From ammonium salts

7.

8.

9.

From an aqueous solution of ammonia

10.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII (Cont'd)

(C) Cont'd

11.

12.

13.

(D) Properties and Determination of Ammonia

1.

2.

3.

4.

5.

6.

Reducing action

7.

Reaction with water

8.

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII (Cont'd)

(D) Cont'd

Volumetric determination of ammonia

10. Total volume of NH_3 solution . . . . . .
Volume of NH_3 solution withdrawn . . . . . .
Volume of $_N$ HCl solution . . . . . .
Normality of NH_3 solution . . . . . .
Weight of NH_3 in the total volume. . . . . .
Calculated weight of NH_4Cl for total volume . . . . . .

Gravimetric determination of ammonia

11. Weight of evaporating dish + NH_4Cl . . . . . .
Weight of evaporating dish . . . . . _____
Weight of NH_4Cl . . . . . .
Weight of NH_4Cl per ml. of solution . . . . . .
Calculated weight of NH_4Cl for total volume . . . . . .

12.

Action on metals

13.

14.

15.

Formation of complex ions

16.

17.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII (Cont'd)

(D) Cont'd

Ammonolysis

18.

19.

20.

(E) Ammonium Salts. *Preparation from ammonia*

1.

Thermal decomposition

2.

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXVIII (Cont'd)

(E) Cont'd

Test for ammonium salts

7.

Experiment XXXIX

OXYGEN COMPOUNDS OF NITROGEN

Discussion. Nitrogen forms oxides in which it possesses oxidation states from +1 to +5 inclusive. Nitrogen in its oxygen acids has oxidation states of +1, +3 and +5 as shown in the following table:

Oxide	Formula	Oxidation State	Acid	Formula	Oxidation State
Nitrous oxide	N_2O	+1	Hyponitrous acid	$H_2N_2O_2$	+1
Nitric oxide	NO	+2			
Nitrogen trioxide	N_2O_3	+3	Nitrous acid	HNO_2	+3
Nitrogen dioxide	NO_2	+4			
Nitrogen tetroxide	N_2O_4	+4			
Nitrogen pentoxide	N_2O_5	+5	Nitric acid	HNO_3	+5

The preparation and properties of the common oxides and oxygen acids of nitrogen are studied in this experiment.

Apparatus and Materials: 10 cm. of white woolen yarn; fine filter paper; 0.05 g. of antimony; hydrogen sulfide gas or its saturated solution; 2 ml. of carbon tetrachloride; pneumatic trough; 0.2 g. of red phosphorus; 2 g. of sodium peroxide.

(A) Preparation of Nitric Acid. 1. By the Action of a Nonvolatile Acid on a Nitrate.* To 1 g. of sodium nitrate in a Pyrex test tube add about 3 ml. of 36*N* sulfuric acid through a funnel to prevent the acid from touching the wall of the tube. Hang a piece of white woolen yarn over the edge of the test tube so that one end of the yarn is about half the distance down the inside of the test tube. Boil the solution gently until the vapors of nitric acid reach the yarn. Note the change in the color of the yarn.[1] The formation of colored xanthoproteic acids with proteins is a characteristic reaction of nitric acid. Discontinue the heating as soon as the end of the yarn changes color.

Place a loose plug of copper turnings about one third of the distance down the test tube. Heat the tube again until the nitric acid reaches the copper. Note the color of the gases evolved and the change in color of the copper.[2] This is a characteristic test for nitric acid; it is studied later in the experiment. *Discontinue* the heating immediately after the effect is noted. What acid other than sulfuric acid could be used in this experiment?[3] Write the equation for the formation of nitric acid.[4]

2. By the Interaction of Solutions of Selected Nitrates and Acids. A solution of nitric acid results when an acid is added to a nitrate whose cation forms an insoluble precipitate with the anion of the acid. For example:

$$Ba^{++} + 2NO_3^- + 2H_3O^+ + SO_4^{=} \rightarrow BaSO_4\downarrow + 2H_3O^+ + 2NO_3^-$$

The two reactants must be mixed in *equivalent amounts.*

* If a retort is available, larger quantities of nitric acid may be prepared and distilled into a cooled receiver.

If the concentration of the dilute sulfuric acid in the desk reagent bottle is 4*N*, calculate the volume of 0.1*N* barium nitrate solution that must be added to 1 ml. of the sulfuric acid.[5] Mix the two solutions, heat the mixture to boiling in order to coagulate the precipitate, and then filter the solution through a *fine* filter paper. A coarse filter paper does not retain the precipitate. Test the solution with litmus paper and with a small piece of calcium carbonate.[6]

On the basis of the general method described in the preceding paragraph, suggest a means for preparing a solution of nitric acid from hydrochloric acid and a suitable nitrate.[7]

3. By the Interaction of Nitrogen Dioxide with Water. Nitric oxide (NO) is formed by the oxidation of ammonia (Ostwald process) or by direct union of nitrogen and oxygen in an electric arc (Birkeland-Eide process). This oxide unites with an excess of oxygen to form nitrogen dioxide which then reacts with water to form nitric acid. Write the equations for the reactions involved in the Ostwald and Birkeland-Eide processes.[8] The reaction of nitrogen dioxide with water is studied in part (G).

(B) Chemical Properties of Nitric Acid. 1. Activity as an Acid. Nitric acid is a strong acid and therefore undergoes reactions characteristic of any strong acid. Test the reaction of 4*N* nitric acid with litmus, with a small lump (0.1 g.) of calcium oxide, and with calcium carbonate (marble chips).[1] Write the equations for the above reactions.[2]

2. Oxidation of an Active Metal. Nitric acid reacts with the metals above hydrogen in the electromotive series to form the nitrates of the metals and various reduction products of nitric acid. The identity of the reduction products depends upon the activity of the metal, the concentration of the nitric acid, and the concentration of the hydronium ion (pH). With zinc, dilute nitric acid forms ammonia, nitrogen, nitrous oxide, and little, if any, hydrogen. In very dilute solutions ammonia is the principal reduction product. In more concentrated solutions, nitric oxide and nitrogen dioxide are formed. Nitrogen dioxide is formed in the greatest proportions when concentrated nitric acid is used.

Mix 3 ml. of 4*N* nitric acid with 3 ml. of water and then add a small piece (0.2 to 0.4 g.) of zinc. Allow the reaction to continue 4 or 5 min. Transfer the solution to a 50-ml. beaker, add 4*N* sodium hydroxide until the solution is strongly alkaline to litmus, and immediately cover the beaker with a watch glass which has a piece of moist red litmus adhering to the under side. What happens to the litmus?[3] Account for the results of this experiment by writing an equation for the reaction between zinc and very dilute nitric acid.[4]

Add 3 ml. of 16*N* nitric acid to a *small piece* (0.05 g.) of mossy or granular zinc. Note the brown color of the nitrogen dioxide liberated in the reaction, then immediately stop the evolution of the gas by pouring the solution into water. This prevents the escape of excessive amounts of nitrogen dioxide into the laboratory. Write the equation for this reaction.[5]

3. Oxidation of Inactive Metals. Place a small amount (0.1 to 0.5 g.) of copper in a test tube and add to it 5 ml. of 4*N* nitric acid. Warm the solution. Note the color of the gases in the test tube after the reaction has proceeded about 1 min., and again after the reaction has gone on for a sufficient length of time to displace all of the air from the tube. Write the equation for the reaction and explain the change in the appearance of the gases in the test tube.[6] Recall the fact that nitric oxide is colorless while nitrogen dioxide is brown.

To a *small piece* of copper (0.05 g. or about the size of a match head) add from 8 to 10 drops of 16*N* nitric acid. (Pour a small amount of the acid into a 50-ml. beaker and then add the drops from a medicine dropper.) Note the color of the gases and then discard the solution immediately. Write an equation for the reaction.[7]

Most metals except gold, platinum, iridium, and rhodium are acted upon by dilute or concentrated nitric acid. Certain elements, for example, antimony, arsenic, tin, molybdenum, and tungsten, are changed to oxides.

Add a few small crystals or a small amount (0.05 g.) of powdered antimony to 3 ml. of 16*N* nitric acid. Gently boil the solution 2 or 3 min. Describe the result and write the equation for the formation of the oxide (Sb_2O_5).[8]

Try the reaction of 12*N* and 4*N* hydrochloric acid with copper. Explain why nitric acid dissolves many of the metals below hydrogen in the electromotive series, whereas hydrochloric acid does not.[9]

4. Oxidation of Nonmetals. Add 3 ml. of 16*N* nitric acid to about 0.2 g. of sulfur in a test tube. If a hood is not available, clamp the test tube to a ring stand and equip the tube with a one-holed stopper and a delivery tube with its end immersed in 4*N* sodium hydroxide. The oxides of nitrogen liberated during the reaction are absorbed by the sodium hydroxide; this prevents the escape of the gases into the laboratory. Boil the nitric acid gently about 5 min. Remove the delivery tube and allow the solution to cool. Pour it into about 20 ml. of water in a small beaker and add 5 ml. of a 0.1*N* solution of lead nitrate or barium chloride. Note that the solution gradually becomes cloudy, and, after 10 or 15 min. a precipitate settles to the bottom of the beaker. What is this precipitate?[10] Write the equation for the oxidation of sulfur by concentrated nitric acid.[11] Dilute nitric acid does not oxidize sulfur. Write an equation for the oxidation of carbon by concentrated nitric acid (Text).[12]

5. Action on Compounds. Add 5 ml. of 16*N* nitric acid to 5 ml. of a saturated solution of hydrogen sulfide or, as an alternative, pass hydrogen sulfide gas through 4*N* nitric acid. Note the formation of an opalescent solution. What is the precipitate that causes this opalescence? Equation?[13]

Precipitate cupric sulfide from 2 ml. of 0.1*N* cupric sulfate solution by the addition of from 8 to 10 ml. of a saturated solution of hydrogen sulfide, *or* dilute the cupric sulfate to 10 ml. and then pass in hydrogen sulfide gas. Transfer half of the mixture to another test tube. To one test tube add 5 ml. of 12*N* hydrochloric acid, and to the other add 5 ml. of 16*N* nitric acid. Note the formation of a gummy mass of sulfur which floats on top of the solution in the latter test tube. Explain the difference between the reaction of nitric acid and hydrochloric acid on sulfides.[14] Write equations to illustrate this difference.[15]

(C) Nitrates. 1. Preparation. With nitric acid as a starting material in each case, write equations to illustrate three different methods for preparing lead nitrate.[1]

2. Thermal Decomposition. Heat about 1 g. of sodium nitrate in a crucible until the substance melts and then begins to decompose. Test for oxygen with a glowing splint.[2] Hold the glowing splint above the molten salt. (**DANGER!** Do not allow the splint to touch the molten salt because an explosion may result.) The other product resulting from the thermal decomposition of the alkali nitrates is a nitrite. Write the equation for the above decomposition.[3]

The nitrates of the less active metals such as lead and mercury are decomposed by heat into an oxide of the metal, nitrogen dioxide, and oxygen. Heat 0.5 g. of lead nitrate in a test tube. If a hood is not available, equip the test tube with a one-holed stopper and a delivery tube the end of which is immersed in a 4*N* solution of sodium hydroxide. Note the color of the gases and of the residue.[4] Write the equation for the decomposition.[5] The formation of nitrous oxide (N_2O) by the thermal decomposition of ammonium nitrate is studied in part (E).

3. The Brown Ring Test for a Nitrate. The nitrate ion (NO_3^-) in the presence of a high concentration of sulfuric acid is reduced by ferrous ion (Fe^{++}) to nitric oxide, NO. Excess ferrous ion then forms a brown complex ion, $[Fe(NO)]^{++}$, with the nitric oxide:

$$3Fe^{++} + NO_3^- + 4H_3O^+ \rightarrow 3Fe^{+++} + NO + 6H_2O$$

$$NO + Fe^{++} \rightarrow \underset{\text{brown}}{[Fe(NO)]^{++}}$$

The nitrites also give the same reaction. A method for distinguishing a nitrate from a nitrite is given in parts (D) and (G).

To 3 ml. of 1*N* ferrous sulfate solution, add a small crystal of a nitrate, or a few drops

of 4*N* nitric acid, or several drops of a solution of any nitrate. Mix thoroughly, incline the test tube, and then carefully pour 36*N* sulfuric acid down the side of the tube. The density of the sulfuric acid is greater than that of the solution, and thus the acid forms a layer below the ferrous sulfate-nitrate mixture. What appears at the boundary between the two layers? [6] Give two reasons why ferric salts cannot be used in place of ferrous salts for the above test.[7]

(D) Nitrous Acid. 1. Preparation from a Nitrite. In part (C) it was shown that sodium nitrite and oxygen resulted from the thermal decomposition of sodium nitrate. Conversion of a nitrate to a nitrite is aided by the addition of lead. The metal is changed to lead monoxide during the decomposition.

Fuse about 1 g. of sodium nitrate in a crucible, and then add about 1 g. of lead. Continue to heat as strongly as possible for 4 or 5 min. Describe the change in the appearance of the lead.[1] Why is less oxygen evolved in the presence of lead than when the nitrate is heated alone? [2] Write the equation for the reaction.[3]

Cool the crucible and add from 5 to 10 ml. of water. Break up the residue with a stirring rod and then filter the solution to remove the lead monoxide. Add 3 ml. of 4*N* hydrochloric acid to the cold solution. Test with litmus to make certain that the solution is acid. Note the slow evolution of a gas. What is this gas? [4] Write the equation for the decomposition of nitrous acid.[5] Reserve the solution for use in the reactions described below.

Look up the ionization constant of nitrous acid and compare it with that of acetic acid [Exp. XXXV, part (D) or Text].[6] Is nitrous acid a weak or a strong acid? [7]

2. Reducing Action. Dilute 2 drops of a 0.1*M* solution of potassium permanganate until it is light-purple in color. Add 1 ml. of 4*N* sulfuric acid to acidify the solution. Now add the solution of nitrous acid drop by drop from a medicine dropper until the color of the permanganate is just discharged. Write the equation for this reaction.[8] How could this reaction be employed to determine the concentration of the nitrous acid in the solution? [9]

3. Oxidizing Action. Add 2 drops of 0.1*N* potassium iodide solution to 5 ml. of water, acidify the solution with 2 drops of 4*N* sulfuric acid, and then add 2 drops of the nitrous acid solution. What change occurs? [10] Add 2 ml. of carbon tetrachloride and then shake the tube. What product of the reaction is shown to be present? [11] Write the equation for the reaction.[12]

4. Tests for a Nitrite. Obtain about 0.2 g. of sodium nitrite crystals. Add to them 4*N* hydrochloric or sulfuric acid. Describe the result and write an equation for the reaction.[13]

Repeat the brown ring test described in part (D), but use a nitrite in place of a nitrate. Describe the result.[14]

Ferrous ion does not reduce a nitrate to nitric oxide in the presence of acetic acid whereas a nitrite is reduced. To 3 ml. of 1*N* ferrous sulfate solution in each of two test tubes add 1 ml. of 4*N* acetic acid. Add 2 drops of a nitrate solution to one of the test tubes and 2 drops of a nitrite solution to the other. Describe the results.[15] Boil the solution obtained with the nitrite. What change in color is observed? Make a statement regarding the stability of the complex ion $[Fe(NO)]^{++}$.[16]

(E) Nitrous Oxide (N_2O). Equip a 20-cm. (8-in.) test tube with a one-holed stopper carrying a delivery tube which extends into a pneumatic trough. Place 6 g. of ammonium nitrate in the test tube and clamp it to a ring stand at an angle of about 30 degrees. Fill the trough with water (warm water if it is available). Heat the test tube gently and steadily with a small flame so that the gas comes over slowly (not faster than one bubble per second). **(DANGER!** Do not become impatient and heat the test tube too rapidly because this may cause an explosion. Do not overheat the test tube near the top of the molten ammonium nitrate.) Discontinue the heating and remove the delivery tube before two thirds of the ammonium nitrate has been decomposed. If more gas is needed, cool the test tube, clean and dry it, and then recharge it with more ammonium nitrate.

After the decomposition has proceeded 2 or 3 min. (the time required to displace the air from the generator and delivery tube) collect one wide-mouthed bottle, preferably a 4-oz. bottle, and two test tubes of the gas. As soon as a test tube is filled, transfer it upside down to a 400-ml. beaker of water in order to prevent it from turning over in the pneumatic trough. If an extra ring stand and clamps are available, the test tubes may be clamped in a vertical position in the pneumatic trough. Remove the delivery tube from the water and discontinue the heating.

Thrust a lighted splint into one test tube of nitrous oxide, and some red phosphorus (burning in a deflagration spoon) into the bottle. Describe the result.[1] What other gas supports combustion in this manner?[2] Nitrous oxide may be distinguished from oxygen by the reaction of the latter with nitric oxide [part (F)]. Reserve the remaining test tube of nitrous oxide for this test.

Examine the upper part of the test tube in which the ammonium nitrate was decomposed. What two products are obtained from the thermal decomposition of ammonium nitrate? Equation?[3] Why was it suggested that warm water be used in the pneumatic trough?[4] Look up the solubility of nitrous oxide in water and make a statement regarding the influence of increased temperature on the solubility of gases in water.[5]

(F) Nitric Oxide (NO). Place about 4 g. of copper in a 20-cm. test tube clamped to a ring stand. Fit the tube with a one-holed rubber stopper and a delivery tube arranged to collect a gas over water in a pneumatic trough. Add 12 ml. of 4*N* nitric acid to the test tube, and then fit the stopper and delivery tube in place. Note the color of the gases in the test tube at the beginning of the reaction and again after the air has been displaced from the tube.[1] Allow the gases to pass through a test tube containing 1*N* ferrous sulfate. Explain the result.[2] What change occurs when the solution is heated?[3]

Completely fill one bottle with the gas; fill another bottle only half full; and then fill two test tubes with the gas. Thrust a glowing splinter into one of the test tubes, and red phosphorus which is burning in a deflagration spoon into the completely filled bottle. Compare the results with those obtained in part (E) for nitrous oxide.[4]

Set up an oxygen generator as illustrated in Fig. 93, or arrange to generate oxygen by heating potassium chlorate with a small quantity of manganese dioxide (Exp. XI). In order to generate oxygen from the sodium peroxide, squeeze the medicine dropper and allow a single drop of water to fall onto the solid. Repeat whenever the flow of oxygen decreases.

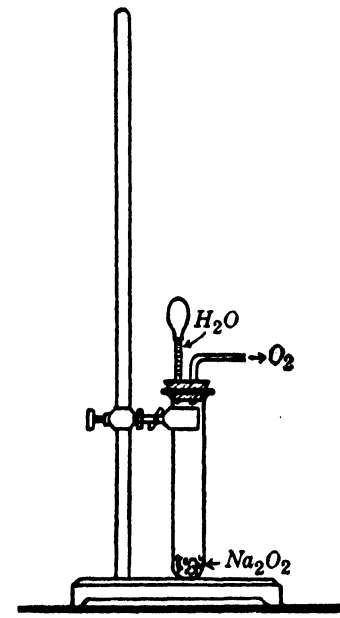


FIG. 93. Preparation of oxygen from sodium peroxide

Mark the level of the water in the bottle that is only partly filled with nitric oxide. Pass in oxygen until the gases in the bottle turn brown. Equation.[5] Remove the delivery tube and swirl the bottle while its mouth is under water. What happens to the brown gas? Equation.[6] Now pass in more oxygen until the gas is again brown. Remove the delivery tube and swirl the bottle. Repeat this process several times. Explain the change in the volume of gas.[7]

Place the test tube of nitrous oxide used in part (E) mouth to mouth with the remaining test tube of nitric oxide. Is there visible evidence of a reaction? Explain.[8] Now open the test tubes to the air. What color change occurs?[9] How could it be determined whether a gas that supports the combustion of a wooden splint is oxygen or nitrous oxide?[10]

(G) Nitrogen Dioxide (NO_2). Fit a test tube with a one-holed stopper and a delivery tube arranged so that a gas may pass through 5 ml. of 1*N* sodium hydroxide (prepared from the 4*N* reagent) contained in a second test tube. Place a piece (0.1 to 0.2 g.) of copper and 3 ml. of 16*N* nitric acid in the first tube, quickly insert the stopper with the delivery tube, and allow the evolved gas to pass through the solution of the base. Note the color of the gas and write an equation for the reaction by which it is formed.[1] When the copper has completely dissolved, remove the stopper from the test tube, and thrust a lighted splinter into the gas remaining in the tube. Result?[2] Compare the oxygen content of the three oxides (N_2O, NO, and NO_2) with their ability to support combustion.[3]

Test the sodium hydroxide solution for the nitrite ion by making 1 ml. of it acid to litmus by the dropwise addition of 4*N* acetic acid, and adding the acidified solution to 2 ml. of 1*N* $FeSO_4$. Result?[4] The appearance of a brown color indicates the presence of a nitrite in the original solution.

In order to determine whether the nitrate ion is also present, the nitrite ion must be removed or destroyed. Neutralize 3 ml. of the solution with dilute sulfuric acid. Add 0.5 g. of ammonium chloride and heat the solution in a beaker of boiling water about 15 min. Note the formation of bubbles of a gas. Write the equation for the reaction by which the gas is formed.[5] Cool the solution and test 1 ml. of it for a nitrite.[6] If the result of the test is negative, add 1 drop of 4*N* sulfuric acid to the remaining 2 ml. of solution. Now add 2 drops of this solution to 3 ml. of 1*N* ferrous sulfate and *slowly* pour the mixture onto 3 ml. of 36*N* sulfuric acid contained in a test tube. Incline the latter tube toward the horizontal during the addition of the ferrous sulfate-nitrate mixture. Result?[7] This is the "brown ring test" for a nitrate.

Recall the equilibrium existing between nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4). (See Exp. XXXII.) Write the equation for this equilibrium and explain the effect of increased temperature (Text).[8]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX

OXYGEN COMPOUNDS OF NITROGEN

(A) Preparation of Nitric Acid. *By the action of a nonvolatile acid on a nitrate*

1.

2.

3.

4.

By the interaction of solutions of selected nitrates and acids

5.

6.

7.

By the interaction of nitrogen dioxide with water

8.

(B) Chemical Properties of Nitric Acid. *Activity as an acid*

1.

2.

Oxidation of an active metal

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX (Cont'd)

(B) Cont'd

4.

5.

Oxidation of inactive metals

6.

7.

8.

9.

Oxidation of nonmetals

10.

11.

12.

Action on compounds

13.

14.

15.

(C) Nitrates. *Preparation*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX (Cont'd)

(C) Cont'd

Thermal decomposition

2.

3.

4.

5.

The brown ring test for a nitrate

6.

7.

(D) Nitrous Acid. *Preparation from a nitrite*

1.

2.

3.

4.

5.

6.

7.

Reducing action

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX (Cont'd)

(D) Cont'd

9.

Oxidizing action

10.

11.

12.

Tests for a nitrite

13.

14.

15.

16.

(E) Nitrous Oxide

1.

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX (Cont'd)

(F) Nitric Oxide

1.

2.

3.

4.

5.

6.

7.

8.

9.

10.

(G) Nitrogen Dioxide

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XXXIX (Cont'd)

(G) Cont'd

5.

6.

7.

8.

Experiment XL

PHOSPHORUS AND ITS COMPOUNDS

Discussion. Nitrogen, phosphorus, arsenic, antimony, and bismuth, all in Group V of the periodic system, form compounds in which these elements may have oxidation states varying from -3 to $+5$. This is in agreement with the presence of five valence electrons in the outer electronic shell of their atoms. Nitrogen and phosphorus are nonmetallic in their properties while the heavier elements are increasingly metallic in character.

While there is a similarity between the properties of the compounds of nitrogen and phosphorus, there are also marked differences. Gaseous nitrogen is rather inactive at ordinary temperatures whereas phosphorus (white) is very active. Nitric acid (HNO_3) is an oxidizing agent; metaphosphoric acid (HPO_3) is not. Ammonia (NH_3) is stable and reacts with water to give a basic solution. The corresponding compound of phosphorus (PH_3) is less stable than ammonia, burns readily in air, and does not react with water. However, phosphine does form phosphonium iodide (PH_4I) corresponding in formula to ammonium iodide (NH_4I).

In this experiment the preparation and properties of the compounds of phosphorus are studied and a comparison is made with the corresponding compounds of nitrogen whenever this is possible.

(A) Allotropic Modifications of Phosphorus. Seal one end of a 20-cm. length of 6-mm. glass tubing. Place in it a small quantity of red phosphorus (0.05 g., or a volume not larger than that of the head of a match). Heat the tube and note whether or not the red phosphorus melts.[1] Note the color of the phosphorus condensed in the cooler part of the tube.[2] While the tube is cooling, test the solubility of red phosphorus in carbon disulfide.[3] Use a *small quantity* of the phosphorus (less than 0.05 g.) and about 1 ml. of carbon disulfide.

Warm the 6-mm. tube gently where the white phosphorus has condensed. Compare the relative melting points of red and white phosphorus.[4] Cool the tube again and add to it 0.5 ml. of carbon disulfide. (**DANGER!** Do not add the carbon disulfide before the tube has cooled. Put out all flames near the carbon disulfide. Do not allow the carbon disulfide solution of phosphorus to touch the hands because the white phosphorus will cause severe burns. Discard excess carbon disulfide solution in the sink and NOT in the waste jars.) Does the white phosphorus dissolve readily in carbon disulfide?[5] Place a filter paper on a wire gauze, or on the base of the ring stand, and then pour the carbon disulfide solution onto the paper. What takes place after the carbon disulfide has evaporated?[6]

(B) Chemical Properties of Phosphorus. White phosphorus is much more reactive than the red modification, but both varieties undergo the same reactions. What evidence was obtained in part (A) for the difference in the reactivity of the two forms?[1]

1. Oxidation by Nitric Acid. Place 0.1 g. of red phosphorus in a test tube equipped with a one-holed rubber stopper and a delivery tube whose lower end is immersed in $4N$ sodium hydroxide solution. Add 3 ml. of $16N$ nitric acid to the phosphorus, clamp the test tube to a ring stand, and then boil the solution gently until brown fumes cease to bubble through the sodium hydroxide solution. What are the brown fumes?[2] Reserve the solution for use in part (D).

2. Reaction with Oxygen. Place about 0.05 g. of red phosphorus in a crucible. Stand the crucible in an evaporating dish and then light the phosphorus with a burning splint.

Cover the crucible at once with a 250-ml. beaker (or a funnel with its stem closed by means of a rubber tube and a clamp). What substance is deposited on the walls of the beaker? [3] Write the equation for the reaction.[4] Allow the beaker to remain in place until the cloud of solid particles has settled. Do not remove the beaker before beginning the experimental work in part (C).

(C) Oxides of Phosphorus. Three oxides of phosphorus are known: P_2O_5, P_2O_4 and P_2O_3. Name these oxides.[1] The first and the last oxides listed are studied in this experiment. Phosphorus pentoxide was the principal product obtained in part (B). How is phosphorus trioxide prepared? (Text) [2]

1. Reaction with Water. Remove the beaker from the evaporating dish (part B) and note the change in appearance of the solid deposited on the walls of the beaker. Explain.[3] Suggest a reason for the high degree of efficiency shown by phosphorus pentoxide as a drying agent (Exp. XXII).[4]

Remove the crucible from the evaporating dish and add 20 ml. of water to the latter. Manipulate the evaporating dish so that the water comes into contact with all of the inside surface. Pour the water into the beaker and repeat the procedure. Use the solution in part (D). Write the equation for the reaction of phosphorus pentoxide and of phosphorus trioxide with water.[5]

(D) Rate of Conversion of Metaphosphoric Acid (HPO_3) to Orthophosphoric Acid (H_3PO_4). Metaphosphoric acid is formed when phosphorus pentoxide is added to water. This acid reacts slowly with water to form orthophosphoric acid. It is desired to measure the rate at which this conversion takes place. The quantity of orthophosphoric acid (H_3PO_4) present at a given time is determined by adding a few drops of the solution to ammonium molybdate reagent. A yellow precipitate of ammonium phosphomolybdate, $[(NH_4)_3PO_4 \cdot 12MoO_3]$, is formed. Metaphosphoric acid does not form a precipitate with this reagent.

Divide the 20 ml. of the solution [reserved from part (C)] between two test tubes. To one of the tubes add 3 ml. of 16*N* nitric acid. Test for the amount of orthophosphate ion present in each test tube by adding 5 drops (use a medicine dropper) of the solution to 3 ml. of the ammonium molybdate reagent and noting the amount of precipitate formed. Place the two test tubes in a beaker containing boiling water. Repeat the test after the solutions have been heated for 5 min., 10 min., and 15 min. Record the results on the form provided on the report sheet.[1] Does nitric acid increase or decrease the rate of conversion of metaphosphoric acid to orthophosphoric acid? [2]

(E) Orthophosphoric Acid. 1. From Phosphates. To about 0.5 g. of tricalcium phosphate, phosphate rock, or bone ash, add 2 ml. of water and 3 ml. of 36*N* sulfuric acid. Heat the mixture about 5 min. Allow it to cool, and then add 10 ml. of water slowly. Stir the mixture constantly. Filter the solution. Neutralize the filtrate with 15*N* ammonia and then acidify it with 4*N* nitric acid. Add 1 ml. of the solution to 3 ml. of ammonium molybdate reagent and warm the mixture to about 60°. Result? [1]

2. From Phosphorus. Test the product obtained from the interaction of concentrated nitric acid and red phosphorus [part (B)] for the presence of the orthophosphate ion with ammonium molybdate reagent. Result? [2] Write the equation for the oxidation of red phosphorus by nitric acid.[3]

3. From Phosphorus Pentachloride. Write the equation for the reaction of phosphorus pentachloride (PCl_5) with water.[4] Carry out the following reaction under the hoods only. Obtain 0.1 g. of phosphorus pentachloride and add it to 5 ml. of water. Test the solution with litmus paper and with ammonium molybdate solution. Result? [5]

4. Dehydration of Orthophosphoric Acid. Show by a series of reactions, the steps in the progressive dehydration of the phosphoric acids beginning with orthophosphoric acid and ending with phosphorus pentoxide.[6]

(F) Ortho-, Meta-, and Pyrophosphates. 1. Tests. To separate 3-ml. portions of 1*M* disodium hydrogen phosphate (Na_2HPO_4) acidified with 1 ml. of 4*N* acetic acid, add 1 ml. of solutions of the following reagents: 0.1*N* silver nitrate, 0.1*N* zinc acetate, and albumin. Record the results in the designated columns of the form on the report sheet.[1]

Prepare a solution of sodium pyrophosphate by dissolving 0.5 g. of the solid in 25 ml. of water. Repeat the tests described in the preceding paragraph.[1]

Add 2 ml. of 4*N* nitric acid and 25 ml. of water to 0.5 g. of sodium metaphosphate. Shake the mixture 2 or 3 min. and then filter it through a fine (highly retentive) filter paper. Test separate 3-ml. portions of the filtrate with 1 ml. of the reagents listed in the first paragraph of this section. Record the results in the table provided on the report sheet.[1]

Test each of the three different phosphate solutions with magnesia mixture (a solution containing magnesium nitrate, ammonium nitrate, and ammonia) as follows: Add 4*N* ammonia solution to 3 ml. of the phosphate solution until it has a distinct odor of ammonia (about 0.5 ml.). Now add 2 ml. of magnesia mixture. Results? [1]

Add 1 ml. of 4*N* nitric acid to 2 ml. of each of the phosphate solutions. Now add 2 ml. of a solution of the ammonium molybdate reagent. Warm the solutions and note the colors of the precipitates.[1]

Nearly all of the phosphates are soluble in strong acids. Add 1 ml. of 0.1*N* silver nitrate solution to 2 ml. of disodium hydrogen phosphate (Na_2HPO_4). Add 4*N* nitric acid a little at a time until the precipitate dissolves. Now add 4*N* ammonia drop by drop until an excess has been added. Describe and explain the results.[2]

2. Thermal Decomposition of the Phosphates. Heat separately 0.5 g. of each of the following substances in a crucible: NaH_2PO_4, $NaNH_4HPO_4$, Na_2HPO_4, and Na_3PO_4. In each case heat the crucible as strongly as possible 3 min. Test the gases liberated from the second substance with moist red litmus paper.[3] Refer to the table prepared in part (F) 1 and test the product in each case to determine which phosphate results from the thermal decomposition. If the decomposition is not complete, a test will be obtained for both the orthophosphate and the product of the decomposition. Record the results in the spaces provided on the report sheets.[4] Write an equation for the thermal decomposition of each of the phosphates.[5]

3. Hydrolysis of the Orthophosphates. Obtain 5 ml. of 1*M* solutions of the following salts: NaH_2PO_4, Na_2HPO_4 and Na_3PO_4. Name these salts.[6] Test each solution with litmus and determine the pH of the solution by adding 2 drops of a universal indicator and then comparing the color produced with the color of the standards supplied in the laboratory.[7] The reaction that accounts for the basic properties of the third salt listed above is:

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^-$$

Write a similar equation for the second salt listed.[8] Explain why the solution of the first salt listed is acidic rather than basic. Equation? [9]

4. Tests with Phosphate Beads. Prepare a small loop in the end of a platinum wire which has been sealed into the end of a glass tube [Exp. II, part (F)]. Heat the wire red-hot and then touch the loop to a small pile of powdered microcosmic salt ($NaNH_4HPO_4$) on a watch glass. Now heat the loop with the solid adhering to it until a clear bead is formed. Touch the hot bead to a *very small speck* of manganese dioxide. Heat the wire in the upper, outer part of the flame (oxidizing flame) until the bead is transparent and uniformly colored. Too much manganese dioxide causes an opaque or cloudy bead; too little causes the color to be too faint. Note the color of the bead after it has cooled.[10]

Change the flame to a reducing one by closing the air holes until the tip of the flame is slightly yellow. Heat the bead 2 min. in the top edge of the inner blue cone where there is an excess of reducing gas. Cool the bead at the base of the blue cone in the nonburning gases. Now remove the bead and note its color.[10]

Remove the bead by melting it and shaking the wire. Dip the latter into 12*N* hydrochloric acid and then heat the wire in the flame. Repeat the operation until no color is imparted to the nonluminous flame. Now repeat the bead test with compounds of copper, nickel, and cobalt. Record the results in the spaces provided on the report sheet.[10]

(G) Phosphorous Acid. Obtain a few drops of phosphorus trichloride in a stoppered test tube. Take it to the *hood*, open the test tube, and blow across the mouth of the tube.[1] Test the fumes with litmus paper.[2] Now dilute the liquid with 5 ml. of water and test the reaction of the solution with litmus.[3] Which acids are formed by the reaction of phosphorus trichloride with water? [4] Equation? [5]

Transfer the solution to a 50-ml. beaker. Evaporate the solution to about 1 ml. or until it becomes syrupy (*not to dryness*). Add 1 ml. of water and a few drops of 0.1*N* silver nitrate solution. Heat the solution to its boiling point. What is the black precipitate? [6] Equation? [7] Compare this reaction with the action of orthophosphoric acid on a solution of silver nitrate.[8]

(H) Phosphine. Add a small piece (0.1 g.) of calcium phosphide to 10 ml. of water in a beaker placed in the hood. [**CAUTION!** Some of the gas ignites when it comes in contact with the air.] Waft some of the gas past the nose and note the odor.[1] Do not inhale the fumes; they are poisonous. Test the gas with moist red litmus paper. Compare the reaction of phosphine (PH_3) with the reaction of ammonia (NH_3) on moist red litmus paper.[2] Test the solution remaining in the evaporating dish with red litmus paper.[3] Write the equation for the reaction of calcium phosphide with water.[4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XL

PHOSPHORUS AND ITS COMPOUNDS

(A) Allotropic Modifications of Phosphorus

1. **2.**

3.

4.

5.

6.

(B) Chemical Properties of Phosphorus. *Oxidation by nitric acid*

1.

2.

Reaction with oxygen

3.

4.

(C) Oxides of Phosphorus

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XL (Cont'd)

(C) Cont'd

5.

(D) Rate of Conversion of Metaphosphoric Acid to Orthophosphoric Acid

1.

Time of Heating	Relative Amount of Precipitate (without HNO_3)	Relative Amount of Precipitate (with HNO_3)
none		
5 min.		
10 min.		
15 min.		

2.

(E) Orthophosphoric Acid

1.

2.

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XL (Cont'd)

(F) Ortho-, Meta-, and Pyrophosphates. *Tests*

1. Record the color of each precipitate obtained and give its formula (except for albumin).

Reagent	Orthophosphate (Na_2HPO_4)	Pyrophosphate ($Na_4P_2O_7$)	Metaphosphate ($NaPO_3$)
$AgNO_3$			
$Zn(CH_3COO)_2$			
Albumin			
Magnesia mixture			
$(NH_4)_2MoO_4$			

2.

Thermal decomposition of the phosphates

3.

4.

Phosphate	Reagents Used to Test the Product	Results of Tests	Decomposition Product
NaH_2PO_4			
$NaNH_4HPO_4$			
Na_2HPO_4			
Na_3PO_4			

Name (last name first) _____ Desk No. _____ Date _____

Experiment XL (Cont'd)

(F) Cont'd

5.

Hydrolysis of the orthophosphates

6.

7.

Phosphate Solution	Reaction with Litmus	pH
NaH_2PO_4		
Na_2HPO_4		
Na_3PO_4		

8.

9.

Tests with phosphate beads

10.

Compound of	Color of Bead in Oxidizing Flame	Color of Bead in Reducing Flame
Mn		
Cu		
Ni		
Co		

Name (last name first) _____ Desk No. _____ Date _____

Experiment XL (Cont'd)

(G) Phosphorous Acid

1. **2.**

3. **4.**

5.

6.

7.

8.

(H) Phosphine

1.

2.

3.

4.

Experiment XLI

ARSENIC, ANTIMONY, AND BISMUTH

Discussion. The compounds of arsenic, antimony, and bismuth show marked similarities in many of their properties. However, there is a regular variation in the properties of these elements and of their compounds with increasing atomic weight of the element. Arsenic, like phosphorus, is largely nonmetallic in its properties. Antimony is nonmetallic, but its compounds in which the element shows an oxidation state of +3 react similarly to the compounds of the metals; bismuth is chiefly metallic in its behavior.

Many of the reactions studied in this experiment illustrate the similarities as well as the variations in the properties of the compounds of the elements in Group V of the periodic system.

(A) Preparation. Place an intimate mixture of 0.05 g. of arsenic trioxide and an equal weight of wood charcoal in a dry test tube. Cover this mixture with a 0.5-cm. layer of the charcoal. Clamp the test tube to a ring stand and then fit the tube with a one-holed stopper and a delivery tube. Immerse the end of the delivery tube in 5 ml. of a saturated solution of barium hydroxide or calcium hydroxide contained in a test tube. Heat the arsenic trioxide-charcoal mixture and note the formation of a black deposit above the charcoal. Determine whether the black substance melts or sublimes when it is heated.[1] What is this substance?[2] Examine the barium hydroxide solution. A cloudy solution or a precipitate indicates the evolution of carbon dioxide; a clear or a slightly turbid solution indicates the evolution of carbon monoxide. Which gas appears to be formed during the reduction of arsenic trioxide by carbon?[3] Write the equation for the reduction.[4] The barium hydroxide solution also prevents the escape of vapors of arsenic and arsenic trioxide into the laboratory.

Antimony and bismuth, as well as many other less active metals, may be obtained from their oxides in this manner. Write the equations for the reduction of the trioxides of antimony and of bismuth with carbon.[5]

(B) Action with Acids. Obtain small pieces (0.05 g.) of arsenic, antimony, and bismuth. Add to each of these substances in separate test tubes 2 ml. of 16*N* nitric acid. Compare the reaction rates of the elements with cold nitric acid.[1] Heat those test tubes in which the reaction is slow. Now compare the reaction mixtures with respect to the appearance of the undissolved solid, and the presence of a cloudy precipitate in the liquid.[2] What oxide of nitrogen is evolved?[3] The other products of the reactions are arsenic acid, antimony pentoxide, and bismuth nitrate respectively. Write the equations for the reactions of arsenic, antimony, and bismuth with concentrated nitric acid.[4]

Look up the position of arsenic, antimony, and bismuth in the electromotive series and predict the solubility of these elements in hydrochloric acid or in other nonoxidizing acids.[5]

(C) Reactions of the Oxides. Place about 0.05 g. of arsenic trioxide, antimony trioxide, and bismuth trioxide in separate test tubes. Add 1 ml. of water to each, and then determine the volume of 12*N* hydrochloric acid required to dissolve each oxide.[1] In the same way determine the volume of 4*N* sodium hydroxide required to dissolve 0.05 g. of each oxide. Designate the oxide as "not dissolved" if solid remains after the addition of 10 ml. of the reagent.[1] On the basis of the generalization that, in a given group in the periodic system, the oxides of the metallic elements dissolve more readily in acids than do the oxides of the nonmetallic elements, which of the three elements, arsenic, antimony, or bismuth, appears

to be most metallic in character? [2] On the other hand, the oxides of the nonmetallic elements are readily soluble in solutions of strong bases. Which of the three elements is found to be most nonmetallic in character? [3] Write the equations for the reactions of the oxides with hydrochloric acid and with sodium hydroxide.[4]

Add 0.05 g. of arsenic trioxide and the same weight of arsenic pentoxide to 10 ml. of water in separate test tubes. Heat the solutions until they begin to boil. Which of the two oxides is more soluble in water? [5] Cool the solutions and test them with litmus paper and with the universal indicator.[5] Which of the oxides forms the more strongly acidic solution? [6] Write equations for the reaction of arsenic trioxide and of arsenic pentoxide with water. [7]

(D) Hydrolysis of the Chlorides. Add 1 ml. of 0.1*N* solutions of arsenic trichloride, antimony trichloride, and bismuth trichloride to separate 10-ml. portions of water. Shake the solutions. In which ones are precipitates formed? Equations.[1] Divide each solution in which a precipitate is formed into three equal volumes. To one portion add 4*N* hydrochloric acid; to another add 4*N* sodium hydroxide; and to the third add a 1*M* solution of sodium potassium tartrate. Record the results in the table provided on the report sheet.[2] Repeat the tests with the remaining solution.[2] Outline a procedure which may be used to determine whether a solution contains arsenic trichloride, antimony trichloride, or bismuth trichloride.[3]

Add a few drops of 0.1*N* bismuth nitrate solution to 10 ml. of water. Shake the mixture. Result? Write an equation to express the formation of the observed product.[4] What use is made of the insoluble compound formed in this reaction? (Text) [5]

(E) Precipitation and Reactions of the Sulfides. Add 2 ml. of 4*N* hydrochloric acid to 3-ml. portions of 0.1*N* solutions of each of the following substances: sodium arsenite, antimony trichloride, and bismuth nitrate. Now pass hydrogen sulfide into the solutions. Describe each precipitate,[1] and write an equation to show how it is formed.[2]

Filter the solution containing the arsenic sulfide. Wash the precipitate with distilled water and then punch a hole in the bottom of the filter paper. Now wash the precipitate into a test tube by means of a stream of water from the jet of the wash bottle. Use as small a volume of water as possible. Pour part of the suspension into another test tube. To one part add 12*N* hydrochloric acid; to the other add 0.1*N* ammonium sulfide solution. If the precipitate dissolves in ammonium sulfide, add a few milliliters of 4*N* hydrochloric acid to the solution. Record all the results in the table provided on the report sheet.[1] Repeat the tests described in this paragraph with the solutions containing the precipitates of antimony trisulfide and bismuth trisulfide.[1] How does the sulfide of bismuth behave differently from the sulfides of arsenic and antimony? [3] Write equations for all of the reactions involved in the tests carried out in this paragraph.[4]

Add 0.05 g. of arsenic trioxide to 12 ml. of water and heat the water until it begins to boil. Cool the mixture, filter it, and then pass hydrogen sulfide into the filtrate. Observe the color of the solution.[5] Compare this result with that obtained when hydrogen sulfide is passed into an acidified 0.1*N* solution of sodium arsenite or arsenic trichloride.[6] Test separately the action of 1-ml. portions of 4*N* hydrochloric acid, 4*N* acetic acid, 1*N* sodium chloride, and about 0.1 g. of sugar on 3-ml. portions of the colloidal solution of arsenic trisulfide. Results? [7] Are electrolytes or nonelectrolytes the more effective in causing the coagulation of colloidal arsenic trisulfide? [8]

Pass hydrogen sulfide into a 0.1*M* solution of disodium hydrogen arsenate. Does a precipitate form? [9] Add 12*N* hydrochloric acid and continue to pass hydrogen sulfide through the solution. Describe any change that occurs.[10] Now boil the solution and again pass in hydrogen sulfide. Result? [11]

(F) Tests. 1. Arsenites and Arsenates. Add 1 ml. of 0.1*N* silver nitrate solution to 3 ml. of a 0.1*M* solution of sodium arsenite and to 3 ml. of a 0.1*M* solution of disodium hy-

drogen arsenate. Describe the precipitates. Equations? [1] Test the solubility of the precipitates in 4*N* nitric acid and in 4*N* ammonia.[2]

Add 1 ml. of magnesia mixture to 3-ml. portions of solutions of 0.1*M* sodium arsenite and 0.1*M* disodium hydrogen arsenate in turn. Results? [3] Filter off the precipitate and then pour onto it 1 ml. of a 0.1*N* solution of silver nitrate. What evidence is there for a chemical change? [4] The reaction with silver nitrate occurs because the silver salt (Ag_3AsO_4) is less soluble than magnesium ammonium arsenate ($MgNH_4AsO_4$). Write the equations for the reactions that occur in this test.[5]

Add 1 ml. of 4*N* nitric acid to 2 ml. of 0.1*M* disodium hydrogen arsenate solution and to 2 ml. of 0.1*M* sodium arsenite solution. To each solution add 5 ml. of a solution of the ammonium molybdate reagent. Results? [6]

Compare the reactions of the arsenates with those of the orthophosphates.[7] Take advantage of the insolubility of arsenic sulfide in devising a procedure designed to accomplish the separation of an arsenate from a phosphate.[8]

2. The Marsh Test for Arsenic. Set up a hydrogen generator (Exp. XVIII, Fig. 58). Place about 10 g. of zinc in the 250-ml. bottle. Add 4*N* sulfuric acid through the thistle tube until the lower end of the tube is covered. After a brisk evolution of hydrogen has proceeded for 2 or 3 min., wrap a towel around the bottle, collect a test tube full of the gas, light the gas in the test tube, and, if it burns quietly, light the jet of hydrogen. (**DANGER!** This procedure must be carried out exactly as described on p. 149 and illustrated in Fig. 60.) What is the color of the hydrogen flame? [9]

Now add through the thistle tube about 1 ml. of 0.1*M* sodium arsenite solution or a solution of any other arsenic compound. Note the change in the color of the flame.[10] Hold a cold porcelain evaporating dish or a crucible cover *in* the hydrogen flame. Result? [11] Add 1 drop of 5 per cent sodium hypochlorite solution to the dark spot. Result? [12] Write the equations for the reactions occurring in this test.[13]

Antimony compounds behave in the same manner except that the black deposit (metallic antimony) is not dissolved by sodium hypochlorite solution. If both arsenic and antimony are present, the hydrogen is generated in an alkaline solution from zinc and sodium hydroxide solution. Antimony compounds are not reduced to stibine under these conditions whereas arsenic compounds are reduced to arsine.

3. The Gutzeit Test for Arsenic. Place about 1 g. of zinc in a test tube and add to it about 5 ml. of 4*N* sulfuric acid. Insert a loose plug of cotton in the upper part of the test tube. Cover a cork with a piece of filter paper, moisten the latter with 0.1*N* silver nitrate solution, and place it loosely in the mouth of the test tube. If the filter paper does not turn black within 2 min., the reagents are free from arsenic.

Now remove the cork and the cotton and add 0.5 ml. of 0.1*N* sodium arsenite solution to the test tube. Replace the cotton and the filter paper. Note the change in the color of the filter paper. Explain.[14] Write the equation for the reaction.[15]

Phosphine and stibine also stain the paper and therefore interfere with the test. Mercuric chloride is sometimes used in place of silver nitrate. Arsine gives a yellow or reddish-brown stain with mercuric chloride.

4. A Test for Antimony. Add about 3 cm. of aluminum wire or about 0.2 g. of aluminum turnings to 1 ml. of 0.1*N* antimony trichloride solution. Add 3 ml. of 4*N* hydrochloric acid, boil the solution, and note the change in the color of the metal.[16] When no further reaction occurs (about 3 min.) filter the solution and pour over the residue 3 ml. of a 1*N* solution of tartaric acid containing about 1 ml. of 4*N* nitric acid. Pour the same solution through the filter paper several times. Finally dilute the solution with 10 ml. of water and pass hydrogen sulfide into it. What is the color of the precipitate? [17] This test identifies antimony in the presence of arsenic. Arsenic is not dissolved by the nitric acid solution of tartaric acid.

In the absence of arsenic, antimony is also identified by means of either the Marsh test or the Gutzeit test.

5. A Test for Bismuth. Add 4*N* ammonia to a 0.1*N* solution of bismuth nitrate until an excess is present. Filter the solution and pour over the residue a freshly prepared solution of sodium stannite. Prepare the latter as follows: Add 4*N* sodium hydroxide drop by drop to 1 ml. of 0.1*N* stannous chloride solution until the precipitate which first forms redissolves. Test the sodium stannite solution to make certain that it is alkaline.

Describe the effect of sodium stannite on bismuth hydroxide.[18] Write an equation for the reaction.[19]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI

ARSENIC, ANTIMONY, AND BISMUTH

(A) Preparation

1. **2.**

3.

4.

5.

(B) Action with Acids

1.

2.

3.

4.

5.

(C) Reactions of the Oxides

1.

Oxide	Volume of HCl	Volume of NaOH
As_2O_3		
Sb_2O_3		
Bi_2O_3		

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI (Cont'd)

(C) Cont'd

2.

3.

4.

5.

Oxide	Relative Solubility	Litmus	pH
As_2O_3			
As_2O_5			

6.

7.

(D) Hydrolysis of the Chlorides

1.

2.

Solution	Precipitate	HCl	NaOH	$KNa(C_4H_4O_6)$
$AsCl_3$				
$SbCl_3$				
$BiCl_3$				

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI (Cont'd)

(D) Cont'd

3.

4.

5.

(E) Precipitation and Reactions of the Sulfides

1.

	Arsenic ($NaAsO_2$)	Antimony ($SbCl_3$)	Bismuth [$Bi(NO_3)_3$]
H_2S			
Conc. HCl + sulfides			
$(NH_4)_2S$ + sulfides			
$(NH_4)_2S$ solution + HCl			

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI (Cont'd)

(E) Cont'd

4.

5.

6.

7.

8.

9.

10.

11.

(F) Tests. *Arsenites and arsenates*

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI (Cont'd)

(F) Cont'd

5.

6.

7.

8.

The Marsh test for arsenic

9.

10.

11.

12.

13.

The Gutzeit test for arsenic

14.

15.

A test for antimony

16.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLI (Cont'd)

(F) Cont'd

17.

A test for bismuth

18.

19.

Experiment XLII

CARBON

Discussion. Carbon, which stands at the head of Group IV in the periodic table, is characteristically nonmetallic. The element does not form simple ions inasmuch as all of its binary compounds such as carbon disulfide (CS_2), methane (CH_4), and carbon tetrachloride (CCl_4), are covalent in character. In ionic compounds carbon usually appears as a constituent of anions such as $CO_3^{=}$, HCO_3^{-}, and $[Fe(CN)_6]^{\equiv}$. Thus, in all but a few of its compounds, carbon *shares* its four electrons with other atoms.

Carbon is unique in that it possesses a remarkable ability to share pairs of electrons with other carbon atoms. Compounds are known in which as many as sixty carbon atoms are directly linked to each other to form long chains. Other systems include rings or combinations of rings and open chains. The study of substances of these types constitutes a major division of chemistry called *Organic Chemistry*.

Elementary carbon is very inert at ordinary temperatures. However, it becomes active at high temperatures and reacts with certain metals (at *very* high temperatures) to form carbides and with sulfur to yield carbon disulfide. Carbon burns in oxygen and in air to form a monoxide or a dioxide (depending upon the amount of oxygen present), and reduces a number of metallic oxides to the free metals. The covalence of carbon in its compounds is 4, except in carbon monoxide in which it is 2.

(A) Forms of Carbon. 1. Graphite. Obtain about 0.2 g. of flake graphite. Note its lustrous appearance. Determine its feel by rubbing a small amount between the fingers.[1] Test its density relative to that of water by placing a small quantity in a test tube containing 5 ml. of water. Shake the tube before reaching a conclusion.[2]

Spread about 0.1 g. of graphite in a very thin layer over the bottom of a porcelain crucible. Now heat the latter 5 min. at the highest temperature obtainable with the burner flame. What can be said about the ease with which graphite is oxidized in the air? [3] Boil a small amount of graphite with 1 ml. of concentrated nitric acid 1 min. Are considerable quantities of nitrogen dioxide evolved? What does the result indicate regarding the ability of the acid to oxidize graphite? [4]

Refer to the text for the melting point of graphite (carbon), and then cite those properties of this form of carbon which make it useful as a lubricant and as a material for making crucibles in which metals may be melted.[5]

2. Charcoal from Sugar. Gently heat 0.1 g. of sugar (do *not* use a larger amount) spread evenly over the bottom of a porcelain crucible. Use a small flame, and heat the sugar very slowly. Record the series of changes that take place.[6] Examine the residue as soon as bubbles cease to be evolved. Feel the product to determine whether or not it is graphite. What is the substance? [7] Now heat the crucible with its contents as strongly as possible. What evidence is there for a chemical change? [8] Write an equation for the reaction.[9] Compare the behavior of charcoal and graphite with regard to their relative ease of oxidation in the air.[10] Continue to heat the crucible until all of the carbon has been burned. Does an ash remain? What does this show regarding the purity of the charcoal prepared from sugar? [11]

3. Charcoal from Wood. Clamp a test tube on a ring stand so that the tube is inclined slightly from a horizontal position. The bottom of the tube should be only a little below the level of its mouth. Fit the tube with a one-holed stopper and a delivery tube which

reaches down into the bottom of another test tube so as to hold the latter in an upright position in a 400-ml. beaker filled with cold water.

Break up a thin wooden splint into about four 2-cm. lengths and place them in the test tube which is held by the clamp on the ring stand. The clamp must hold the test tube as near the mouth as possible because the tube is to be heated about one half of its length. Replace the stopper with its delivery tube and then heat the test tube strongly from the bottom up toward the top by moving the burner flame back and forth. What is the first evidence of the decomposition being brought about by this destructive distillation of the wood? [12] Vaporize tarry liquids by heating the droplets as soon as they condense in the upper portion of the tube. Continue the heating until all volatile products have been driven off from the wood.

Examine the small amount of liquid distillate. Note its odor, and then add to it 5 ml. of water. Test the solution with litmus paper. What substance formed in the decomposition of wood is responsible for the action on the litmus? (Text) [13] Consult the text and then list the other products of the distillation.[14]

Shake the remaining pieces of wood charcoal out of the test tube which has been used as a still,* and place them in a porcelain crucible. Heat the crucible until all of the charcoal has burned. What remains in the crucible? [15] Does its presence mean a higher or a lower degree of purity for the wood charcoal as compared with the charcoal made from sugar? Explain.[16]

4. Charcoal as an Adsorbent. Heat 1 g. of animal charcoal strongly in a *covered* crucible until the bottom of the crucible becomes red-hot. This process drives adsorbed gases and volatile liquids out of the charcoal, and thus serves to *activate* the substance. Continue the heating about a minute and then allow the charcoal to cool in the *covered* crucible for 10 min. Why must the cover be kept on the crucible throughout the activation and the cooling? [17]

Place about 0.1 g. of the charcoal in a test tube and add to it 5 ml. of iodine water. Shake the tube several minutes and then filter the liquid. Allow all of it to drain through even although the filtrate may contain suspended carbon. If this is the case, pour the suspension through the same filter and catch the filtrate in a clean test tube. What is the color of the clear filtrate? What does this indicate? [18] Test this point by adding 2 drops of starch solution to the liquid. Result? [19] What has become of the iodine? [20] How could it be recovered? [21]

Dilute several drops of 0.1*M* sodium thiosulfate solution to 5 ml., and then add the same number of drops of 4*N* sulfuric acid. Warm the solution to hasten the precipitation of sulfur. Filter the milky suspension. Result? [22] Filter again through the same paper. Why is the sulfur not retained by the filter paper? [23] Now add 0.1 g. of the activated charcoal to the milky suspension, shake it 1 min. and then filter it. If the filtrate is not clear, pour it through the same paper once more. Result? [24]

Other forms of charcoal, such as that prepared from wood, are also active adsorbents. What part does charcoal play in the refining of sugar? (Text) [25] Liquids and gases are also adsorbed by various kinds of charcoal. What is the purpose of the charcoal in the canister of the gas mask? [26]

5. Charcoal as a Reducing Agent. Place 0.2 g. of powdered cupric oxide (or cupric oxide wire) in a 10-cm. Pyrex test tube, and then add enough of the activated animal charcoal to form a layer about 2 cm. in depth. Mix the oxide and the charcoal by shaking them in the test tube. Now clamp the tube at an angle of about 45 degrees and heat it strongly 5 min. If at any time a layer of the solid begins to rise in the tube, tap the latter sharply to cause the solid to drop back.

Allow the tube to cool to room temperature, and then pour its contents into a 50-ml.

* Do not clean the test tube at this time; reserve it for use in the section on coal and coke.

beaker. Add 30 ml. of water and stir the mixture vigorously. Decant the suspension. Repeat the procedure until practically all of the carbon has been removed in this manner. Describe the heavy residue. What is it? [27] Write an equation to show its formation from its oxide.[28]

6. Lampblack. Hold a porcelain evaporating dish in a luminous gas flame. Note the extremely fine state of division of the deposit. Why does this feature make the substance especially suitable as a pigment in black inks and paints? [29] Point out any similarities between this method of preparation and the commercial process used for making lampblack (Text).[30]

7. Coal and Coke. Use the same test tube in which wood charcoal was prepared as a still for the destructive distillation of several small lumps (about the size of a pea) of bituminous (soft) coal. Carry out this experiment by the same procedure used for wood but place 5 ml. of water in the receiving tube before the coal is heated.

Test the distillate with litmus paper. What substance is responsible for the change in the color of the litmus? [31] What substance remains after the volatile matter has been driven out of bituminous coal? [32] List some of the materials obtainable from the tarry product (Text).[33]

(B) Preparation and Properties of Carbon Dioxide. 1. From Carbon and Carbonaceous Compounds. Recall the direct union of carbon with oxygen to form carbon dioxide (Exp. XIII), and also the products of combustion of any carbonaceous compound in an excess of air or oxygen. Write an equation to show the combustion of ethyl alcohol (C_2H_5OH).[1]

2. By a Biological Process. Blow the breath through a glass tube into 3 ml. of a saturated solution of barium hydroxide ($Ba(OH)_2$) contained in a test tube. Repeat with a saturated solution of calcium hydroxide (limewater). Results? Write equations for the reactions.[2] Suggest a procedure and an apparatus in which the percentage by volume of carbon dioxide in exhaled breath might be determined.[3]

3. By Thermal Decomposition of Carbonates and Bicarbonates. Heat 0.5 g. of anhydrous sodium carbonate in a Pyrex test tube. Incline the tube at an angle of about 45 degrees and then test for carbon dioxide by holding a drop of limewater (on the end of a glass rod) at the mouth of the tube. What does the result show with regard to the stability of sodium carbonate toward heat? [4] [*Note:* do not dip the glass rod into the bottle of limewater on the reagent shelf; obtain several milliliters of the solution in a test tube and then dip the rod into this.] Care must be taken to prevent the drop from falling into the hot test tube. Why? [5] Repeat this test with a marble chip heated to the highest temperature obtainable with the burner flame. A white scum formed on the surface of the drop indicates the presence of carbon dioxide. The drop of limewater should be held at the mouth of the tube at least 3 min. before a conclusion is reached. Make the result of this test the basis of a statement regarding the relative degree of stability of sodium carbonate and calcium carbonate toward heat.[6] What industry uses this reaction to make its product? [7] Write the equation for the reaction.[8] Add 5 ml. of water to the marble which has been heated. Raise the temperature of the water to the boiling point and then test the solution with litmus paper. Result? [9] Write equations to show how the substance in solution was formed.[10]

Heat 0.5 g. of anhydrous sodium bicarbonate ($NaHCO_3$) in a test tube. Test for carbon dioxide with a drop of limewater. Is the result positive or negative? [11] Does this decomposition take place more or less readily than that of marble? [12] Write an equation to express the decomposition.[13] Pure carbon dioxide may be prepared in this way from pure sodium bicarbonate.

4. By the Action of Acids on Carbonates. Test the action of 4*N* sulfuric acid on a 0.1 g. portion of each of the following: sodium carbonate, sodium bicarbonate, barium carbonate,

and magnesium carbonate. Results? Write equations to express the reactions.[14] Characterize carbon dioxide with regard to its odor.[15] Make a general statement covering the action of a carbonate with an acid.[16]

Select two marble chips of about the same size and place one in each of two test tubes. Add 5 ml. of 4*N* hydrochloric acid to one tube, and an equal volume of 4*N* acetic acid to the other. Compare the rates at which the gases are evolved. Explain.[17]

5. Laboratory Preparation. Set up a 250-ml. Erlenmeyer flask with a delivery tube arranged to collect carbon dioxide over water in a pneumatic trough. Place in the flask 10 g. of marble (or any other form of calcium carbonate) and 100 ml. of a solution of hydrochloric acid made by the addition of 20 ml. of the 12*N* acid to 80 ml. of water. Allow 4 or 5 min. to elapse before proceeding with the collection of the gas. Why?[18] Now fill two 250-ml. bottles, one 20-cm. test tube, and one 15-cm. test tube with the gas. If the gas is evolved too slowly near the end of the collection, warm the generator.

6. Reaction with Water. Add about 5 ml. of water to the small test tube, close the mouth of the tube with the thumb, and then shake the tube vigorously. Test the solution with blue litmus paper. Result? Write an equation to show the formation of the substance dissolved in the water.[19] Boil the solution 30 sec., and again test it with litmus paper. Result?[20] What conclusion is reached with regard to the effect of increased temperature on a solution of carbonic acid?[21]

7. Effect on Combustion. Light a wooden splint and then quickly turn the larger tube containing carbon dioxide upside down just above the splint. Do not thrust the splint up into the tube. What conclusions may be reached regarding the ability of the gas to support combustion,[22] and the density of carbon dioxide relative to that of air?[23] *Calculate* the density of carbon dioxide (air = 1).[24]

Thrust a burning, 7-cm. length of magnesium ribbon into one of the bottles filled with carbon dioxide. Describe what takes place.[25] Name the black deposit which has collected on the walls of the bottle and write an equation to show its formation.[26]

Light a small amount (0.05 g.) of red phosphorus in a deflagration spoon and quickly introduce it into the second bottle filled with carbon dioxide. Result?[27] Draw a conclusion regarding the advisability of using carbon dioxide to extinguish a fire.[28]

8. Action with Limewater. Pass a stream of carbon dioxide through limewater 5 min. Describe the changes taking place during this time.[29] Write equations for the reactions.[30] Boil the solution. Result? Equation to express the reaction?[31]

(C) Carbonates. 1. Hydrolysis. Add 2 drops of a universal indicator (Appendix F) to 5 ml. of a 1*M* solution of sodium bicarbonate and to 5 ml. of a 1*M* solution of sodium carbonate. Compare the color of each solution with those of the standards in the laboratory. Estimate the pH of each solution.[1] Calculate the concentration of the hydroxide ion in each solution and then the percentage hydrolysis of each substance [Exp. XXXV, part (E)].[2] Write equations for the hydrolyses.[3] Test the action of each of the solutions on litmus paper. Result?[4]

2. Solubility. Add 1 ml. of a 1*N* solution of ammonium carbonate to 3 ml. of each of the following 0.1*N* solutions: $SrCl_2$, $MnCl_2$, $NiSO_4$, and KCl. Which of the cations in these solutions yield insoluble carbonates?[5] Make a general statement covering the solubility of the carbonates (Text).[6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII

CARBON

(A) Forms of Carbon. *Graphite*

1.

2.

3.

4.

5.

Charcoal from sugar

6.

7. **8.**

9.

10.

11.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII (Cont'd)

(A) Cont'd

Charcoal from wood

12.

13.

14.

15.

16.

Charcoal as an adsorbent

17.

18.

19.

20.

21.

22.

23.

24.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII (Cont'd)

(A) Cont'd

25.

26.

Charcoal as a reducing agent

27.

28.

Lampblack

29.

30.

Coal and coke

31. **32.**

33.

(B) Preparation and Properties of Carbon Dioxide. *From carbon and carbonaceous compounds*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII (Cont'd)

(B) Cont'd

By a biological process

2.

3.

By thermal decomposition of carbonates and bicarbonates

4.

5.

6.

7.

8.

9.

10.

11.

13.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII (Cont'd)

(B) Cont'd

By the action of acids on carbonates

14.

15.

16.

17.

Laboratory preparation

18.

Reaction with water

19.

20.

21.

Effect on combustion

22.

23. **24.**

25.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLII (Cont'd)

(B) Cont'd

26.

27.

28.

Action with limewater

29.

30.

31.

(C) Carbonates. *Hydrolysis*

1. **2.**

3.

4.

Solubility

5.

6.

Experiment XLIII

SELECTED EXPERIMENTS IN ORGANIC CHEMISTRY

This series of exercises studies the methods used to identify the isomeric forms of an alcohol, and gives the experimental procedures employed in the preparation and purification of several organic compounds.

I. The Identification of a Butyl Alcohol *

Discussion. This exercise shows the effect of structure on physical and chemical properties, and how the differences in properties observed for the isomeric forms of a compound may be used in identifying these isomers.

Apparatus and Materials: A 150-ml. distilling flask; 150° thermometer; water-jacketed condenser; melting-point tubes; small chips of porous plate and one unbroken plate; 50 ml. of one of the four butyl alcohols; 5 ml. of 95 per cent ethyl alcohol; 0.3 g. of 3,5-dinitrobenzoic acid; 0.4 g. of phosphorus pentachloride; special zinc-chloride reagent.†

(A) The Boiling Point of Butyl Alcohol. In the chemical literature, the boiling points of the butyl alcohols at 760 mm. are given as follows:

Alcohol	B.P.
n-butyl	117.7°
*iso*butyl	108.4°
sec-butyl	99.5°
tert-butyl	82.8°

Since there are considerable differences between the boiling points of these isomers, a determination of the value for this property should indicate the identity of a fairly pure sample of any one of these alcohols.

Request an order from the laboratory instructor for a 50-ml. sample of a butyl alcohol.‡ Place the sample and several chips of porous plate in a 150-ml. distilling flask, and set up an apparatus similar to that illustrated in Fig. 64. Distill the liquid slowly, and at as steady a rate as possible, into a 100-ml. graduate. Record the temperature at each of the following stages in the distillation: [1]

1. First drop falls into graduate
2. Volume of distillate is 5 ml.
3. " " " " 10 ml.
4. " " " " 15 ml.
5. " " " " 20 ml.
6. Volume of distillate is 25 ml.
7. " " " " 30 ml.
8. " " " " 35 ml.
9. " " " " 40 ml.
10. " " " " 45 ml.

Discontinue the distillation, and plot the data on the sheet of graph paper furnished with the report sheets.[2] Record the boiling-point range of the sample and, using this as the basis, state which butyl alcohol comprises the sample.[3] The value for the boiling point is to be regarded only as supporting evidence inasmuch as tests of a chemical nature must be carried out before the final decision on the identity is reached.

* Adapted from a procedure developed by Dr. W. M. Lauer of the University of Minnesota.

† Prepared in the stockroom by dissolving 136 g. of anhydrous zinc chloride in 88 ml. of 12*N* HCl.

‡ The sample of the unknown is to be obtained at the stockroom.

(B) Identification of a Butyl Alcohol by Its Chemical Properties. 1. Reactions with 12*N* HCl. Saturated monohydric alcohols are classified as primary, secondary, and tertiary. A convenient method of distinguishing between these three classes makes use of the difference in the ease with which the different types of alcohols react with hydrochloric acid. Alcohols containing the grouping—CH_2OH are primary; those with $\rangle CHOH$ are secondary; and those with $-COH$ are designated as tertiary. Write the structural formulas of the butyl alcohols, classify each one as primary, secondary, or tertiary, and name each one according to the Geneva system.[1]

Tertiary alcohols react with cold concentrated (12*N*) hydrochloric acid to form the corresponding chlorides. Since the alkyl chlorides are not appreciably soluble in water, a separate layer appears if the alcohol is converted to the chloride. Thus, a visible change accompanies the conversion.

Secondary alcohols do not react with cold 12*N* hydrochloric acid with sufficient speed to give a visible result in a short time. However, they do react rapidly with a solution containing the 12*N* acid and zinc chloride.

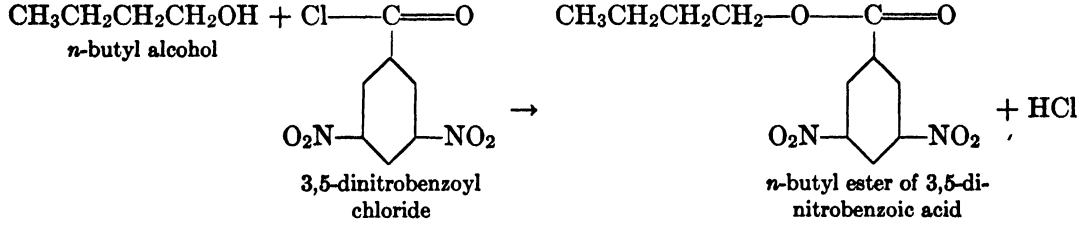
Primary alcohols do not react with either of the two aforementioned reagents to produce a visible result under the same conditions.

A procedure that takes advantage of the above differences is now carried out. Place in a test tube 2 ml. of the distillate obtained in part (A) and 12 ml. of a special hydrochloric acid-zinc chloride reagent (see **Apparatus and Materials**). The clear solution obtained becomes cloudy after a few minutes if the secondary or tertiary alcohol is present; the solution remains clear if the sample is the primary butyl alcohol. Record the result, and state the conclusion reached.[2]

If the above result shows the presence of a secondary or tertiary alcohol, a further test is needed to distinguish between them. Place 2 ml. of the sample in a test tube and add to it 10 ml. of 12*N* HCl. The tertiary alcohol reacts quickly to form the insoluble chloride, which rises to form an upper layer of liquid. The solution of a secondary alcohol remains clear. Give the result and the conclusion on the basis of this test.[3]

2. The Use of Butyl Esters to Identify the Alcohols. The preparation of derivatives of organic compounds and their comparison with the same derivatives of compounds of *known* constitution is an important step in the identification of an organic substance. For this purpose it is customary to prepare solid derivatives, and then to use the convenient melting-point and mixed melting-point determinations as the basis of the identification (Exp. VI).

Solid esters are commonly used to identify alcohols. Such esters are conveniently prepared by the action of an acid chloride on the alcohols. In this case the acid chloride of 3,5-dinitrobenzoic acid is used. The equation for the reaction between *n*-butyl alcohol and the acid chloride is



If the acid chloride is available, it is used in **b** below; if it is not obtainable, it is readily prepared from 3,5-dinitrobenzoic acid according to the directions in **a**.

a. Preparation of 3,5-dinitrobenzoyl chloride. Carry out this preparation *in duplicate* because two separate portions of the acid chloride are required. One of them is used to

prepare an ester from the unknown sample, and the other is needed to esterify an authentic sample which the tests described in parts (A) and (B)1 indicate to be identical with the unknown sample.

Heat gently 0.3 g. of 3,5-dinitrobenzoic acid and 0.4 g. of phosphorus pentachloride in a dry test tube. Move the test tube constantly over a low flame. The mixture liquefies and a vigorous evolution of hydrogen chloride sets in. At this point remove the test tube from the flame. When the evolution of gas ceases, boil the liquid gently 5 sec. Allow the product to cool, whereupon it should solidify. It consists of 3,5-dinitrobenzoyl chloride (m.p. 68°) and a small amount of phosphorus oxychloride (a liquid at ordinary temperatures). The acid chloride should be used at once because it is quickly hydrolyzed by moisture taken up from the air.

b. The esterification of butyl alcohol. Place in a test tube 0.4 g. of 3,5-dinitrobenzoyl chloride obtained from the stockroom, or one of the portions of the acid chloride just prepared, and immediately cover it with 0.5 ml. of the unknown sample. Repeat these operations, but use an authentic sample of the butyl alcohol (stockroom) which the tests carried out in parts (A) and (B)1 indicate is identical with the unknown sample. Now carry out the following procedure with the contents of each tube.

Boil the alcoholic solution of the acid chloride 10 sec. over a low flame. The esterification should be complete at the end of this time. Quickly pour the hot liquid onto a small watch glass, and allow it to solidify until it becomes a pasty mass.

By means of a spatula transfer the solid to a piece of porous clay plate. Use the spatula to rub the pasty solid on the plate until the admixed liquid has been absorbed by the plate. Now scrape the nearly dry solid from the plate, and transfer the substance to a test tube. Add 5 ml. of 95 per cent ethyl alcohol, heat the mixture to the boiling point in order to dissolve the ester, and then quickly filter the hot solution into a test tube through a filter paper which is not more than 9 cm. in diameter. Keep the filtrate near its boiling point by moving the tube in and out of a low flame, and add distilled water drop by drop (use a medicine dropper) until a faint turbidity persists in the hot solution. Now allow the contents of the tube to cool. Shake the tube frequently until crystals begin to appear. Allow the crystallization to continue 15 min., and then filter the mixture through a small filter paper. Remove the paper from the funnel, spread it out on a watch glass, and place it in the desk to dry until the next laboratory period.

c. Conclusive identification of butyl alcohol. Determine the melting point of (1) the ester prepared from the unknown sample,[4] (2) the ester prepared from the authentic sample,[5] (3) a mixture of the two esters.[6] Make these determinations according to the directions given in Exp. VI. Compare the results with the known melting points of the butyl esters of 3,5-dinitrobenzoic acid, and with the melting point of 3,5-dinitrobenzoic acid itself (204–5°). If the product obtained by the procedure followed in **b** is the acid, then the original sample is the tertiary alcohol. This is true because the only solid product of the reaction between *tert*-butyl alcohol and 3,5-dinitrobenzoyl chloride is 3,5-dinitrobenzoic acid. Now make the final decision on the identity of the original alcohol obtained as an unknown.[7]

MELTING POINTS OF ESTERS

Ester	Melting Point
n-butyl	64°
*iso*butyl	83°
sec-butyl	75°

II. The Preparation of Ethyl Acetate

Discussion. The interaction of an alcohol and an acid is a reversible reaction. However, it differs from most reversible inorganic reactions because it requires a considerable

time to reach a condition of equilibrium. It is a matter of days before the maximum amount of ethyl acetate is formed from ethyl alcohol and acetic acid at room temperatures. If a mole of the acid is allowed to react with a mole of the alcohol, the reaction mixture contains about 0.66 mole of the ester at equilibrium.

The rate of the esterification may be increased by (1) raising the temperature, (2) increasing the concentration of the reactants, and (3) by adding a catalyst. Hydronium ion is a convenient catalyst for this reaction. In fact, the rate of esterification is proportional to the concentration of this ion *over certain ranges of concentration.* However, it must be recalled that, unless the concentration of the acid is high, a catalyst does not change the position of the equilibrium point (Text). Also worthy of mention is the slight effect of temperature on the esterification equilibrium. In this particular case, about 66 per cent of the theoretical yield is obtained at 60° and also at 200° in a sealed tube.

Insofar as the influence of concentration is concerned, it is evident that this factor may, according to the law of mass action, influence the yield of ester obtained. Thus, the use of a considerable excess of alcohol increases the yield of ester per mole of acid present.

Finally, the equilibrium may be shifted by the removal of one of the products, that is, the ester or the water. Sulfuric acid, if present in a considerable amount, reduces the effective concentration of the water, and thus slows the rate of hydrolysis.

Apparatus and Materials: Water-jacketed (Liebig) condenser; 150-ml. distilling flask; 250° thermometer; 100-ml. separatory funnel; 20 ml. of absolute ethyl alcohol; 25 ml. of 95 per cent ethyl alcohol; 25 ml. of glacial acetic acid; 25 ml. of 36*N* sulfuric acid; porous anhydrous calcium chloride.

Experimental Procedure. Fit a distilling flask with a cork carrying a 250° thermometer and a glass tube, bent as shown in Fig. 94. Place 20 ml. of absolute alcohol in a 100-ml. beaker, and then slowly pour 25 ml. of 36*N* H_2SO_4 into the alcohol. Stir the liquid constantly during the addition of the acid. Now stopper the flask with the cork carrying the thermometer and the glass tube, and attach to the latter a 100-ml. separatory funnel containing a solution of 25 ml. of glacial acetic acid in an equal volume of 95 per cent alcohol. Connect the flask with a water-jacketed condenser set up for distillation.

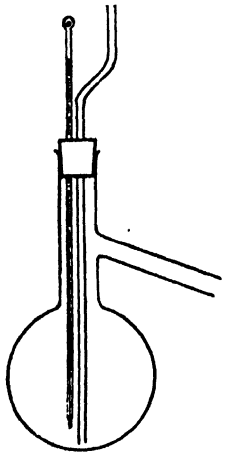


Fig. 94. Distilling flask with thermometer

Heat the contents of the flask to a temperature of 140°, and then allow the solution in the separatory funnel to flow into the flask as rapidly as the ethyl acetate which is formed distills into a conical flask that is used as the receiver. During this time maintain the temperature of the reaction mixture at 140 to 145°. Discontinue the distillation several minutes after the last of the acetic acid-alcohol solution has been added. Do not forget to close the stopcock as soon as the funnel is empty.

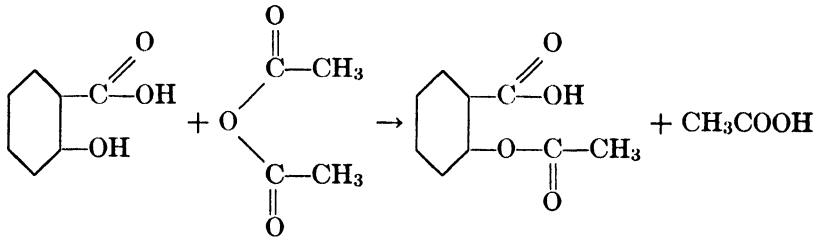
Transfer the distillate to a 250-ml. beaker, add slowly a 2*N* solution of sodium carbonate until, after stirring the mixture in the beaker, effervescence practically ceases. Sometimes the effervescence is very slight. Pour the mixture into a separatory funnel, and drain the lower layer of water from the upper one of ethyl acetate. Do not remove the ester from the funnel, but wash it several times by shaking it in the funnel with 10-ml. portions of a 1*N* solution of sodium chloride. Drain the salt solution after each washing. Now transfer the ester to a conical flask of appropriate size, and add to it about a half-dozen pieces of anhydrous calcium chloride. Stopper the flask, and allow it to stand until the next laboratory period.

Filter the ester into a dry distilling flask, and then distill the liquid slowly through a water-jacketed condenser into a conical flask. Transfer the ester to a graduate, record the volume,[1] and then calculate the weight.[2] (The density of the ester is 0.901 at 20°.) Calculate

the percentage yield on the basis of the weight of the acetic acid used.[3] (The density of glacial acetic acid is 1.049 at 20°.)

III. The Preparation of Acetylsalicylic Acid (Aspirin)

Discussion. The introduction of the acetyl group $\left(CH_3C\overset{O}{\diagup\!\!\diagdown}\right)$ into a compound is called acetylation. Acetyl chloride and acetic anhydride are effective acetylating agents. They react readily with compounds containing an active hydrogen atom, such as is found in amines and phenols. The latter are not acetylated satisfactorily in aqueous solution. Salicylic acid, a phenolic substance, and acetic anhydride are the starting materials in this experiment. The reaction is:



salicylic acid — acetic anhydride — acetylsalicylic acid (Aspirin)

Sulfuric acid serves as a catalyst in this reaction.

The physiological effect of aspirin is due in greater part to the action of acetylsalicylic acid itself, since from 75 to 90 per cent of it is absorbed unchanged in the intestines; from 10 to 25 per cent is hydrolyzed to salicylic acid and acetic acid.

Apparatus and Materials: Porous plate, small beam balance; 1 g. of salicylic acid, 2 ml. of acetic anhydride, ice.

Experimental Procedure. Place 1 g. of salicylic acid and 2 ml. of acetic anhydride in a 50-ml. beaker. Be careful to bring all of the solid into contact with the liquid. Note the absence of a visible change. Now add 2 drops of 36*N* H_2SO_4, and stir the mixture for a minute or two. Result? [1] Allow the solution to stand from 5 to 10 min. and then, regardless of the formation of crystals, rub the mixture vigorously with a stirring rod. Place ice-water in an evaporating dish, and cool the beaker until its contents stiffen to a paste.

Now thoroughly mix the contents of the beaker with 20 ml. of water, and rub the mixture until a thin paste is obtained. Filter the mixture, and then dry the solid by rubbing it on a porous plate. Weigh the dry solid on a small beam balance. Record the weight and calculate the yield on the basis of the weight of salicylic acid used.[2] Try to determine the melting point of aspirin. Describe the behavior of the substance as it is heated in the melting-point tubes.[3] Test the solubility of aspirin in water and in benzene.[4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIII

SELECTED EXPERIMENTS IN ORGANIC CHEMISTRY

I. The Identification of a Butyl Alcohol

(A) The Boiling Point of Butyl Alcohol

1.

Volume of Distillate	B.P.	Volume of Distillate	B.P.
1 drop		25 ml.	
5 ml.		30 ml.	
10 ml.		35 ml.	
15 ml.		40 ml.	
20 ml.		45 ml.	

2. Graph

3.

(B) Identification of a Butyl Alcohol by Its Chemical Properties

Reactions with 12N HCl

1.

2.

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIII (Cont'd)

(B) Cont'd

The use of butyl esters to identify the alcohols

4. M.p. of ester from unknown:

5. M.p. of ester from authentic sample:

6. M.p. of a mixture of the two esters:

7.

II. The Preparation of Ethyl Acetate

1. Volume of ester = **2.** Weight of ester =

3. Percentage yield =

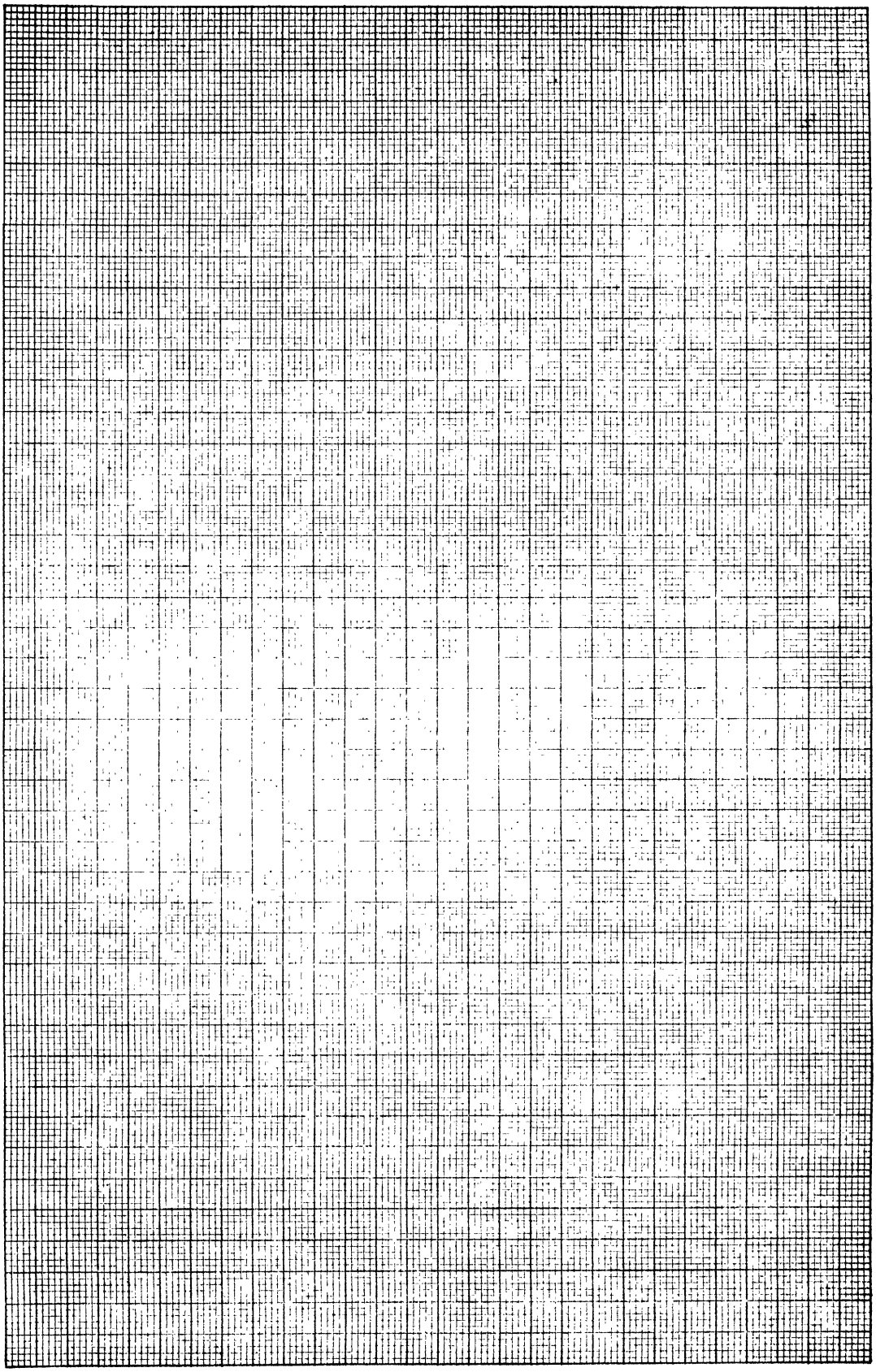
III. The Preparation of Acetylsalicylic Acid (Aspirin)

1.

2.

3.

4.



Experiment XLIV

SILICON AND BORON

Discussion. Although silicon and boron occur in different groups in the periodic arrangement, the two elements show marked resemblances in their behavior. Both are nonmetallic in their chemical properties. They form high-melting, nonvolatile, acidic oxides (B_2O_3 and SiO_2). These compounds react with basic oxides at high temperatures to yield stable compounds. Many of the latter are derivatives of polyacids of the general formula $mH_2O \cdot nB_2O_3$, in which m is usually 1, 2, or 3, and n may be as large as 6. Certain of the hypothetical acids of silicon are represented in the following formulas: $H_6Si_2O_7$ or $3H_2O \cdot 2SiO_2$, $H_8Si_3O_{10}$ or $4H_2O \cdot 3SiO_2$, and $H_{10}Si_4O_{13}$ or $5H_2O \cdot 4SiO_2$. However, while most of the silicates are derived from ortho- or metasilicic acid, and thus contain the groups $SiO_4^{\equiv}$ and $SiO_3^{=}$, very few salts of orthoboric acid (H_3BO_3) are known.

(A) Reaction of Silicon with an Alkali. Test the action of 5 ml. of 4*N* NaOH on 0.1 g. of silicon. Warm the mixture gently if there is no reaction in the cold. What takes place? [1] Heat the tube strongly, and test the vapors with a lighted splint. What is the gas? [2] Write the equation for the reaction by which it is formed.[2] Boil the solution several minutes, and then set it aside until the evolution of gas ceases. Now add 4*N* HCl drop by drop until the solution is acid to litmus. Tell what the insoluble substance is, classify it as crystalline or gelatinous, and write the equation for the reaction by which it is formed.[3]

(B) Silicon Dioxide (Silica). 1. A Test for Silica and the Silicates. Use a steel spatula to thoroughly mix 0.2 g. of calcium fluoride with 0.5 g. of fine sand on a piece of paper. Transfer the mixture to a *dry* 10-cm. test tube, add 10 drops of 36*N* H_2SO_4, and then warm the tube gently. Test the vapors at the mouth of the tube with a drop of water held on the end of a glass rod or in a loop of a Nichrome or platinum wire. Observe and describe the change in the appearance of the water.[1] This is a test for silica or a silicate. Write equations for the reactions concerned.[2]

2. Preparation of Sodium Silicate from Silica. Prepare a clear, transparent sodium carbonate bead in a loop of a Nichrome or platinum wire. Touch the hot bead to some finely divided sand, and then heat the bead strongly until it once more becomes transparent. Note the evolution of a gas accompanying the solution of the sand. Write the equation for the reaction.[3] Touch the hot bead to the sand once more, and then heat the bead for a period of 3 min. If the bead has not become transparent by this time, touch it to sodium carbonate and reheat it. If this treatment does not produce a transparent bead within 3 min., repeat it until the desired result is obtained.

Snap off the molten bead into a mortar, and pulverize it as soon as it is cool. Transfer the powder to a test tube containing 1 ml. of water. Heat the tube until the solid dissolves, then drop in a small piece of litmus paper, and add 4*N* HCl dropwise until the litmus changes color. Describe the precipitate that is formed.[4] For what is its formation a test? [5] Explain the alkaline reaction shown by a solution of a silicate.[6]

(C) Silicic Acid and Silica Gel. Add 1 ml. of a solution of water glass * (sodium metasilicate) to 5 ml. of water, mix the resulting solution thoroughly, and then add to it 2 ml. of 4*N* HCl. Result? [1] Now dilute 2 ml. of 4*N* HCl with 5 ml. of water. Add 1 ml. of water glass to this solution. How does the result differ from the preceding one? Explain.[2]

* 36 per cent solution.

Thoroughly mix 5 ml. of water glass with 15 ml. of water in a 50-ml. beaker. Now pour in 4.5 ml. of 4*N* HCl, swirl the liquid, and then allow the beaker to stand undisturbed 5 min. Describe the product.[3] Use the steel spatula to cut out a small piece of the gel. Transfer it to a test tube, add 5 ml. of 4*N* NaOH, and then warm the tube. Result?[4] Cut out another piece of the gel and place it in a porcelain crucible. Gently heat the crucible a few minutes and then raise its temperature to a dull-red heat. Describe the changes undergone by the gel.[5] Continue the heating 5 min. Now allow the crucible and its contents to cool, and then transfer the silica to a test tube. Test the solubility of the solid in 5 ml. of a boiling 4*N* solution of sodium hydroxide. Compare the result with that obtained by the action of the base on silica gel.[6] After strong ignition, substances often do not show their ordinary reactions.

Cut out a cube of the silica gel, place it on a watch glass, and set it aside in the desk until the next laboratory period. Explain the change in the size and the appearance of the cube.[7]

(D) Silicates. 1. Solubility of Silicates. Dilute 6 ml. of water glass with 12 ml. of water. Distribute the solution equally in six test tubes. Test separately the action of each of the following ions with the metasilicate ion: K^+, NH_4^+, Ca^{++}, Al^{+++}, Fe^{+++}, and Co^{++}. On the basis of these tests, classify each of the silicates as soluble or insoluble. Include the formula of each.[1] Make a general statement regarding the solubility of the simple metasilicates.[2]

2. The Chemical Garden. If a crystal of a salt containing the ions of a heavy metal is placed in a solution of sodium metasilicate, a little of the salt dissolves, and the crystal soon becomes covered with a film of the insoluble silicate. A film of this kind acts as a semipermeable membrane. It separates the saturated solution of the salt immediately surrounding the crystal from the solution of sodium silicate. Water from the latter solution passes through the membrane and dissolves more of the salt. Consequently, the volume of this solution increases, and the membrane is subjected to an increasing pressure which finally becomes great enough to rupture the film. As soon as this occurs, the solution of the salt flows out into the silicate solution to form additional insoluble silicate as an outgrowth on the original film. This projection grows upward to the surface of the liquid. Use of heavy-metal ions of various colors produces a formation called "the chemical garden."

Place in a 50-ml. beaker a solution made by diluting 20 ml. of water glass with an equal volume of water. Drop into this solution a crystal or a lump (about the size of the head of a match) of each of the following substances: manganous sulfate, cupric sulfate, cobalt nitrate, and nickel chloride. Space the crystals as far from each other as is possible on the bottom of the beaker. Watch the solids carefully for several minutes, and describe what takes place.[3] At the end of an hour, make another observation. Describe the "garden."[4]

(E) Glass. Make a clear sodium carbonate bead in a loop of a Nichrome or platinum wire. Touch the hot bead to fine sand, and then reheat it to dissolve the sand. Now cause powdered calcium carbonate to adhere to the bead. Heat the bead strongly until it is once more transparent. If it does not remain clear when it has cooled, reheat it, and continue to touch it to the three substances in turn until a transparent glass is obtained. Write equations for the reactions.[1]

Moisten a small amount of powdered glass in a test tube with several drops of distilled water. Add 1 drop of a solution of phenolphthalein, and then shake the tube. Explain the result.[2] Why is the same result not obtained with the distilled water which has been in contact with the glass wash bottle?[3]

(F) Boric Acid. Place 5 g. of borax ($Na_2B_4O_7 \cdot 10H_2O$) and 15 ml. of water in a 50-ml. beaker. Boil the water to dissolve the borax, and add 15 ml. of 4*N* H_2SO_4 to the solution. Let the mixture stand 1 hr., and then filter it. Wash the precipitate on the filter with two

5-ml. portions of icewater. Now transfer the boric acid to a test tube containing 10 ml. of water, and boil the mixture until all of the solid has dissolved. Immediately filter the hot solution into a 50-ml. beaker, and allow the latter to stand a half-hour in an evaporating dish partly filled with crushed ice. Transfer the contents of the beaker to a filter, allow the liquid to drain, and then wash the solid by pouring 5 ml. of icewater through the filter. Take the filter paper out of the funnel without removing the acid from the paper, open the paper, and spread it out on a watch glass. Allow the paper and the acid to dry in the air at the temperature of the laboratory.

Write the equation for the reaction by which orthoboric acid is prepared from sodium tetraborate.[1] Record the weight of the dry acid.[2] Calculate the theoretical yield [3] and the percentage yield.[4] Reserve 1 g. of the acid for use in part (G).

Heat about 0.1 g. of the acid in a 10-cm. test tube. What volatile product is observed? [5] Write equations to show the series of reactions that take place when boric acid is decomposed by heat.[6]

Dissolve 0.1 g. of boric acid in 5 ml. of water. Test the solution with litmus paper. Result? [7] What can be said about the strength of boric acid? [8]

(G) Borax. 1. Preparation from Boric Acid. Calculate the volume of 2*N* NaOH required to react with 1 g. of boric acid to form sodium tetraborate.[1] Place 1 g. of the boric acid, prepared in part (F), in a test tube, and add to it the calculated volume of 2*N* NaOH. Heat the tube until all of the solid has gone into solution. Now add 5 ml. of water, and cool the solution by holding the tube in running water from the tap. Set the tube aside 5 min. If the solution does not deposit crystals at the end of this time, add a few crystals of borax. What is this procedure for inducing crystallization called? [2]

Remove 1 ml. of the saturated solution of borax, dilute it to a volume of 10 ml., and then test the reaction of this solution toward litmus. Result? [3] Explain by writing a series of equations to represent the hydrolysis of this salt.[4]

2. Tests for Boric Acid and Borates. Add 0.1 g. of sodium tetraborate to 10 ml. of methanol contained in a 50-ml. conical flask. Now slowly pour in, drop by drop, a 5-ml. portion of 36*N* H_2SO_4. This must be done slowly and carefully because of the large amount of heat developed. Close the flask with a one-holed rubber stopper carrying a 7.5-cm. length of glass tubing that extends just below the bottom of the stopper. Boil the liquid in the flask, and then light the vapor as soon as it is seen to issue from the end of the tube. What is the color of the flame? [5] The volatile compound of boron responsible for the color is the methyl ester of boric acid ($B(OCH_3)_3$). Write equations to show how it is formed in this experiment.[6] A procedure of this kind may be used to test for boron when the element is present originally as boric acid or as a compound that may be converted into boric acid.

Dissolve 0.1 g. of borax in 10 ml. of water, drop into it a small piece of litmus paper, and acidify the solution with 4*N* HCl. Dip a strip of turmeric paper into the solution, and then dry the paper by placing it on a watch glass over a beaker in which water is boiling. Remove the paper as soon as it is dry, and then touch it with a drop of 4*N* NaOH held on the end of a stirring rod. Result? [7] The appearance of this color is a test for a borate.

3. Borax Beads. Make a small loop in the end of a platinum or Nichrome wire that has been sealed into the end of a glass tube or rod. Now repeat the section in Exp. XL, part (F), dealing with "Tests with Phosphate Beads," but use borax in place of microcosmic salt ($NaNH_4HPO_4$). Record the results on the form provided on the report sheet.[8]

(H) Sodium Perborate. 1. Preparation. Dissolve 5 g. of borax and 1 g. of sodium hydroxide in 5 ml. of boiling water contained in a test tube. Cool the solution to a temperature of 5° by placing the test tube in crushed ice contained in a 400-ml. beaker. Measure out 30 ml. of a 3 per cent solution of hydrogen peroxide into a 30-cm. test tube, and cool this solution to a temperature of 5°. Now slowly pour the cold solution of borax into the hydrogen peroxide solution. Stir the solution in the large test tube throughout the addition of the

borax. Prepare a freezing mixture by mixing about 15 g. of coarse salt with the ice in the beaker. Transfer the solution from the large test tube to a 50-ml. beaker, and allow the latter to stand in the ice-salt mixture 1 hr. Filter the mixture in the beaker at the end of this time. First wash the crystals of sodium perborate with 5 ml. of icewater, then with two 5-ml. portions of cold 95 per cent ethanol, and lastly with 5 ml. of ether. [**CAUTION!** Extinguish all burner flames within a distance of 6 ft. from the filter!] Allow the crystals to remain exposed to the air until the odor of ether can no longer be detected. The composition of the compound is indicated by its formula ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$).

2. Properties. Place 0.3 g. of the crystals in a 10-cm. test tube containing 4 ml. of water and several drops of 4*N* HCl. Warm the mixture. Use a glowing splint to test the gas being evolved. On the basis of the result, write an equation to account for the formation of the gas.[1]

Dissolve about 0.1 g. of sodium perborate in 3 ml. of water, and add to it drop by drop a very dilute solution of potassium permanganate (made by adding water to a drop of 0.1*M* $KMnO_4$ until the color of the solution is pink). Describe the result, and write the equation for the reaction.[2] What would be the equation for the reaction if it were carried out in an acid solution? [3]

Test the action of a solution of sodium perborate on a neutral and on an acidified 0.1*N* solution of potassium iodide. Write equations for the reactions.[4]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV

SILICON AND BORON

(A) Reaction of Silicon with an Alkali

1.

2.

3.

(B) Silicon Dioxide (Silica). *Test for silica and the silicates*

1.

2.

Preparation of sodium silicate from silica

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV (Cont'd)

(C) Silicic Acid and Silica Gel

1.

2.

3.

4.

5.

6

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV (Cont'd)

(C) Cont'd

7.

(D) Silicates. *Solubility of silicates*

1.

2.

The chemical garden

3.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV (Cont'd)

(D) Cont'd

4.

(E) Glass

1.

2.

3.

(F) Boric Acid

1.

2. **3.** **4.**

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV (Cont'd)

(F) Cont'd

6.

7.

8.

(G) Borax. *Preparation from boric acid*

1. **2.**

3.

4.

Tests for boric acid and borates

5.

6.

7.

Borax beads

8.

Compound of	Color of Bead in Oxidizing Flame	Color of Bead in Reducing Flame
Mn		
Cu		
Ni		
Co		

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIV (Cont'd)

(H) Sodium Perborate

1.

2.

3.

4.

Experiment XLV

THE ALKALI METALS AND THEIR COMPOUNDS

Discussion. Lithium, sodium, potassium, rubidium, and cesium are among the most strongly electropositive elements. Thus, from the point of view of their chemical properties, they are entirely metallic in their behavior. The alkali metals are very reactive, and enter into combination by the loss of their single valence electron to form simple positive ions in which their oxidation state is always +1. Most of the salts of the alkali metals are soluble in water.

Ammonium ion (NH_4^+) is grouped with the ions of the alkalies because it so strongly resembles these ions in its chemical reactions. Thus, in analytical procedures, ammonium ion is found along with those of sodium and potassium. Lithium, cesium, and rubidium are not studied in this experiment because they and their compounds are not commonly met with.

(A) Action of the Alkali Metals on Water. Recall the action of sodium on water (Exp. XVI). Look up the position of potassium in the electromotive series and then state whether it is more or less electropositive than sodium.[1] Would the action of potassium on water be more or less vigorous than that of sodium?[2] Write the equation for the reaction between potassium and water.[3]

(B) Preparation and Chemical Properties of Sodium Hydroxide. 1. Preparation of a Solution of Sodium Hydroxide. Add hot water slowly to 6 g. of powdered calcium oxide until a thin paste is formed. Note the strongly exothermic character of this reaction in which lime is "slaked." Equation?[1] Add the slaked lime to a boiling solution of 10.6 g. (0.1 mole) of anhydrous sodium carbonate dissolved in 100 ml. of water. Boil the mixture for several minutes, allow the solid to settle, and then decant the supernatant liquid through a filter. Wash the remaining solid onto the filter with a stream of water from the jet of the wash bottle (Fig. 48, Exp. VIII). Wash the precipitate on the filter three times with 15-ml. portions of water, and then dilute the filtrate to a volume of 150 ml.

Obtain a 10-ml. pipette, withdraw this volume of the sodium hydroxide solution, and place it in a 250-ml. Erlenmeyer flask containing 75 ml. of water. Add 2 drops of methyl orange and then titrate the solution with standard 1*N* hydrochloric acid. Calculate the normality of the base,[2] and also the percentage yield (based upon the weight of sodium carbonate used).[3] Reserve the solution of sodium hydroxide for further use in this experiment.

Make a schematic drawing of the apparatus in which sodium hydroxide is prepared electrolytically (Text).[4] Write equations for the reactions occurring at the electrodes.[5]

2. Reaction with Metals. Test the action of 10 ml. of the solution of sodium hydroxide on 0.1 g. of powdered zinc. Result? Write the equation for the reaction.[6] Recall the action of sodium hydroxide on aluminum [Exp. XVI, part (C)], and write the equation for this reaction.[7]

3. Reaction with Cations. Place in separate test tubes 1 ml. of 0.1*N* solutions containing the following ions: Al^{+++}, Co^{++}, Cr^{+++}, Cu^{++}, Fe^{++} (use 0.1*M* ferrous ammonium sulfate), Fe^{+++} (0.1*M*), Pb^{++}, Mn^{++}, Hg^{++}, Ag^{+}, Sn^{++} (0.1*M*), and Zn^{++}. Add to each solution 1 ml. of the sodium hydroxide solution prepared in this experiment. Record the color and the formula of each precipitate in the proper places in the table on the report

sheet.[8] Note the fact that *oxides*, and not *hydroxides*, are formed by silver and mercury. Now add excess sodium hydroxide drop by drop to each tube and note whether or not the precipitate is soluble.[8] Make a general statement regarding the solubility in water of the hydroxides of the heavy metals.[9] All hydroxide bases are soluble in acids. What term is applied to hydroxides which are soluble both in acids and in bases? [10]

4. Action on Wool and Cotton. Dissolve 1 g. of sodium hydroxide in 4 ml. of water and then divide the solution equally between two test tubes. Boil the solution in one of the tubes and drop into it about 1 cm. of white woolen yarn. Result? [11] Repeat the test with cotton in place of wool. Result? [12] Outline a procedure which might be used to determine the percentage of wool in textiles.[13]

(C) Preparation of Sodium Bicarbonate by the Solvay Process. Shake 10 ml. of 15*N* ammonia solution with 3 g. of sodium chloride and 1 g. of powdered ammonium carbonate in a stoppered 50-ml. Erlenmeyer flask. The ammonia solution must be saturated with sodium chloride.

Now set up a 250-ml. Erlenmeyer flask as a carbon dioxide generator. Arrange the delivery tube so that it extends to the bottom of a test tube which stands in a vertical position in an empty 400-ml. beaker placed on the desk. Decant the ammonia solution from the undissolved salts into the test tube, and then charge the generator with 25 g. of marble chips and a solution of hydrochloric acid made by mixing 40 ml. of the 12*N* acid with 60 ml. of water.

Place a loose plug of cotton in the neck of the generator flask, and then pass carbon dioxide through the ammonia solution for a half-hour. At the end of this time remove the delivery tube and filter off the precipitated sodium bicarbonate at once. Shake the solid remaining in the tube with a few milliliters of cold water and then quickly pour the liquid through the filter. After the liquid has been drained off, remove the filter paper with its contents, and spread it out on a watch glass to dry. Reserve the sodium bicarbonate for further use in this experiment.

Write equations to show the formation of sodium bicarbonate by this process.[1] A precipitate of potassium bicarbonate is not formed when potassium chloride is used in place of sodium chloride in this preparation. Suggest a reason for this fact.[2] Dissolve about 0.1 g. of the dry sodium bicarbonate in 6 ml. of water. Divide the solution equally between two test tubes and then test the solutions separately for ammonium ion [Exp. XXXVIII, part (E)] and for chloride ion (curdy white precipitate with Ag^+, insoluble in nitric acid). Are the results of these tests positive or negative? [3] Consider the difference in solubility of ammonium chloride and sodium bicarbonate (Text) and then suggest a method by which the sodium bicarbonate might be purified.[4]

(D) Baking Powders. The sodium bicarbonate found in all baking powders is the source of the carbon dioxide whose liberation in and eventual escape from dough leaves the latter light and porous. Present also is a certain substance which furnishes the hydronium ion necessary for the liberation of carbon dioxide from the bicarbonate. This constitutes the "leavening process" used in making bread, cakes, and other bakery products.

Baking powders differ chiefly in the substances used as a source of hydronium ions. The compounds most frequently used for this purpose are potassium hydrogen tartrate (cream of tartar, $KHC_4H_4O_6$); primary calcium phosphate, $(Ca(H_2PO_4)_2)$; and sodium aluminum sulfate, $(NaAl(SO_4)_2)$. Make a solution of each one of these compounds by dissolving 0.1 g. of the solids in 5-ml. portions of water. Test each solution with blue litmus paper. Results? [1] Write equations to show how hydronium ions are formed from these substances when they are dissolved in water.[2] Add about 0.05 g. of sodium bicarbonate to each of the solutions. Results? [3]

Starch is also present in baking powders. Why? (Text) [4] How could its presence be detected? [5]

(E) Tests for the Ions of the Alkali Metals. 1. Flame Tests. Heat a platinum or Nichrome wire in the nonluminous flame until the flame is colorless. If this result is not attained after heating several minutes, dip the wire into a few milliliters of 12*N* hydrochloric acid contained in a test tube and again heat the wire. Now obtain 3-ml. portions of 1*N* solutions of ammonium chloride, sodium chloride, and potassium chloride in separate test tubes. Dip the wire into the solution of ammonium chloride and then introduce the wire into the nonluminous flame. Note the appearance of the flame, clean the wire as before, and then test, in turn, the solutions of potassium chloride and sodium chloride. Clean the wire after each test. Record the results on the form provided on the report sheet.[1]

Now view the sodium flame through a light filter made by filling a flat 60-ml. bottle with a 0.1*M* solution of chrome alum.* Result? [2] Clean the wire, and repeat with the potassium flame. Result? [3] Mix the solutions of sodium chloride and potassium chloride. What color is given to the flame by this mixture? [4] View this same flame through the light filter. Describe the result and tell whether this test might be used to detect potassium in the presence of sodium.[5] *Do not omit the cleaning of the wire between each test,* because a very small amount of sodium masks the color given by a relatively large amount of potassium when the flame is not viewed through the light filter.

2. Difficultly Soluble Salts. Acidify 5 ml. of a 1*N* solution of potassium chloride with several drops of 4*N* acetic acid. Now add 1 ml. of a 0.5*N* solution of sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$. The precipitate is $K_2Na[Co(NO_2)_6]$. Repeat with 1*N* ammonium chloride in place of potassium chloride. Record the results.[1]

Make 2 ml. of a 1*N* solution of sodium chloride alkaline with several drops of 1*N* potassium hydroxide solution and then add 4 ml. of a saturated solution of potassium pyroantimonate ($K_2H_2Sb_2O_7$). Test a 1*N* solution of ammonium chloride in the same way. If precipitation does not occur at once, it may be hastened by scratching the inside of the tube with a glass rod just below the surface of the solutions. Record the results.[1]

Acidify 1 ml. of a 1*N* solution of sodium chloride with several drops of 4*N* acetic acid, and then add 5 ml. of a solution of uranyl zinc acetate reagent.† The precipitate is $NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$. Repeat the test with 1*N* potassium chloride and with 1*N* ammonium chloride respectively. Record the results.[1]

Study the table in which the results of the above tests are summarized, and then point out those cases in which ammonium ion interferes with tests for sodium ion and potassium ion.[6] How would it be possible to remove an ammonium salt from a mixture containing the solid chlorides of sodium, potassium, and ammonium? [7] [Exp. XXXVIII, part (E)] What is the test for the ammonium ion? [8] [Exp. XXXVIII, part (E)]

(F) Analysis of an Unknown. On the basis of the information gained in part (E), devise a procedure which might be used to detect and identify the ions of the alkali metals in the presence of each other.[1] [**Note:** Begin the procedure by testing for ammonium ion in a *separate* portion of the solution containing all three ions.]

What error would be introduced by testing for the ammonium ion in the entire volume of the solution which was to be used for the analysis? [2] What step would be omitted if the test for ammonium ion in an unknown solution showed this ion to be absent? [3]

Have the suggested procedure checked by the laboratory instructor. If the procedure is approved, obtain an unknown and analyze it for ammonium, sodium, and potassium ions. Record the results of the analysis.[4]

* A piece of cobalt glass may also be used as a light filter.

† Thirty g. of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 80 g. of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, and 10 ml. of glacial acetic acid dissolved in enough water to make 250 ml. of solution.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLV

THE ALKALI METALS AND THEIR COMPOUNDS

(A) Action of the Alkali Metals on Water

1.

2.

3.

(B) Preparation and Chemical Properties of Sodium Hydroxide. *Preparation of a solution of sodium hydroxide*

1.

2.

3.

4.

5.

Reaction with metals

6.

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLV (Cont'd)

(B) Cont'd

Reaction with Cations

8.

Oxides Precipitated by NaOH		Hydroxides Precipitated by NaOH; Soluble in Excess		Hydroxides Precipitated by NaOH; Insoluble in Excess	
Color	Formula	Color	Formula	Color	Formula

9.

10.

Action on wool and cotton

11.

12.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLV (Cont'd)

(B) Cont'd

13.

(C) Preparation of Sodium Bicarbonate by the Solvay Process

1.

2.

3.

4.

(D) Baking Powders

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLV (Cont'd)

(D) Cont'd

5.

(E) Tests for the Ions of the Alkali Metals. *Flame tests*

1.

Ion	Color in Flame	Reaction with $Na_3Co(NO_2)_6$	Reaction with $K_2H_2Sb_2O_7$	Reaction with Uranyl Zinc Acetate
NH_4^+ Na^+ K^+				

2.

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLV (Cont'd)

(F) Analysis of an Unknown

1.

2.

3.

4.

Experiment XLVI

COLLOIDS

Discussion. The preparation and properties of a number of colloidal dispersions are studied in this experiment. An important piece of information about a colloid is the sign of the charge on its particles. Knowledge of the sign is obtained by observing the effectiveness of ions in causing the particles to coagulate. If Al^{+++} is more effective than Ca^{++}, which in turn is more effective than Na^{+}, the colloidal particles carry a negative charge. On the other hand, if $PO_4^{\equiv}$ is more effective than $SO_4^{=}$, which in turn is more effective than Cl^{-}, the particle carries a positive charge. Mutual precipitation may also be employed to determine the sign of the charge. If the particles of a colloid are positively charged, they are coagulated by a sol which contains negatively charged particles (As_2S_3) and are not affected by a sol containing particles with a positive charge ($Fe(OH)_3$).

Illustrations of a number of experimental techniques used in the study and applications of colloidal dispersions are given.

Special Materials. An 8- × 8-in. sheet of untreated cellophane; 4 ml. of 2 per cent formaldehyde solution; 1 ml. of 0.1 per cent gelatin solution; 8 ml. of 10 per cent $NaNO_3$ solution; 1 ml. of 0.1 per cent solutions of egg albumen and tragacanth; 10 ml. of either kerosene, benzene, or an oil; 20 ml. of 1 per cent soap solution; 0.1 g. magnesium or aluminum stearate (see footnote, p. 405); 0.05 g. of vaseline or petroleum jelly; 3 g. of soap; 1 ml. of a saturated solution of calcium acetate; 10 ml. of 95 per cent alcohol; 0.5 g. PbS; 1 ml. of pine oil.

(A) Preparation of Sols. 1. Sulfur. To 5 ml. of a saturated aqueous solution of sulfur dioxide add an equal volume of a saturated solution of hydrogen sulfide (or add 5 ml. of water and then pass H_2S into the solution). Describe the result and write the equation for the reaction.[1] Try to filter out the sulfur. Now add about 0.5 g. of solid NaCl and then shake the tube vigorously. Result? [2] Filter the mixture and wash the sulfur several times with water. Explain why the sulfur is peptized.[3]

2. Arsenic Trisulfide. To 10 ml. of a saturated aqueous solution of As_2O_3 add an equal volume of a saturated solution of H_2S. Describe the result and write the equation for the reaction.[4] Determine the number of drops of 0.5*N* NaCl, 0.01*N* $BaCl_2$, and 0.01*N* $AlCl_3$ required to cause the coagulation of separate 2-ml. portions of the As_2S_3 sol.[5] What is the sign of the charge carried by the particles? [6] Reserve the remainder of the sol.

3. Ferric Hydroxide. To 50 ml. of boiling water add dropwise 2 ml. of 0.1*M* $FeCl_3$. Describe the result.[7] Determine the number of drops of 0.1*N* solutions of NaCl, Na_2SO_4, and Na_3PO_4 required to cause the coagulation of separate 2-ml. portions of the ferric hydroxide sol.[8] What is the sign of the charge on the particles? [9]

Mix 2 ml. of the arsenic trisulfide sol with an equal volume of the ferric hydroxide sol. Explain the result and give the term used to describe the process which takes place.[10]

4. Silver Halides. Place 1 ml. of 0.1*N* $AgNO_3$ in one test tube, and an equal volume of 0.1*N* KBr in another. Add 5 ml. of water to each tube and then mix the contents of the two tubes. Result? [11]

Repeat the experiment, but this time dilute 2 ml. of 0.1*N* $AgNO_3$ with 5 ml. of water, and 1 ml. of 0.1*N* KBr with 5 ml. of water. Mix the two solutions, and compare the result with that obtained when equivalent amounts of $AgNO_3$ and KBr were used.[12] To one 2-ml. portion of this solution add 2 ml. of the ferric hydroxide sol, and to another 2-ml. portion

add 2 ml. of the arsenic trisulfide sol. Explain how this procedure proves the sign of the charge on the particles in the silver bromide sol.[13]

Prepare another silver bromide sol from solutions made by diluting 1 ml. of 0.1*N* $AgNO_3$ with 5 ml. of water, and 2 ml. of 0.1*N* KBr with 5 ml. of water. To one 2-ml. portion of this sol add 2 ml. of the ferric hydroxide sol, and to another add 2 ml. of the arsenic trisulfide sol. What is the sign of the charge on these AgBr particles? [14]

Which ions account for the charge and the stability of each of the two silver sols formed by the foregoing procedures? [15]

(B) Properties of a Sol (Silver). 1. Preparation. Place in a 400-ml. beaker 100 ml. of water and 4 ml. of 0.1*N* $AgNO_3$. To this solution add 100 ml. of a dilute solution of potassium bromide (0.5 ml. of 0.1*N* KBr in 100 ml. of water) and then 4 ml. of 2 per cent formaldehyde solution. Lastly, add rapidly and with vigorous stirring a solution of sodium hydroxide containing 0.5 ml. of 4*N* NaOH in 50 ml. of water. Continue to stir the solution several minutes. Describe the results.[1] Reserve this sol for use in **2.** In alkaline solution, formaldehyde reduces silver salts to free silver and in the presence of bromide ion or other stabilizing ions a colloidal dispersion is formed.

2. Dialysis. Wet a sheet (8 × 8 in.) of untreated (not waterproofed) cellophane or parchment paper and tie it firmly to a two-holed cork or rubber stopper in the manner shown in Fig. 95. Pour about **100** ml. of the silver sol (just prepared) through the funnel into the bag. Now support the funnel so that the level of the liquid in the bag is just slightly above the level of the distilled water in the beaker. After 15 min. test the water in the beaker for OH^- by adding 1 drop of phenolphthalein to a 5-ml. portion; for NO_3^- by the brown-ring test (p. 335); and for Na^+ by the uranyl zinc acetate test (p. 395). Results? [2] Did any silver pass through the membrane? [3] Explain the mechanism of the purification of colloidal solutions by dialysis.[4]

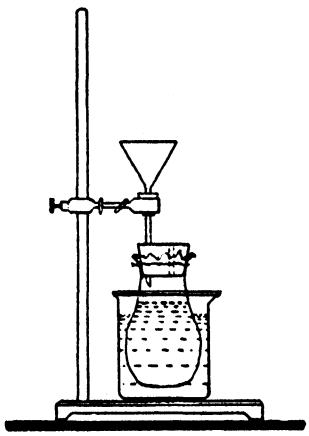


FIG. 95. Apparatus for dialysis

3. Determination of the Charge. Determine the sign of the charge on the silver particles by one of the methods described in part (A). State the method used and describe the results which indicate the sign of the charge.[5]

4. Determination of the Precipitation Value. This value is *the concentration in millimoles per liter of a specified electrolyte required to cause the coagulation or precipitation of a given colloid within a specified time* (usually 12 or 24 hrs.). The concentration of sodium nitrate which brings about a change in the color of the silver sol from yellow to green causes the particles to coagulate in 12 hrs. This concentration is taken as the precipitation value of the silver sol.

Place 10-ml. portions of the silver sol in ten separate test tubes. Dilute 1 ml. of 0.1*N* $NaNO_3$ to 10 ml. with distilled water. Rapidly mix this solution with one of the 10-ml. portions of the silver sol. Shake the mixture, and note whether or not a color change occurs. Now test a second portion of the silver sol with a solution made by diluting 2 ml. of 0.1*N* $NaNO_3$ to a volume of 10 ml. Continue in this manner, using successively 3, 4, 5, 6, 7, 8, and 9 ml. of 0.1*N* $NaNO_3$ diluted each time to a volume of 10 ml.; finally, use 10 ml. of 0.1*N* $NaNO_3$. Which of these solutions contains a sufficiently high concentration of $NaNO_3$ to bring about a color change from yellow to green? [6] Calculate the concentration (in millimoles per liter) of the $NaNO_3$ in the solution which caused a color change to occur, and record this value as the precipitation value of the silver sol.[7]

5. Protective Colloids. The "silver number" of a protective colloid is *the number of milligrams of a protective colloid that, when added to 10 ml. of a standard silver sol, just fails*

to prevent the yellow to green color change on the addition of 1 ml. of a 10 per cent solution of sodium nitrate. The silver number is of value as a measure of the relative protecting power of various agents for a given sol.

Place 10-ml. portions of the silver sol in four test tubes. Dilute 1 ml. of 0.1 per cent gelatin solution to a volume of 10 ml. and add 1 drop of it to the first tube, 5 drops to the second, 10 drops to the third, and 20 drops to the fourth. Shake the tubes 3 min. and then add to each 1 ml. of 10 per cent $NaNO_3$ solution. In which tubes is there a color change from yellow to green? [8] Select the tube in which the gelatin just fails to prevent the color change, and calculate the number of milligrams of the protective agent present (assume 20 drops per milliliter).[9]

Repeat the above procedure but replace the gelatin with 0.1 per cent egg albumen and with 0.1 per cent tragacanth. Do not dilute the tragacanth solution and, if necessary, use more than 20 drops of it.

Arrange these three protective agents in the order of their ability to stabilize the silver sol, and place the value of the silver number in parentheses following the name of the substance.[10] Explain the protective action of these substances.[11]

(C) Emulsions. 1. Preparation. Place in a test tube 10 ml. of water and 10 ml. of kerosene, benzene, or an oil. In another tube place 10 ml. of 1 per cent soap solution with the immiscible liquid used in the first tube. Shake the tubes vigorously and explain the difference in the behavior of the mixtures.[1]

In order to "break" an emulsion it is necessary to add a substance which reacts with or diminishes the effectiveness of the emulsifying agent. To a 5-ml. portion of the stable emulsion add 1 ml. of 4*N* HCl or 5 ml. of 0.1*N* $CaCl_2$. Note whether or not the emulsion separates into two phases after standing from 5 to 10 min.[2]

2. Types. If an emulsion is an oil-in-water type, the addition of *water* does not produce a second phase; if the emulsion is a water-in-oil type, the addition of *oil* does not cause a second phase to appear.

To one 5-ml. portion of the stable emulsion just prepared, add 5 ml. of water, and to a second 5-ml. portion add 5 ml. of the other liquid used in the emulsion. Results? [3] Which type of emulsion is indicated? [4]

To the remaining 5 ml. of the emulsion prepared in 1 add about 0.1 g. of solid magnesium stearate or aluminum stearate.* Shake the tube vigorously, and then determine whether or not an inversion of the type has occurred. State the result and describe the procedure used in arriving at the decision.[5]

3. Detergent Action. Mix about 0.05 g. of bone black with a few drops of an oil or an equivalent amount of vaseline or petroleum jelly. Smear part of the mixture on three small pieces of white cloth. Shake one of them with 10 ml. of water, another with 10 ml. of carbon tetrachloride, and the remaining one with 10 ml. of 1 per cent soap solution. Explain the differences in results.[6]

(D) Gels. 1. Soap Gels. When certain colloids are treated in particular ways they form gels of a brush-heaplike structure (Text) with the dispersion medium trapped within their interstices.

Place 15 ml. of water and 1 g. of soap in one beaker, and 50 ml. of water and 1 g. of soap in another. Heat the beakers until the soap disperses and then allow the dispersions to cool. Describe the results.[1]

2. Calcium Acetate Gel (Solid Alcohol). Add 10 ml. of 95 per cent alcohol all at once to 1 ml. of a saturated solution of calcium acetate contained in a 50-ml. beaker. Result? [2] Touch a lighted match to the gel.

* If neither of these stearates is available, prepare magnesium stearate by mixing 10 ml. of soap solution with an equal volume of 0.1*N* $MgCl_2$. Filter the mixture, and dry the solid by pressing it between sheets of filter paper.

3. Silica Gel. To 10 ml. of a 36 per cent solution of sodium silicate (density 1.38) in a small beaker add rapidly, while stirring, 10 ml. of 1*N* CH_3COOH made by diluting 2.5 ml. of the 4*N* acid to a volume of 10 ml. After about 15 min. cut out a piece of the gel with a spatula and place it on a watch glass to dry. Describe the product.[3]

4. Adsorption with Silica Gel. Gases and vapors are strongly adsorbed on silica gel which has been properly prepared. If commercial silica gel is available,* use it in the following tests.

Fill a test tube with ammonia by the method described in Exp. XXXVIII, part (D)**1.** Quickly add to the tube several grams of silica gel and tightly cover the mouth of the tube with the thumb. Shake the closed tube several minutes. If any effect is noticeable, describe it.[4] Now remove the thumb from the mouth of the tube and then determine by the odor whether or not appreciable quantities of ammonia have been adsorbed by the gel.[5]

Add a few drops of methyl violet to 10 ml. of water in a test tube, and then drop into it 1 g. of silica gel. Shake the tube and describe the result.[6]

(E) Flotation. Mix 0.5 g. of finely powdered lead sulfide (galena) with an equal weight of pulverized silica (or sand) in a conical flask. Add to the mixture 50 ml. of water and 1 ml. of pine oil. Stopper the flask and shake it vigorously. Describe the result.[1] Explain why the solid floats even though it is much heavier than water (Text).[2] List certain applications of the flotation process.[3]

* Granular silica gel may be purchased from the Silica Gel Corporation, Baltimore, Md.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVI

COLLOIDS

(A) Preparation of Sols. *Sulfur*

1.

2.

3.

Arsenic trisulfide

4.

5. Drops of: 0.5*N* NaCl ____; 0.01*N* $BaCl_2$ ____ ; 0.01*N* $AlCl_3$ ____

6.

Ferric hydroxide

7.

8. Drops of: 0.1*N* NaCl ____ ; 0.1*N* Na_2SO_4 ____; 0.1*N* Na_3PO_4 ____

9.

10.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVI (Cont'd)

(A) Cont'd

Silver halides

11.

12.

13.

14.

15.

(B) Properties of a Sol (Silver). *Preparation*

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVI (Cont'd)

(B) Cont'd

Determination of the charge

5.

Determination of the precipitation value

6. **7.**

Protective colloids

8.

9.

10.

11.

(C) Emulsions. *Preparation*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVI (Cont'd)

(C) Cont'd

2.

3.

4.

5.

Detergent action

6.

(D) Gels. *Soap gels*

1.

Calcium acetate gel (solid alcohol)

2.

Silica gel

3.

Adsorption with silica gel

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVI (Cont'd)

(D) Cont'd

6.

(E) Flotation

1.

2.

3.

Experiment XLVII

COMPOUNDS OF THE ALKALINE-EARTH METALS

Discussion. Calcium, strontium, and barium are in Group II of the periodic system. In all of their compounds the elements are present in the oxidation state of +2, that is, both electrons are lost from the outer shell. Most of the compounds of these elements are ionic and are therefore completely ionized in aqueous solutions. The reactions of the ions of these elements are therefore an important part of the chemistry of the three elements. A number of the reactions which are often employed in analytical chemistry are studied in the first part of this experiment.

Compounds of the alkaline-earth metals, particularly those of calcium, are used extensively in building materials. A few of these substances are studied.

When water comes into contact with minerals, rocks, and soil, certain compounds of the alkaline-earth metals, along with other substances, are dissolved. The ions of the alkaline-earth metals form insoluble, curdy precipitates with soap, which is largely sodium stearate ($C_{17}H_{35}COONa$). Water containing the ions of calcium, magnesium, or iron is said to be "hard water." If bicarbonate ions are also present as a result of the action of carbonic acid on limestone, the water is called "temporary" hard water. This temporary hardness is removed by boiling the solution or by adding a basic substance such as ammonia or calcium hydroxide.

If the water contains calcium and magnesium ions after the water is boiled, it is known as "permanently" hard water. This type of hard water also contains sulfate and chloride ions in amounts at least equivalent to the calcium and magnesium ions that cause the water to be permanently hard. Thus a solution of calcium sulfate or of calcium chloride is a permanently hard water.

Both types of hard water are "softened" by the addition of softening agents which form slightly soluble compounds or slightly dissociated complex ions with the ions of calcium, magnesium, and iron.

(A) Tests for the Ions of Calcium, Strontium and Barium. 1. Flame Tests. Prepare a small loop on the end of a platinum, Nichrome, or Chromel wire which has been sealed into a glass tube. Dip the wire into a 0.1*N* solution of calcium chloride and then hold it in the upper part of a nonluminous flame. Note the color imparted to the flame, and the approximate length of time that the flame is colored.[1] Clean the wire thoroughly by first dipping it into 12*N* hydrochloric acid contained in a test tube. Now heat the wire steadily several minutes. Repeat the procedure until no color is imparted to the flame.

Repeat the above experiment with solutions of strontium chloride and barium chloride. Record the results in the table provided on the report sheet.[1]

2. Reactions with Anions. Record the results of the following tests in the table provided on the report sheet.[2] In each case use 3 ml. of 0.1*N* solutions of calcium chloride, strontium chloride, and barium chloride in separate test tubes:

a. Add 3 ml. of 4*N* sodium hydroxide.[2]

b. Add 3 ml. of 4*N* ammonia.[2] Explain the difference in the reactions of solutions of ammonia and sodium hydroxide with the ions of the alkaline-earth metals.[3]

c. Add a few drops of 4*N* ammonia to make the solutions alkaline and then 3 ml. of 1*N* ammonium carbonate solution.[2] Test the solubility of the precipitates in 4*N* acetic acid.[2]

d. Add a few drops of 4*N* ammonia and 3 ml. of 0.1*N* ammonium oxalate.[2] Divide each suspension into two equal parts. Add 4*N* acetic acid to one portion, and 4*N* hydrochloric acid to the other.[2] Explain, with the aid of equations, the difference in the action of the two acids.[4] List the oxalates of the three elements in the order of their decreasing solubility in acids.[5]

e. Add a few drops of 4*N* ammonia and 3 ml. of a 0.1*M* solution of sodium chromate or potassium chromate. Result?[2] Divide the suspension of each precipitate between two test tubes. To one test tube add 4*N* acetic acid, and to the other add 4*N* hydrochloric acid. Result?[2] Explain the difference in the action of the two acids. Equations.[6] List the chromates of the three elements in the order of their decreasing solubility in acids.[7]

f. Add 3 ml. of 4*N* sulfuric acid to each solution. Test the solubility of each precipitate in 4*N* hydrochloric acid.[2]

g. Add 3 ml. of a saturated solution of calcium sulfate. Result?[2]

h. Add a saturated solution of strontium sulfate. Result?[2] List the sulfates of calcium, strontium and barium in the order of their decreasing solubility.[7]

Write the equations for the formation of each precipitate in the preceding tests.[8]

(B) Analysis of an Unknown. Make up 3 ml. of a solution containing Ca^{++}, Sr^{++}, and Ba^{++} from the 0.1*N* solutions on the reagent shelf. Acidify the solution with 4*N* acetic acid and add 1 ml. of a 0.1*M* solution of potassium chromate. A precipitate indicates the presence of barium ion. Filter the solution, add 1 or 2 drops of 4*N* hydrochloric acid to the precipitate, touch a platinum wire to the latter, and confirm the presence of barium by means of the flame test.

Divide the filtrate into two equal parts. To one part add 5 ml. of a saturated solution of calcium sulfate and heat the mixture to the boiling point. A precipitate indicates the presence of strontium. Filter off the precipitate, add 1 or 2 drops of 4*N* hydrochloric acid to the residue and confirm the presence of strontium by means of the flame test.

To the second part of the filtrate add 3 ml. of a 0.1*N* solution of ammonium sulfate. Filter off the strontium sulfate and add to the filtrate 2 ml. of a 0.1*N* solution of ammonium oxalate. A precipitate indicates the presence of calcium ion. Filter the solution, add 1 or 2 drops of 4*N* hydrochloric acid to the residue, and confirm the presence of calcium by means of the flame test.

Obtain an unknown which may contain any one of the three ions or any combination of them. Analyze the solution by the procedure described above. Record the number of the unknown and list the ions found.[1]

(C) Building Materials. 1. Mortar. Place about 10 g. of lime in a small beaker and add about 5 ml. of water. Feel the beaker. What evidence is there for a chemical reaction?[1] Equation?[2] This process is called the slaking of lime. The product, calcium hydroxide, is known as slaked lime.

Stir into the slaked lime-water mixture about 10 g. of sand until the mixture has the consistency of a thick paste. Place part of the mortar on a watch glass, and part of it in a crucible. Carefully submerge the crucible in water contained in a beaker. Set both portions of the mortar aside and examine them at the next laboratory period. Compare the two samples.[3] Add 4*N* hydrochloric acid to a small piece of the mortar from the watch glass. What gas is evolved?[4] Explain the mechanism of the setting or hardening of mortar and explain why the one submerged in water did not set.[5] Write the equation for the carbonation which takes place during the setting of mortar.[6]

2. Cement. Mix 10 g. of Portland cement with about 20 g. of sand in a beaker or evaporating dish. Add water a little at a time and work the mixture with a spatula until a thick homogeneous paste is obtained. Pour part of the paste into a match box or another small container and immerse it in water; mold the remaining part into a convenient form on

a piece of cardboard. Examine both samples at the next laboratory period. Does cement set under water? [7] Explain the difference between the setting of cement and of mortar.[8]

3. Plaster of Paris. Weigh about 7 g. of plaster of Paris thoroughly and mix it with about 5 ml. of water in a beaker or in an evaporating dish. Mold the mixture into a form on a piece of cardboard and note the time required for the mixture to set.[9] While the mixture is still wet and soft, rub a film of vaseline or paraffin on a coin or a key and press it into the top of the mass. After the plaster of Paris has set, remove the coin. Give a few practical applications of plaster of Paris.[10] Write the equation for the setting of plaster of Paris.[11]

Weigh out two more 7-g. portions of plaster of Paris. Mix one portion with 5 ml. of 1*N* sodium chloride solution and the other portion with 5 ml. of an albumen or a gelatin solution. Measure the length of time required for each to set.[12] Compare the speeds of setting with the speed noted with pure water.[13]

(D) Hard Water. 1. Temporary Hardness. Pass carbon dioxide into 15 ml. of calcium hydroxide solution (saturated) until the precipitate which forms at first is redissolved. Equations? [1] If the solution is still cloudy after 10 min., discontinue the passage of carbon dioxide, and filter out the remaining precipitate. (See Exps. XXV and XLII for methods of preparing carbon dioxide.)

Obtain about 50 ml. of standard soap solution. (One milliliter of this solution is equivalent to approximately 0.6 mg. of calcium carbonate.) Dilute 5 ml. of the bicarbonate solution to 25 ml. with distilled water and pour it into a 250-ml. Erlenmeyer flask. Add successively from a burette 0.3-ml. portions of soap solution until, following a vigorous shaking after each addition, a lather forms over the entire surface and persists for 3 min. Record the volume of soap solution required for the titration.[2]

Boil the remaining portion of the calcium bicarbonate solution about 10 min. Dilute 5 ml. of this solution to 25 ml. with distilled water and titrate the solution with the standard soap solution in the same manner described above. Record the volume required to produce the permanent lather.[3] Compare this with the value required before the solution was boiled.[4] Write the equation for the reaction that accounts for the removal of temporary hardness by boiling.[5] What percentage of the original hardness was removed.[6]

Bicarbonates of magnesium and iron are also decomposed at the boiling point of water.

2. Permanent Hardness. Dilute 5 ml. of a saturated solution of calcium sulfate to 25 ml. and carry out the titration described in the previous section. How many milliliters of soap solution are required to produce the permanent lather? [7] Boil 5 ml. of the calcium sulfate solution, dilute it to 25 ml., and then repeat the titration.[8] Explain why the permanent hardness is not removed by boiling.[9]

(E) Degree of Hardness of Tap Water.* Determine the total hardness of the tap water by titrating 25 ml. of the water with standard soap solution. How many milliliters of soap solution are required? [1]

The hardness of water is often expressed by stating the number of milligrams of calcium carbonate required to consume the same quantity of soap as would be consumed by 1 liter of the water. Assume that 1 ml. of the soap solution is equivalent to 0.6 mg. of calcium carbonate (or obtain a more accurate value from the instructor). Calculate the total hardness of the tap water in milligrams of calcium carbonate per liter of water. This value is sometimes referred to as the hardness in parts per million (p.p.m.).

Boil gently for 10 to 15 min. about 50 ml. of tap water. Cool the water, measure out 25 ml., and titrate it with standard soap solution. What volume of soap solution was required? [2] Calculate the hardness (in p.p.m.) not removed by boiling the water (permanent

* If the tap water has been softened, prepare a synthetic hard water for use in the laboratory, or obtain some natural hard water from a lake or river.

hardness).[3] Calculate the hardness removed by boiling the water (temporary hardness).[4] What percentage of the total hardness is due to permanent hardness? [5]

(F) Relative Effectiveness of Water Softeners. To separate 25-ml. portions of the tap water (or hard water prepared in the laboratory) add about 0.5 g. of the following substances: (1) trisodium phosphate (Na_3PO_4); (2) borax [sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)]; (3) sodium hexametaphosphate $(NaPO_3)_6$, known commercially as Calgon; (4) sodium carbonate [washing soda ($Na_2CO_3 \cdot 10H_2O$ or Na_2CO_3)]. Titrate each with standard soap solution. Record the results in the table provided on the report sheet.[1] List these substances in the order of their decreasing efficiency as water-softening agents.[2] Note that the solution containing sodium hexametaphosphate does not become cloudy when soap is added to water containing it. This is because the alkaline-earth-metal ions react with the sodium hexametaphosphate to form a soluble slightly dissociated complex ion that does not precipitate the soap. Other substances, such as the silicates, ammonia, and lime mixed with sodium carbonate, are also employed as water-softening agents.

Connect a rubber tube carrying a screw clamp to the end of a calcium chloride tube. Clamp the tube in a vertical position with the rubber tube at the bottom. Close the clamp, pour some distilled water into the tube, and then add about 25 g. of a zeolite (natural greensand or Permutit). Open the clamp and allow the water to run out slowly. Add tap water when the level of the water is about even with the surface of the zeolite. Discard the first 25 to 30 ml. of tap water that passes through the zeolite, and then collect 25 ml. and titrate it with standard soap solution. Record the result in the table on the report sheet.[1] Explain the mechanism of the softening of water with zeolites (Text).[3] How are zeolites regenerated? [4] Return the zeolite to the bottle provided for it.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII

COMPOUNDS OF THE ALKALINE-EARTH METALS

(A) Tests for the Ions of Calcium, Strontium, and Barium. *Flame tests*

1.

Solution of	Color of Flame	Approximate Time that the Flame Remains Colored
$CaCl_2$ $SrCl_2$ $BaCl_2$		

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII (Cont'd)

(A) Cont'd

Reactions with anions

2. Record the color, type, and formula of each precipitate formed. Indicate the solution of a precipitate by "dissolves."

Reagents	Ca^{++}	Sr^{++}	Ba^{++}
(a) $NaOH$			
(b) NH_3			
(c) $NH_3 + (NH_4)_2CO_3$			
CH_3COOH + precipitates			
(d) $NH_3 + (NH_4)_2C_2O_4$			
CH_3COOH + precipitates			
HCl + precipitates			
(e) $NH_3 + Na_2CrO_4$			
CH_3COOH + precipitates			
HCl + precipitates			
(f) H_2SO_4			
HCl + precipitates			
(g) $CaSO_4$			
(h) $SrSO_4$			

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII (Cont'd)

(A) Cont'd

3.

4.

5.

6.

7.

8.

(B) Analysis of an Unknown

1.

Reagents Added	Result	Flame Test	Ion Present
$CH_3COOH + Na_2CrO_4$			
$CaSO_4$			
$(NH_4)_2C_2O_4$			

(C) Building Materials. *Mortar*

1. **2.**

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII (Cont'd)

(C) Cont'd

3.

4.

5.

6.

Cement

7.

8.

Plaster of Paris

9.

10.

11.

12.

13.

(D) Hard Water. *Temporary hardness*

1.

2. **3.**

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII (Cont'd)

(D) Cont'd

5.

6.

Permanent hardness

7. **8.**

9.

(E) Degree of Hardness of Tap Water

1. **2.**

3.

4.

5.

(F) Relative Effectiveness of Water Softeners

1.

Softening Agent	Initial Reading of the Burette	Final Reading of the Burette	Volume of Soap Solution
Na_3PO_4			
$Na_2B_4O_7 \cdot 10H_2O$			
$(NaPO_3)_6$			
Na_2CO_3			
Zeolite			

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVII (Cont'd)

(F) Cont'd

2.

3.

4.

Experiment XLVIII

MAGNESIUM

Discussion. A density of 1.74 at 20° makes magnesium the lightest of the rigid metals. The element has been prominent in the news of recent years because of the tremendously increased demand for light alloys and because of its use in making flares and incendiary bombs.

Reference to a table of oxidation-reduction potentials (Text) shows this metal to be chemically active, standing just below calcium and sodium. Thus, it readily displaces hydrogen from acids and unites directly with most nonmetals. It is permanent in air because of a coherent film of oxycarbonate which forms in the presence of moisture.

(A) Reactions of Magnesium Ion, Mg^{++}. Dip the wire used for flame tests into a solution of a magnesium salt and then hold the wire in the upper part of a nonluminous flame. Result? [1]

Add several drops of 4*N* NaOH to 1 ml. of a 0.1*N* solution of magnesium chloride. Describe the result and write an equation for the reaction.[2] Repeat with another 1-ml. portion of the solution of magnesium chloride, substituting 4*N* NH_4OH for sodium hydroxide. Note any observable difference in the result.[3] Test a third 1-ml. portion of magnesium chloride solution, adding first 5 drops of a 1*N* solution of ammonium chloride, and then a few drops of 4*N* NH_4OH. Explain the difference from the result obtained in the test in which ammonium chloride was not added.[4]

Add several drops of 1*N* NH_4Cl and the same amount of 4*N* NH_4OH to a 0.1*N* solution of magnesium chloride. Add about 6 drops of 1*N* $(NH_4)_2CO_3$ to the mixture. Explain the result.[5] Repeat this test, but substitute 1*M* $(NH_4)_2HPO_4$ for the ammonium carbonate. Record the result and write an equation for the reaction that has taken place.[6] Filter the mixture, wash the precipitate with distilled water, and then dissolve it by pouring 2 ml. of 4*N* HCl through the filter. To the filtrate add 1 drop of *p*-nitrobenzeneazo-α-naphthol reagent. Note the color of the solution and then add 4*N* NaOH to it drop by drop. Describe the result.[7] The formation of the blue "lake" is a very sensitive test for the Mg^{++}; it will detect as little as 2×10^{-7} g. of Mg^{++} per milliliter.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLVIII

MAGNESIUM

(A) Reactions of Magnesium Ion

1.

2.

3.

4.

5.

6.

7.

Experiment XLIX

COPPER AND SILVER

Discussion. Copper and silver, together with gold, have long been known as the coinage metals. They are not very active chemically and thus occur free in nature. Copper is an extremely important metal in peacetime and is indispensable in the conduct of modern warfare. During World War II there was presented the apparently curious spectacle of silver, a precious metal, being used as a substitute for copper, one of the base metals. There were, however, two factors which made this situation a logical one. A plentiful supply of silver was built up, and the metal is unsurpassed as a conductor of heat and electricity.

Copper and silver stand below hydrogen in the activity series, and are not attacked by nonoxidizing acids in the absence of oxygen. Fused alkalies have only a slight effect on the metals.

(A) Copper and Its Compounds. 1. Copper. a. Form a helix by winding 10 cm. of 18-gauge copper wire around a lead pencil. Take the helix off the pencil, grasp one end of the wire with the crucible tongs, and heat the wire in the oxidizing part of a gas flame. Remove the wire before it melts, and note any change in its appearance. Record the melting point of copper (Text), and name the coating on the wire.[1] Now heat the wire to redness, and quickly drop it into a test tube containing 5 ml. of methanol (wood alcohol). Describe what takes place and note the odor of the gaseous oxidation product of the alcohol.[2] The odorous substance is formaldehyde; it is a reducing agent.

b. Test separately the action of the following acids on small amounts of copper turnings or short lengths (about 3 mm.) of copper wire: 4*N* and 12*N* HCl; 4*N* and 16*N* HNO_3; 4*N* and 36*N* H_2SO_4. If no action occurs in the cold, try the effect of heat. Tabulate the results on the report sheet.[3] Write equations for all reactions taking place.[4]

2. Cuprous Compounds. a. Dissolve 5 g. of $CuCl_2 \cdot 2H_2O$ in 20 ml. of water in a 100-ml. beaker. Add 20 ml. of 12*N* hydrochloric acid together with 2.5 g. of copper wool. Boil the mixture vigorously (***HOOD!***) until the greenish color of the solution changes to a clear amber. The color change should occur after boiling for about 2 min. What is indicated by the disappearance of the greenish tint? [5] Write an equation for the reaction that takes place and tell in what capacity the metallic copper acts.[6]

Reserve 5 ml. of the solution for use in **b,** and pour the remainder into a beaker containing 200 ml. of water. What is the precipitate? [7] Allow it to settle, and then decant the clear liquid from the solid. To the latter add 50 ml. of water, stir thoroughly, and filter. Wash the precipitate on the filter by pouring through it a mixture of 23 ml. of water and 2 ml. of 12*N* hydrochloric acid. Divide the washed cuprous chloride into three equal parts.

Place one portion of the moist cuprous chloride in a test tube, and wash the salt down into the bottom of the test tube with approximately 5 ml. of water. Quickly cover the water with half its volume of kerosene, and add 3 ml. of 15*N* ammonium hydroxide. Stir the solution carefully with a small glass rod until all the salt dissolves. If any remains undissolved, add more ammonium hydroxide. Note the color of the aqueous layer. Bubble air through the ammoniacal solution. Note the deepening of the color. Write the equation for the action of ammonium hydroxide on cuprous chloride. Why was the kerosene added? [8] What is the effect of air on the solution? [9]

Add 12*N* hydrochloric acid to another portion of the solid cuprous chloride. Write an equation for the reaction that takes place.[10] Explain the solubility of cuprous chloride in ammonium hydroxide and in hydrochloric acid.[11]

Save the third portion of the solid cuprous chloride for use in part (A) **5 b.**

b. To 5 ml. of the acidic solution of cuprous chloride prepared in **a** add a slight excess of 4*N* sodium hydroxide solution. What is the precipitate? Write an equation for the reaction.[12] After the precipitate has settled, decant the supernatant liquid, add 10 ml. of water to the precipitate, and filter it off. Wash the solid once more by pouring 20 ml. of water through the filter.

Take a small portion of the cuprous oxide and heat it in a test tube with 10 ml. of 4*N* sodium hydroxide solution. Is the oxide amphiprotic? Give the reason for the answer.[13]

Test separately the action of small portions of cuprous oxide with 12*N* hydrochloric acid and with 4*N* ammonium hydroxide. Note the results, and write an equation for each reaction.[14] Explain the solubility of cuprous oxide in ammonium hydroxide.[15]

Suspend a small quantity of the cuprous oxide in 5 ml. of water in a test tube. Shake the tube continually several minutes. Now add 5 ml. of 4*N* NH_4OH. Note the result and draw a conclusion as to the stability of cuprous oxide in the presence of air and moisture.[16]

c. Add 0.1*N* KI, drop by drop, to 10 ml. of 0.1*N* $CuSO_4$ until precipitation is complete. Note carefully what occurs.[17] Add an excess of 2 ml. of 0.1*N* KI, filter off the precipitate, and wash it *thoroughly* with water. Do not allow the washings to run into the original filtrate. Dilute 1 ml. of the latter with 10 ml. of water and add 3 ml. of carbon disulfide. What is extracted by the carbon disulfide?[18] To 1 ml. of the original filtrate, diluted with 10 ml. of water, add a little starch solution. Show that the result confirms the answer to the preceding question; note the color of the solid on the filter paper and tell what the substance is.[19] Write equations to express the steps by which its formation takes place.[20] What can be said as to the stability of cupric iodide?[21]

3. Reactions of Cupric Compounds. For each of the following tests use 3-ml. portions of 0.1*N* cupric sulfate.

a. Add several drops of 4*N* NaOH to 3 ml. of 0.1*N* cupric sulfate solution. Describe the appearance of the precipitate and tell what it is.[22] Now add 5 ml. more of the 4*N* NaOH. Note whether or not any appreciable quantity of the precipitate dissolves, and then boil the mixture. What does the result indicate with regard to the amphiprotic nature of the compound?[23]

b. Add a few drops of 0.1*N* potassium ferrocyanide to another portion of the cupric sulfate solution. Describe the result and tell what the precipitate is.[24] Add one drop of 0.1*N* $CuSO_4$ to 50 ml. of water contained in a 100-ml. conical flask. Swirl the liquid to insure thorough mixing and add to it 1 drop of 0.1*N* $K_4Fe(CN)_6$. Describe the result.[25] This is a sensitive test for cupric ion.

c. Place separate 3-ml. portions of 0.1*N* $CuSO_4$ in three test tubes. To one tube add a small piece of aluminum; to the second, a piece of zinc; and to the third, a piece of tin. Write an equation for each reaction, and explain the results.[26]

d. Precipitate cupric sulfide by adding 3 ml. of 0.1*N* ammonium sulfide to 3 ml. of 0.1*N* $CuSO_4$. Filter off the precipitate and wash it (on the paper) with distilled water until the odor of hydrogen sulfide is no longer perceptible. Test separately the solubility of small amounts of the solid in 4*N* and in 12*N* HCl, and in a special sodium hydroxide-sodium sulfide-sulfur reagent.* If an action does not occur in the cold, try the effect of raising the temperature. Tabulate the results.[27]

e. Write an equation for the reaction that occurs upon the addition f 1 drop of 4*N* NH_4OH to 3 ml. of 0.1*N* $CuSO_4$.[28] Now add an excess of 4*N* NH_4OH. Note the result,

* This reagent, used in qualitative analysis, contains 120 g. of NaOH, 80 g. of $Na_2S \cdot 9H_2O$, and 0.1 g. of S in a liter of aqueous solution.

write an equation to express the reaction, explain the solubility of the precipitate in the excess of ammonia, and name the deeply colored product of the reaction.[29] Pass H_2S into this solution. Explain the result and write an equation for the reaction.[30]

4. Preparation of Tetramminecupric Sulfate. Pulverize 10 g. of cupric sulfate crystals and dissolve the powder in a solution of ammonium hydroxide prepared by the addition of 10 ml. of water to 15 ml. of 15*N* ammonium hydroxide. If the resulting deep-blue solution contains any insoluble material, it should be filtered through a thin mat of asbestos wool placed in a funnel. Now stir the clear solution vigorously while slowly adding to it 15 ml. of 95 per cent alcohol. Bluish-purple crystals of tetramminecupric sulfate, $[Cu(NH_3)_4]SO_4 \cdot H_2O$, precipitate. Set these aside for an hour, and then filter. Wash the crystals by first pouring through the filter 20 ml. of a mixture of equal volumes of 95 per cent alcohol and 15*N* ammonium hydroxide, and then 10 ml. of alcohol alone. By the use of a spatula transfer the compound from the filter paper to a watch glass, and allow the crystals to dry at the temperature of the laboratory. Weigh the dry crystals on a beam balance. Record the weight,[31] and calculate the percentage yield.[32] Note carefully the color of the crystals, and set them aside in the desk for examination at the next laboratory period. Decide whether a color change is noticeable and, on this basis, make a statement as to the stability of the compound at ordinary temperatures.[33]

5. The Cuprocyanide Ion. a. Dilute 2 ml. of 0.1*N* $CuSO_4$ with an equal volume of water. Add 1 drop of 1*N* potassium cyanide solution **(Care, POISON!)**. Describe the precipitate [34] and then add 1*N* KCN drop by drop until the precipitate dissolves. Record the color of the resulting solution, write equations for the reactions that have taken place, and name the complex compound formed.[35] Pass H_2S into the solution. Result? [36]

b. Test the action of 1*N* KCN on the cuprous chloride reserved from **2a**. Describe the result, write an equation to express the reaction, and explain the solubility of the chloride in the solution of the cyanide.[37]

c. Prepare a solution of tetramminecupric sulfate by the addition of an excess of 4*N* ammonia to 3 ml. of a 0.1*N* solution of cupric sulfate. Now add 1*N* KCN drop by drop. What marks the end point of this reaction? [38] Write the equation for the reaction, and tell why it goes to completion.[39] Pass H_2S into this solution. On the basis of this result and that obtained in part (A) **3a** make a statement regarding the relative values of the instability constants of the ammoniocupric ion and the cuprocyanide ion.[40]

(B) Compounds of Silver. 1. The Silver Halides. a. Add several drops of 4*N* HCl to 5 ml. of 0.1*N* $AgNO_3$. Precipitate silver bromide and silver iodide from 5-ml. portions of 0.1*N* $AgNO_3$ by the addition of 5-ml. portions of 0.1*N* KBr and 0.1*N* KI respectively. Note the color of each of the silver halides.[1] Add 5 ml. of water to each mixture, and shake them until the precipitates settle readily on standing. Decant the liquid from the precipitates, shake them with fresh 5-ml. portions of water, and again decant the liquid. Finally, add 5 ml. of water to each of the washed halides and reserve them for use in **b**.

b. Transfer a small portion of each of the halides prepared in **a** to another test tube and test its action with 4*N* ammonia. Carefully note any differences in the behavior of the individual halides.[2] Now filter the solutions in which any silver halide remains undissolved. Acidify these filtrates, and also the solution containing silver chloride dissolved in ammonia, with 4*N* HNO_3. State the results, and tell what they prove with regard to the solubility of the silver halides in ammonia.[3] Write the equations for the interaction of ammonia with a silver halide, and the reprecipitation with nitric acid.[4] Dissolve another small portion of silver chloride in 4*N* ammonia. Add to this solution a few drops of a 0.1*N* solution of potassium iodide. Note the result and draw a conclusion as to the relative solubility of AgCl and AgI in water. Explain.[5] Tell why silver iodide fails to dissolve in ammonia.[6]

Try the action of 1*N* KCN on each of the silver halides. Results? [7] Write an equation for one of these reactions.[8] Recall the failure of silver iodide to dissolve in ammonia, and

then decide whether the instability constant of the diamminesilver ion or that of the argenticyanide ion has the smaller value; explain.[9] Expose a little silver chloride to direct sunlight. Describe the result and give a brief statement of the application of this reaction to photography.[10]

Test the action of a 0.1*M* solution of sodium thiosulfate on one of the silver halides. Result? [11] Write an equation for the reaction and tell briefly the application of this reaction to photography.[12]

Add a few drops of 0.1*N* sodium fluoride to 1 ml. of a 0.1*N* solution of silver nitrate. Result? [13] Look up and record the solubility of AgF in water.[14]

2. Silver Oxide. Add a drop of 4*N* ammonium hydroxide to 3 ml. of 0.1*N* $AgNO_3$. Describe the result and write an equation for the reaction.[15] Now add an excess of the ammonia. Write an equation to express the reaction which results in the solution of the precipitate.[16] In the same way test the action of 4*N* NaOH on 0.1*N* $AgNO_3$. What does the test show with regard to the amphiprotic nature of silver oxide? [17]

3. Silver Chromate. Note the characteristic color of the precipitate formed on the addition of 0.1*M* potassium chromate to 2 ml. of 0.1*N* $AgNO_3$. Divide the precipitate between two test tubes and test its solubility in 4*N* HNO_3 and in 4*N* CH_3COOH. Explain the results.[18]

Add 3 ml. of a 0.1*N* solution of sodium chloride to 3 ml. of 0.1*N* $AgNO_3$. Shake the tube to bring about the coagulation of the silver chloride. Allow the precipitate to settle and add to the mixture 1 drop of 0.1*N* NaCl. If no further precipitation occurs, filter the mixture. If precipitation is not complete, add several more drops of 0.1*N* NaCl and then filter. If the filtrate is not clear, pour it back through the same filter. Now add a few drops of 0.1*M* K_2CrO_4 to the filtrate. Note the result, and decide whether the halide or the chromate is the less soluble salt.[19] Repeat this experiment, using 0.1*N* sodium (or potassium) iodide. Is silver iodide or silver chromate the less soluble of these two salts? [20]

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX

COPPER AND SILVER

(A) Copper and Its Compounds. *Copper*

1.

2.

3.

4.

Cuprous compounds

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(A) Cont'd

7.

8.

9.

10.

11.

12.

13.

14.

15.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(A) Cont'd

16.

17. **18.**

19.

20.

21.

Reactions of cupric compounds

22.

23.

24.

25.

26.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(A) Cont'd

27.

28.

29.

30.

Preparation of tetramminecupric sulfate

31. **32.**

33.

The cuprocyanide ion

34.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(A) Cont'd

35.

36.

37.

38.

39.

40.

(B) Compounds of Silver. *The silver halides*

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(B) Cont'd

3.

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(B) Cont'd

9.

10.

11.

12.

13.

Silver oxide

15.

16.

17.

Name (last name first) _____ Desk No. _____ Date _____

Experiment XLIX (Cont'd)

(B) Cont'd

Silver chromate

18.

19. **20.**

Experiment L

ZINC, CADMIUM, AND MERCURY

Discussion. Zinc, cadmium, and mercury exhibit a rather close family resemblance. Their normal valence of 2 is in keeping with their position in Group II of the periodic system. Mercury shows a formal oxidation state of +1, inasmuch as it exists in the form of the Hg_2^{++} in the mercurous series of compounds.

(A) Properties and Reactions of Compounds of Zinc. 1. Zinc Hydroxide. a. Add 2 drops of 4*N* NH_4OH to 3 ml. of a 0.1*N* solution of zinc nitrate. Describe the precipitate that forms.[1] Now add drop by drop more 4*N* ammonia and shake the mixture after each addition of ammonia. Note the effect produced by an excess of ammonia, and write equations for the reactions that have taken place.[2]

b. Repeat **a**, using 4*N* NaOH instead of ammonium hydroxide. Write the equations for the reactions.[3] Now precipitate $Zn(OH)_2$ by the addition of 4*N* NaOH to 0.1*N* $Zn(NO_3)_2$ and then acidify the mixture with 4*N* HCl. On the basis of these tests, make a statement regarding the amphiprotic character of zinc hydroxide.[4]

2. Zinc Sulfide. a. Acidify two separate 3-ml. portions of 0.1*N* $Zn(NO_3)_2$, the one with 4 or 5 drops of 4*N* acetic acid, the other with the same amount of 4*N* HCl. Pass hydrogen sulfide into each solution. Explain the results.[5] On the basis of these results, explain why zinc sulfide would be more completely precipitated by hydrogen sulfide from a solution of zinc acetate than from a solution of zinc nitrate.[6] Why would zinc sulfide be precipitated more completely from zinc nitrate by ammonium sulfide than by hydrogen sulfide?[7]

b. A 0.3*M* solution of hydrochloric acid readily dissolves ZnS or prevents its formation. In this experiment 3 ml. of a zinc nitrate solution were acidified with 5 drops of 4*N* HCl. Calculate the molarity of this solution with respect to HCl. Assume the volume of a drop to be 0.05 ml. Disregard the hydrolysis of the hydrated zinc ion.[8]

(B) Properties and Reactions of Cadmium Compounds. 1. Cadmium Hydroxide. Add 5 drops of 4*N* NaOH to 3 ml. of a 0.1*N* solution of cadmium nitrate. Describe the result.[1] Now determine whether or not the hydroxide is amphiprotic.[2]

2. The Tetramminecadmium Ion. a. Add 4*N* NH_4OH, drop by drop, to 3 ml. of 0.1*N* $Cd(NO_3)_2$ until the precipitate first formed goes into solution. Write equations for the reactions involved.[3] Divide the solution into three equal portions and reserve them for further use in this experiment.

b. Pass hydrogen sulfide into one portion of the solution just prepared. Note the result, and write an equation for the reaction.[4] Now prepare a solution of tetramminecupric sulfate from 1 ml. of 0.1*N* $CuSO_4$ and the necessary quantity of 4*N* NH_4OH. Mix the tetramminecupric sulfate solution with a portion of the tetramminecadmium nitrate (from **a**) and pass H_2S into this mixture. Describe the result.[5] Recall the result obtained with H_2S in Exp. XLIX, part (A)**3e**, and conclude whether or not cadmium could be detected by the precipitation of its sulfide from a mixture of the ammonia complexes of copper and cadmium; explain.[6]

3. The Cyanocadmium Ion. a. Add a drop of 1*N* KCN to 2 ml. of 0.1*N* $Cd(NO_3)_2$. Describe the precipitate formed, and write an equation for the reaction.[7] Now add 1*N* KCN until the precipitate just dissolves. Write an equation for the reaction that has taken

place.[8] Pass H_2S through the solution containing the complex cyanocadmium ion. Note the result and express the reaction by an equation.[9]

b. To the remainder of the solution of tetramminecadmium nitrate prepared in **2a** above, add 0.5 ml. of 1*N* KCN. This converts the ammonia complex to the cyanocadmium ion. Write the equation for this reaction.[10] Now prepare a solution of tetramminecupric sulfate from 1 ml. of 0.1*N* $CuSO_4$, and then convert it into potassium cuprocyanide by the dropwise addition of 1*N* KCN (see Exp. XLIX, part (A)**5c**). Mix this solution with the one containing the cyanocadmium ion, and then pass H_2S into the mixture. Describe the result, and tell whether or not this procedure may be used to detect cadmium in the presence of copper.[11] What does the result indicate as to the relative degree of dissociation of these complex ions of cadmium and copper? [12]

4. Cadmium Sulfide. a. Precipitate CdS from 3 ml. of 0.1*N* $Cd(NO_3)_2$. Filter the mixture and wash the precipitate on the filter until the odor of H_2S is no longer perceptible. Reserve a small portion of the sulfide for use in **b.** Now prepare HCl of the following concentrations, using 0.5 ml. of the 4*N* acid and the required amount of water: 0.1*N*, 0.2*N*, 0.3*N*, 0.4*N*, and 0.5*N*. Test the solubility of small portions of the sulfide in each of these acid solutions. Results? [13] On the basis of these results decide upon the maximum acid concentration permissible in a solution from which cadmium sulfide is to be precipitated.[14]

b. Test the solubility of cadmium sulfide in the sodium sulfide—sodium hydroxide—sulfur reagent (see footnote to Exp. XLIX, part (A)**3d**) by gently boiling a small amount of CdS with 3 ml. of the reagent for a period of 2 min. Result? [15]

(C) Properties and Reactions of Compounds of Mercury. 1. Mercurous Chloride. Add several drops of 4*N* HCl to 2 ml. of a 0.1*N* solution of mercurous nitrate. Describe the result, and write an equation for the reaction.[1] Filter the mixture, wash the precipitate on the filter paper, and then add a few drops of 4*N* NH_4OH to the precipitate. Result? [2] Write an equation for the reaction (Text).[3]

2. Mercuric Chloride. a. Add several drops of 4*N* HCl to 2 ml. of 0.1*N* mercuric nitrate. Compare the result with that obtained in **1a**, and make a statement with regard to the solubility of mercuric chloride in water.[4] Confirm this statement by reference to a table of solubilities (Text). Record the solubility of $HgCl_2$.[5]

b. Add 6 drops of a 0.1*N* solution of stannous chloride to 3 ml. of a 0.1*N* solution of mercuric chloride. Note the color of the precipitate, and write the equation for the reaction.[6] Now add an excess of the stannous chloride solution. Tell what change is noted.[7] Write the equation for the reaction and state the function of the stannous ion in this and in the preceding reaction.[8]

3. Mercuric Iodide. Treat 2 ml. of a 0.1*N* solution of mercuric chloride with 1 drop of 0.1*N* KI. Record the appearance of the precipitated HgI_2.[9] Does it change color on standing for several minutes? [10] Now add 0.1*N* KI drop by drop until a change occurs. Explain what takes place, and write the equation for the reaction.[11]

Name (last name first) _____ Desk No. _____ Date _____

Experiment L

ZINC, CADMIUM, AND MERCURY

(A) Properties and Reactions of Compounds of Zinc. *Zinc hydroxide*

1.

2.

3.

4.

Zinc sulfi

5.

6.

7.

REPORT SHEET [*Exp. L*]

Name (last name first) _____ Desk No. _____ Date _____

Experiment L (Cont'd)

(A) Cont'd

8.

(B) Properties and Reactions of Cadmium Compounds. *Cadmium hydroxide*

1.

2.

The tetramminecadmium ion

3.

4.

5.

6.

Name (last name first) _____ Desk No. _____ Date _____

Experiment L (Cont'd)

(B) Cont'd

The cyanocadmium ion

7.

8.

9.

10.

11.

12.

Cadmium sulfide

13.

14.

Name (last name first) _____ Desk No. _____ Date _____

Experiment L (Cont'd)

(C) Properties and Reactions of Compounds of Mercury. *Mercurous chloride*

1.

2.

3.

Mercuric chloride

4.

5.

6.

7.

8.

Name (last name first) _____ Desk No. _____ Date _____

Experiment L (Cont'd)

(C) Cont'd

Mercuric iodiae

9. **10.**

11.

Experiment LI

ALUMINUM

Discussion. Aluminum is the most commonly occurring and the only industrially important metal among all the elements placed in Group III of the periodic system. Its position in the activity series of the metals shows it to be an active element. As such, its atom readily loses three electrons to form trivalent ions. However, its solid crystalline halides—with the exception of the fluoride—are essentially nonionic in character. This fact is indicated by their relatively low melting points, their solubility in organic solvents, and their low degree of conductivity in the molten state. The fluoride is difficultly soluble in water, but the other halides are readily soluble to yield the hydrated aluminum ion and the halide ions.

(A) Properties and Reactions of Aluminum and Its Compounds. 1. Aluminum. a. Place a few aluminum turnings in each of three test tubes and try the action of the metal with $4N$ HCl, with $4N$ HNO_3, and with $4N$ H_2SO_4. Warm the solutions, if necessary, to start the reactions. Tell with which acid the metal acts most readily, and with which the least readily.[1] Now test the action of both cold and hot $16N$ HNO_3 on a few turnings of the metal. Note the results, and give a possible reason for the observed behavior.[2] Which acid might be used safely to remove the deposit from an aluminum container in which hard water had been boiled? [3]

b. Test the action of $4N$ NaOH on aluminum turnings. If a reaction does not take place in the cold, try the effect of heat. As soon as a vigorous reaction sets in, introduce a lighted wooden splint into the tube. Tell which gas is evolved, and write the equation for the reaction.[4]

2. Aluminum Hydroxide. a. Add 3 drops of $4N$ NaOH to 3 ml. of $0.1N$ $Al(NO_3)_3$. Name and describe the precipitate formed.[5] Now add, drop by drop, $4N$ NaOH until an excess of the reagent brings about a noticeable change. Shake the test tube during the addition of the sodium hydroxide. Describe the result, and write the equation for the reaction.[6]

b. Repeat **a**, using $4N$ NH_4OH in place of sodium hydroxide. Note the observed difference in the results.[7]

c. Precipitate aluminum hydroxide from 3 ml. of $0.1N$ $Al(NO_3)_3$ by the use of $4N$ NH_4OH. Filter the mixture, wash the precipitate with distilled water, and then transfer part of the hydroxide to a small watch glass. Now add $4N$ HCl to the hydroxide. Give the result, and write the equation for the reaction.[8] On the basis of this behavior, and that noted in **a**, how is this hydroxide to be classified? [9] Give a possible explanation for the failure of aluminum hydroxide to dissolve in a solution of ammonia.[10]

3. Hydrolysis of Aluminum Salts. Test separately, with litmus paper, $0.1N$ solutions of aluminum chloride, sulfate, and nitrate. Record the results, and explain them by means of equations.[11] How does the reaction of the hydrated aluminum ion with water cause this substance to be classified according to the Brönsted-Lowry theory of acids and bases? [12]

4. Aluminum Sulfide. Treat 5 ml. of $0.1N$ $AlCl_3$ with 1 ml. of a $1N$ solution of ammonium sulfide. Describe what takes place.[13] Filter the mixture and wash the precipitate with water until the odor of hydrogen sulfide is no longer perceptible. How could it be ascertained whether or not the precipitate is aluminum sulfide? [14] Test the procedure, record the result, and state the conclusion reached.[15] Write equations to show what actually takes place on the addition of a solution containing sulfide ion to a solution of an aluminum salt.[16] (Text) Explain the completeness of the hydrolysis of aluminum sulfide.[17] Suggest a means of preparing aluminum sulfide.[18]

5. Tests for the Aluminum Ion. a. Add a drop of a 0.1*N* solution of cobalt nitrate, ($Co(NO_3)_2$), to 3 ml. of 0.1*N* $Al(NO_3)_3$, and then add an excess of 4*N* NH_4OH. Place a few small pieces of shredded asbestos at the bottom of a filter paper placed in a funnel, and then filter the foregoing mixture through this paper. Wash the precipitate several times with small amounts of water. Carefully collect the asbestos, with the adhering precipitate, in the loop of a platinum or nichrome wire. Heat the material on the wire in the hottest part of a gas flame until the dark-blue color of cobalt aluminate appears. Write an equation to express the formation of this compound.[19]

b. To 1 ml. of 0.1*N* $AlCl_3$ add drop by drop 4*N* NaOH until the precipitate of aluminum hydroxide just dissolves, and then add 1 drop of phenolphthalein solution. Acidify the solution by the dropwise addition of 4*N* acetic acid (**Care!** Not more than 1 drop in excess) and add to it 1 drop of a 0.1 per cent solution of aluminon * and 2 ml. of 1*N* $(NH_4)_2CO_3$. Result? [20] The bright-red precipitate of the dye adsorbed on or combined with aluminum hydroxide is a sensitive test for the aluminum ion. This precipitate is known as a "lake." [See part (B).]

(B) Lakes. a. Hydroxides of certain metals, such as aluminum, chromium, and iron, are often partly colloidal when precipitated in neutral or slightly acid solutions. These colloidal hydroxides are positively charged, while the dyes used to give the color to the lakes are negatively charged and are therefore adsorbed by the hydroxides. In basic solutions the hydroxides are negatively charged and do not adsorb negatively charged dyes. However, once these lakes are formed they are stable in alkaline solutions. Certain lakes are true inner complex salts (Text).

Add 0.1 g. of eosin (stockroom) to 5 ml. of water which has been made ammoniacal with several drops of 4*N* NH_4OH. Now add 5 ml. of 0.1*N* $Al_2(SO_4)_3$, shake the mixture, and then heat it to boiling. Filter the mixture and thoroughly wash the precipitate with water. Note whether or not the color is removed during the process of washing.[1] Record the color of the lake.[2]

(C) Aluminum Hydroxide as a Mordant. Place a piece of cotton cloth in a test tube containing 10 ml. of 0.1*N* $Al_2(SO_4)_3$. Boil the solution 3 min. and then transfer the cloth to a test tube containing a dilute solution of ammonia (1 ml. of 4*N* NH_4OH + 6 ml. of water). Bring the liquid to the boiling point and then shake the contents of the tube 2 min. Now the cloth is said to be mordanted with aluminum hydroxide.

Obtain 10 ml. of an aqueous suspension of alizarin and mix it well with 50 ml. of water contained in a beaker. Immerse in this suspension the mordanted cloth and also a piece which is untreated. Heat the mixture to its boiling point and stir the pieces of cloth 10 min. with a glass rod. At the end of this time remove the cloths, and wash them in running water from the tap. Record the results, and account for the difference observed.[1]

(D) Preparation of Ordinary Alum. Give the general formula of an alum.[1] Dissolve 0.02 of a gram-molecular weight of $Al_2(SO_4)_3 \cdot 18H_2O$ in 25 ml. of water. Record the calculated weight,[2] and check with the laboratory instructor as to its correctness. Now heat the solution to boiling, and then add to it the calculated amount [3] of finely powdered potassium sulfate. Keep the solution at its boiling point and stir it until all of the potassium sulfate has dissolved. Filter the hot solution into a small beaker, cover the beaker with a watch glass, and set it aside in the desk until the next laboratory period. Usually a single large mass, composed of smaller crystals, will be formed. Remove the alum and dry it by pressing it between sheets of filter paper. Weigh the alum on a trip balance. Record the weight,[4] and calculate the percentage yield.[5] Are the crystals of all alums isomorphous? [6] List the other trivalent elements that form alums.[7] Does a solution of an alum contain a complex ion? [8] Try to precipitate aluminum hydroxide from a solution of alum. Record the result and tell whether or not it confirms the answer to the preceding question.[9]

* The ammonium salt of aurin tricarboxylic acid.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LI

ALUMINUM

(A) Properties and Reactions of Aluminum and Its Compounds

Aluminum

1.

2.

3.

4.

Aluminum hydroxide

5.

6.

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LI (Cont'd)

(A) Cont'd

8.

9.

10.

Hydrolysis of aluminum salts

11.

12.

Aluminum sulfide

13.

14.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LI (Cont'd)

(A) Cont'd

15.

16.

17.

18.

Tests for the aluminum ion

19.

20.

(B) Lakes

1. **2.**

Name (last name first) _____ Desk No. _____ Date _____

Experiment LI (Cont'd)

(C) Aluminum Hydroxide as a Mordant

1.

(D) Preparation of Ordinary Alum

1. **2.** **3.**

4. **5.**

6. **7.**

8. **9.**

Experiment LII

TIN AND LEAD

Discussion. Tin and lead are the commonly occurring metals in the *A* division of Group IV of the periodic system; germanium, the other member of this division, is widely distributed in nature but occurs only in very small amounts. Tin and lead are moderately strong reducing agents in acid solution and show a powerful reducing action in alkaline solution. The metals exist in oxidation states of +2 and +4. In the latter state their compounds are chiefly covalent in character. As examples of this fact, the tetrachlorides of both metals are liquids at ordinary temperatures.

(A) Properties and Reactions of Tin and Its Compounds. 1. Tin. a. Place about 0.2 g. of mossy tin in a test tube and add to it 5 ml. of 12*N* HCl. Note the relative rate—slow or rapid—of evolution of the gas.[1] Pure tin does not evolve hydrogen readily with acids because of overvoltage effects. Boil the mixture 1 min., then dilute it to a volume of 20 ml., and saturate it with hydrogen sulfide. Note the color of the precipitate and write the equation for its formation.[2]

b. Treat about 0.2 g. of mossy tin with 3 ml. of 16*N* HNO_3. If no action occurs, add 1 or 2 drops of water. What is the product of the reaction? (Text) [3] What is the oxidation state of tin in the white solid? [4]

c. Place about 0.2 g. of mossy tin in a small evaporating dish and add to it 10 ml. of 4*N* NaOH. Bring the solution to its boiling point in order to cause the solution of the metal. Add more sodium hydroxide, if necessary, to dissolve the tin, and then transfer the solution to a small conical flask. Drop in a piece of litmus paper and acidify the solution with 12*N* HCl. Do not add an excess of the acid. Now saturate the solution with hydrogen sulfide. Compare the color of the precipitate with that of the sulfide obtained in **a.**[5] Write equations for all the reactions that have taken place.[6]

2. Stannous Chloride. Place 10 ml. of 1*N* $SnCl_2$ in a 50-ml. beaker and set it aside in the desk until the next laboratory period. At that time test the action of 2 drops of this solution on 3 ml. of a 0.1*N* solution of mercuric chloride. Result? [7] Recall the action of stannous chloride on mercuric chloride (Exp. L, part (C)**2b**) and tell what must have taken place during the exposure of the solution of stannous chloride to the air.[8]

3. Hydrated Stannous Oxide (Stannous Hydroxide). Add 1 ml. of 4*N* NaOH to 4 ml. of 1*N* $SnCl_2$. Divide the mixture into two equal parts. To one part add an excess of 4*N* NaOH (reserve this solution for use in **4**) and to the other an excess of 4*N* HCl. On the basis of these results classify the hydrated oxide as basic, acidic, or amphiprotic.[9] Write equations for all the reactions.[10] (Consult the text for the action of sodium hydroxide on stannous chloride.)

4. Reducing Action of the Stannite Ion. Precipitate bismuth hydroxide from 0.1*N* $Bi(NO_3)_3$ by the action of 4*N* NH_4OH. Filter the mixture, and wash the precipitate on the paper until the odor of ammonia is no longer perceptible. Treat the precipitate with the solution of sodium stannite prepared in **3.** Describe the result, and write the equation for the reaction.[11]

5. Stannic Chloride. a. Test the action of several drops of a 0.1*M* solution of stannic chloride on 1 ml. of 0.1*N* $HgCl_2$. Result? [12] Place an iron nail in a solution made by adding 2 ml. of 4*N* HCl to 5 ml. of 0.1*M* $SnCl_4$. When the evolution of hydrogen has ceased, test

the resulting solution by adding to it a few drops of 0.1*N* $HgCl_2$. Explain the result and write an equation to express the change undergone by the stannic chloride.[13]

b. Add 4*N* NaOH drop by drop to 2 ml. of 0.1*M* $SnCl_4$ until the precipitate formed dissolves. Write equations for the reactions.[14] Reserve this solution for use in **6.**

6. Stannic Sulfide. Drop a piece of litmus paper into the solution of sodium stannate reserved from **5b** and then add 4*N* HCl to the solution until it is acid to litmus. Saturate this solution with hydrogen sulfide, filter the mixture, and then wash the precipitate on the filter with small amounts of water. Test the washings separately with litmus, and, when they are no longer acid in reaction, pour 5 ml. of hot sodium sulfide-sodium hydroxide-sulfur reagent through the filter. If no action is apparent, reheat the reagent and pour it through the filter again and again until the precipitate dissolves. Now add 4*N* HCl dropwise to the solution. Result? [15] Compare the color of the precipitate with that of the sulfide formed in part (A)**1c** and that of the sulfide precipitated above with hydrogen sulfide.[16] What are these precipitates? [17] Write equations for all the reactions carried out in this paragraph.[18] Explain why stannic sulfide dissolves in the sodium sulfide reagent.[19]

(B) Properties and Reactions of Compounds of Lead. 1. The Halides of Lead. a. Place separate 3-ml. portions of 0.1*N* $Pb(NO_3)_2$ in four test tubes. To the first tube add 1 drop of 0.1*N* NaI. Shake the tube, and then add more 0.1*N* NaI drop by drop (shake the tube after the addition of each drop) until a permanent precipitate is obtained. Repeat this procedure with each of the other three solutions of $Pb(NO_3)_2$, but use separately 0.1*N* solutions of NaF, NaCl, and NaBr. Describe the results and tell which of the halides is the least soluble.[1] Consult a table of solubilities and arrange these halides in the order of decreasing solubility; include the solubility values.[2]

b. Precipitate lead chloride by adding 3 drops of 4*N* HCl to 2 ml. of 0.1*N* $Pb(NO_3)_2$. Heat the mixture. What does the result show regarding the relative solubility of lead chloride in hot and in cold water? [3] Reprecipitate the lead chloride by cooling its solution under running water from the tap. Now add 12*N* HCl dropwise to the mixture until a total of from 1 to 2 ml. of the acid has been added. *Explain* what takes place.[4]

c. Precipitate lead chloride from 4 ml. of 0.1*N* $Pb(NO_3)_2$ by the addition of 6 drops of 4*N* HCl. Filter the mixture, divide the filtrate equally between two test tubes, and then add 1 ml. of 1*N* CH_3COONH_4 to each tube. Pass hydrogen sulfide into one of the solutions and add several drops of 0.1*M* K_2CrO_4 to the other. Describe the results and write an equation for each of the reactions.[5] What do these tests show with regard to the relative extent to which lead ions are removed by chloride ions and by sulfide or chromate ions? [6]

2. Lead Hydroxide. Determine whether or not lead hydroxide is amphiprotic by adding an excess of 4*N* NaOH to 2 ml. of 0.1*N* $Pb(NO_3)_2$. State the conclusion reached, and write equations for the reactions that have taken place.[7] Repeat this procedure, using 4*N* NH_4OH in place of the sodium hydroxide. Record the result and explain the observation made.[8]

3. Lead Sulfate. Precipitate lead sulfate by the addition of 1 ml. of 4*N* H_2SO_4 to 4 ml. of a hot 0.1*N* solution of lead nitrate. Filter the mixture and wash the lead sulfate on the filter paper. Test the solubility of separate small amounts of the sulfate in 2 ml. of (*a*) 4*N* NaOH, (*b*) 36*N* H_2SO_4, and (*c*) 6*N* CH_3COONH_4. Try the effect of heat if no change is apparent at ordinary temperatures; it may be necessary to boil the mixture of lead sulfate and ammonium acetate. Record the results.[9] Write an equation to express each reaction, and give an explanation of the solubility of lead sulfate in each of these reagents.[10] Reserve each of the solutions for further tests.

Pour the solution of lead sulfate in 36*N* H_2SO_4 into 15 ml. of water. Tell what takes place, and write equations to explain the result.[11]

4. Lead Chromate. Add several drops of 0.1*M* K_2CrO_4 to the solution made by dissolving lead sulfate in 6*N* CH_3COONH_4. What does the result show with regard to the

relative concentration of the lead ion in the solution just tested, and in a saturated solution of lead chromate?[12] Repeat the test, using 0.1*M* K_2CrO_4 and the solution of sodium plumbite prepared by dissolving lead sulfate in sodium hydroxide. Explain the difference in the result of this test and the preceding one.[13]

5. Lead Sulfide. Pass hydrogen sulfide through 4 ml. of a 0.1*N* solution of lead acetate. Filter the mixture and wash the precipitate on the filter paper until the odor of hydrogen sulfide is no longer perceptible. Transfer part of the precipitate to a 50-ml. beaker and test its solubility in the sodium hydroxide-sodium sulfide-sulfur mixture by boiling the lead sulfide 1 min. with 10 ml. of the reagent. Is there a noticeable diminution in the quantity of the black sulfide?[14] Confirm the observation by filtering the mixture and then acidifying the filtrate with 4*N* HCl. Note the presence or absence of a precipitate of lead sulfide, and, on the basis of this observation, draw a conclusion as to the solubility of lead sulfide in the reagent.[15]

Name (last name first) _____ Desk No. _____ Date _____

Experiment LII

TIN AND LEAD

(A) Properties and Reactions of Tin and Its Compounds. *Tin*

1.

2.

3. **4.**

5.

6.

Stannous chloride

7.

8.

Hydrated stannous oxide (*stannous hydroxide*)

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LII (Cont'd)

(A) Cont'd

10.

Reducing action of the stannite ion

11.

Stannic chloride

12.

13.

14.

Stannic sulfide

15.

16. **17.**

Name (last name first) _____ Desk No. _____ Date _____

Experiment LII (Cont'd)

(A) Cont'd

18.

19.

(B) Properties and Reactions of Compounds of Lead. *The halides of lead*

1.

2.

3.

4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LII (Cont'd)

(B) Cont'd

6.

Lead hydroxide

7.

8.

Lead sulfate

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LII (Cont'd)

(B) Cont'd

10.

11.

Lead chromate

12.

13.

Lead sulfide

14.

Experiment LIII

CHROMIUM

Discussion. Chromium has three oxidation states, of which the maximum is +6 in chromium trioxide (CrO_3) and the related chromates ($CrO_4^{=}$) and dichromates ($Cr_2O_7^{=}$). In chromous compounds the chromous ion (Cr^{++}) is in an oxidation state of +2, and in chromic compounds and chromites (CrO_2^{-}) the element is in an oxidation state of +3. Chromous ion (Cr^{++}) is a powerful reducing agent, as is shown by the electrode potential of −0.41 volts for $Cr^{++} \rightleftharpoons Cr^{+++} + 1\epsilon$. On the other hand, the dichromate ion ($Cr_2O_7^{=}$) is a strong oxidizing agent in acid solution. The oxidation-reduction potential of

$$Cr_2O_7^{=} + 14H_3O^{+} + 6\epsilon \rightleftharpoons 2Cr^{+++} + 21H_2O$$

is +1.36 volts.

(A) Chromous Chloride. Prepare a solution of chromous chloride as directed in Exp. XVIII part (C)**3,** but use a solution made from 0.5 g. of chromic chloride ($CrCl_3 \cdot 6H_2O$) in 5 ml. of water instead of the 0.1*M* solution of $CrCl_3$. Add 2 ml. of 12*N* HCl to the chromic chloride solution, and then carry out the reduction with 1 g. of mossy zinc. After the evolution of hydrogen ceases, quickly pour about 1 ml. of the chromous chloride solution into a test tube containing approximately 0.2 g. of solid cupric sulfate (*Do not shake the tube containing this mixture!*) and then immediately replace the stopper in the tube containing the chromous chloride. What is the finely divided reddish powder formed by the reaction? [1] Write the equation for the chemical change.[2] Now test the action of the solution of chromous chloride on 0.1*N* $HgCl_2$. Note carefully what occurs, describe the results, and write equations for the reactions that have taken place.[3]

(B) Properties and Reactions of Chromic Compounds. a. Add 4*N* NH_4OH drop by drop to 2 ml. of 0.1*M* $CrCl_3$ until no more precipitate is formed. Describe the precipitate, and then determine whether or not it is soluble in an excess of ammonia.[1]

b. Add 4*N* NaOH dropwise to 2 ml. of 0.1*M* $CrCl_3$ until the precipitate that forms at first is completely dissolved. Write equations to show what reactions have taken place.[2] Name the ion of which the chromium is now a constituent.[3] Now boil the solution 1 min. Result? [4] Test the solubility of this precipitate in an excess of 4*N* NaOH. Result? [5]

c. Add 0.5 ml. of 1*N* $(NH_4)_2S$ to 3 ml. of 0.1*M* $CrCl_3$. Filter the mixture and wash the precipitate on the filter until the odor of hydrogen sulfide is no longer perceptible. Propose a test to determine whether or not the precipitate is a sulfide.[6] If the laboratory instructor approves the test, try it out. Tell the result of the test, and write equations to show how the precipitate was formed.[7]

(C) Chromates and Dichromates. a. Prepare a solution of sodium chromite from 3 ml. of 0.1*M* $CrCl_3$ and a 4*N* solution of sodium hydroxide. Stir 3 per cent H_2O_2 into the resulting solution until the liquid assumes a bright-yellow color. Tell what the colored ion is, and write an equation to show its method of formation.[1] Now add 1 ml. of 2*N* Na_2CO_3 to the solution and boil the resulting liquid until it is about half of its original volume. This treatment decomposes any excess of hydrogen peroxide.

b. To the solution from **a** add 4*N* H_2SO_4 drop by drop until the solution is distinctly acid to litmus. What is the cause of the change in color? Write the equation for the reaction.[2]

c. To the solution from **b** add 4*N* NaOH until the mixture is alkaline to litmus. Tell what color change is observed and write the equation for the reaction.[3]

d. Test the action of several drops of each of the following solutions on 1-ml. portions of 0.1*M* K_2CrO_4: 0.1*N* $AgNO_3$, 0.1*N* $BaCl_2$, 0.1*N* $Pb(CH_3COO)_2$, and 0.1*N* $ZnSO_4$. Record the formula, name, and color of each precipitate.[4]

e. Add 3 drops of 4*N* H_2SO_4 to a solution containing 3 drops of 0.1*M* $K_2Cr_2O_7$ in 5 ml. of water. To the acidified solution add 5 ml. of diethyl ether (ordinary ether). Place the thumb over the mouth of the test tube, and shake the mixture. Note whether or not a colored substance is extracted by the ether, and then add a drop or two of 3 per cent H_2O_2. Shake the tube again and then allow the liquid to separate into its two layers. Result?[5] How could this test be applied if the chromium was originally present as Cr^{+++}?[6] An excess of either the dichromate or the hydrogen peroxide renders the test less delicate or may destroy the colored substance entirely. What is said to be the formula of the blue compound? (Text)[7]

(D) Preparation of Chrome Alum. Cover 5 g. of finely powdered potassium dichromate in a 100-ml. beaker with 20 ml. of water, and add to the mixture the calculated amount of 36*N* H_2SO_4 necessary to form the sulfates of potassium and chromium. Stir the mixture during the addition of the acid. Record the weight of sulfuric acid needed and also the volume of 36*N* H_2SO_4 which contains the required weight of the acid.[1] The addition of the sulfuric acid should raise the temperature enough to bring about the solution of the dichromate, but, if it is necessary, heat the solution a little longer. When all of the solid has dissolved, cool the solution to 40° by placing the beaker in an evaporating dish containing a mixture of ice and water. Remove the beaker from the dish, stir the liquid vigorously with a thermometer, and add 95 per cent alcohol drop by drop until the temperature begins to rise. Again cool the solution to 40° or below, and then continue the dropwise addition of alcohol until a total of 10 ml. has been added. Throughout the addition of alcohol the temperature should be kept between 35 and 45°. If the temperature begins to rise suddenly, and should get as high as 50°, drop a piece of ice into the solution. The addition of too much alcohol at one time may cause the reaction to proceed so violently that part of the solution will be ejected from the beaker. After all the alcohol has been added, set the solution aside in the desk until the next laboratory period. Crystallization takes place during the intervening time.

What is the reducing agent in this reaction?[2] Name the odorous oxidation product of alcohol formed in the reaction.[3] Write the equation for the reaction by which the dichromate is reduced.[4]

Filter the crystals on a suction filter and free them from liquid. Dry the crystals between sheets of filter paper or paper towels, and then weigh the alum. Record the weight, and calculate the percentage yield.[5]

In order to prepare large deep-purple crystals of the alum, make a saturated solution of it at 35°, decant the solution from undissolved solute, and warm the clear liquid to 45°. Now drop in 2 or 3 very small crystals to serve as nuclei, and then set the solution aside until the next laboratory period. The large crystals obtained should be quickly dried and then preserved in a stoppered bottle to prevent efflorescence.

Write the formula of solid chrome alum, and tell whether it is isomorphous with ordinary alum.[6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment LIII

CHROMIUM

(A) Chromous Chloride

1.

2.

3.

(B) Properties and Reactions of Chromic Compounds

1.

2.

3. 4.

5.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LIII (Cont'd)

(B) Cont'd

6.

7.

(C) Chromates and Dichromates

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LIII (Cont'd)

(C) Cont'd

5.

6.

7.

(D) Preparation of Chrome Alum

1.

2. **3.**

4.

5.

6.

Experiment LIV

MANGANESE

Discussion. It is interesting to note that, although manganese is one of the more abundant elements, masurium and rhenium, in the same subgroup with manganese, exist in very small amounts.

Manganese is known to exist in six oxidation states. Of these, the +1 state is by far the least common; it is found in the coordination complex $K_5[Mn(CN)_6]$. In the +2 series are the familiar manganous compounds; the only stable Mn^{+3} compounds capable of being prepared in aqueous solution are those which are slightly soluble, or are slightly dissociated complexes, for example, K_2MnF_5; the well known MnO_2 is the only very stable representative of Mn^{+4}, although fairly stable manganites, as $CaMn_2O_5$, may be prepared; manganates and permanganates, containing Mn^{+6} and Mn^{+7} respectively, are the chief representatives of these two oxidation states.

The +2 and +3 oxidation states are basic, the +4 is amphiprotic, while the two higher states are acidic.

(A) Properties and Reactions of Manganous Compounds. Place 2 ml. of a 0.1*M* solution of manganous nitrate in one test tube, and in a second tube place another 2-ml. portion of the same solution and 1 ml. of 1*N* NH_4Cl. To the first tube add several drops of 4*N* NaOH. Describe the result and tell what the precipitate is.[1] Shake the contents of the tube and allow the mixture to remain exposed to the air for a time. What change is observed?[2] Write the formula of the substance formed and make a general statement covering the ease with which various manganous salts are oxidized in the air (Text).[3]

To the second tube, containing a mixture of manganous nitrate and ammonium chloride, add 4 or 5 drops of 4*N* NH_4OH. What is the immediate result?[4] What is the result after exposure to the air for a time?[5] Identify the product of the reaction.[6] Make a statement in regard to the solubility of manganous hydroxide in ammonium salts.[7]

(B) Manganese in an Oxidation State of +3. To 2 ml. of 0.1*M* $Mn(NO_3)_2$ add several drops of 4*N* NaOH and 1 ml. of 3 per cent H_2O_2. Record the result, and complete and balance the following equation:[1]

$$Mn^{++} + O_2^{=} \rightarrow MnO(OH)\downarrow$$

Filter off the precipitate, wash it first with several milliliters of water containing 5 drops of 4*N* NaOH, and then with 2 ml. of water. Now treat the precipitate on the paper with a mixture of 2 ml. of 4*N* HNO_3 and from 8 to 10 drops of 3 per cent H_2O_2. Result?[2] Complete and balance the equation for the reaction:[3]

$$MnO(OH) + H_2O_2 \rightarrow Mn^{++} + O_2\uparrow$$

What class of agent is hydrogen peroxide in this reaction?[4]

(C) The Permanganate Ion. **a.** Boil 2 ml. of 0.1*M* $Mn(NO_3)_2$ with 0.5 g. of lead dioxide and 5 ml. of 16*N* HNO_3. After the solution has been boiled about 1 min., allow it to stand until suspended solid settles. Note the color of the supernatant liquid, and write the equation for the reaction.[1]

b. Acidify 2 ml. of 0.1*M* $Mn(NO_3)_2$ with 0.5 ml. 4*N* HNO_3 and then add a small amount (about 0.02 g.) of solid sodium bismuthate, $NaBiO_3$. Shake the mixture several

minutes and then allow the undissolved material to settle. Compare the color of the solution with that obtained by the action of lead dioxide and nitric acid on manganous ion.[2] Write the equation for the reaction.[3] This reaction as well as the one carried out in **a** are often used as tests for manganese.

c. Place a 2-ml. portion of 0.1*M* $KMnO_4$ in each of two test tubes. Dilute each solution with 2 ml. of water, and then add 0.5 ml. of 4*N* H_2SO_4 to one tube, and the same volume of 4*N* NaOH to the other. Now pass hydrogen sulfide through each tube until the color of the permanganate ion disappears. Describe the contents of the tubes.[4] Write an equation to express each of the reactions.[5] What fraction of a molecular weight of potassium permanganate is the equivalent weight in an acid solution, and in a basic solution? [6]

Name (last name first) _____ Desk No. _____ Date _____

Experiment LIV

MANGANESE

(A) Properties and Reactions of Manganous Compounds

1.

2.

3.

4.

5.

6.

7.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LIV (Cont'd)

(B) Manganese in an Oxidation State of +3

1.

2.

3.

4.

(C) The Permanganate Ion

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____

Experiment LIV (Cont'd)

(C) Cont'd

5.

6.

Experiment LV

IRON, COBALT, AND NICKEL

Discussion. It is not surprising that these three transition elements possess many properties in common because such differences as there are result merely from the number of 3 *d* electrons in their atoms.

Oxidation of the elements to the +2 state is readily brought about, but the removal of another electron to give +3 ions becomes more difficult with increasing atomic number. In accordance with this fact, ferric ion (Fe^{+++}) is a good oxidizing agent, whereas the corresponding nickelic ion is not known. An oxidation-reduction potential of +1.86 volts for the couple $Co^{++} \rightleftharpoons Co^{+++} + 1\epsilon$ in acid solution shows cobaltic ion (Co^{+++}) to be a powerful oxidizing agent, and indicates the extreme ease with which this ion reverts to the +2-oxidation state. These three elements also exist in a number of unusual oxidation states, as 0 and +1 for nickel in complex cyanides and +6 for iron in a ferrate (K_2FeO_4).

An outstanding characteristic of iron, cobalt, and nickel is their ability to form coordination compounds. In fact, there are many more *known* complex compounds of cobalt than of any other element.

(A) Tests for Ferrous Ion, Fe^{++}, and Ferric Ion, Fe^{+++}. 1. Ferrous ion. Divide 9 ml. of a freshly prepared 0.1*M* solution of ferrous ammonium sulfate equally among three test tubes.* To the first tube add several drops of a 0.1*N* solution of potassium ferrocyanide; to the second, several drops of 0.1*N* potassium ferricyanide; and to the third, a drop of 0.1*N* potassium or ammonium thiocyanate. Describe what occurs and write equations for the reactions that take place (Text).[1]

2. Ferric ion. Repeat part (A)**1**, but use 0.1*M* $FeCl_3$ in place of the ferrous ammonium sulfate. Record the results, and write equations for the reactions (Text).[2]

Tabulate the results (colors of solutions or precipitates) obtained in part (A)**1** and **2** on the form provided on the report sheet.[3] On the basis of the results, outline a procedure that could be used to detect ferrous and ferric ions in a solution containing a mixture of these two ions.[4]

(B) Properties and Reactions of Ferrous Compounds. Use a freshly prepared 0.1*M* solution of ferrous ammonium sulfate for the following experiments. This solution is referred to hereafter as the *ferrous test solution.*

1. Ferrous Hydroxide. a. Dilute 5 drops of the ferrous test solution to a volume of 5 ml. Treat this solution with several drops of 4*N* NaOH. Quickly note the color and form of the precipitate.[1] Now shake the tube persistently 2 or 3 min. and describe what occurs.[2] Compare the present color of the precipitate with that of one obtained by adding 2 drops of 4*N* NaOH to 2 ml. of 0.1*M* $FeCl_3$.[3] Draw a conclusion as to the action of air on ferrous hydroxide.[4] Confirm the conclusion by dissolving the precipitate, obtained by exposing ferrous hydroxide to the air, in 4*N* HCl, and then adding a drop or two of 0.1*N* KSCN to the solution. Result?[5] Complete and balance the following equation:[6]

$$Fe(OH)_2 + O_2 + H_2O \rightarrow ?$$

---

* This solution should either be prepared by the stockroom on the day the reagent is to be used in the laboratory, or the student should make an approximately 0.1*M* solution by dissolving 0.4 g. of the salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ in 10 ml. of water.

b. Determine whether or not ferrous hydroxide is amphiprotic by adding 3 ml. of 4*N* NaOH to 0.5 ml. of the ferrous test solution. Result? [7]

2. Ferrous Sulfide. Place separate 2-ml. portions of the ferrous test solution in two test tubes. Acidify one of these solutions with the volume of 4*N* HCl required to make the solution 1*N* with respect to HCl, and then pass hydrogen sulfide through both solutions. Describe the result, and make a statement with regard to the precipitation of ferrous sulfide in 1*N* acid solution.[8]

3. Oxidation of Ferrous Ion. a. To 1 ml. of the ferrous test solution add 3 drops of 4*N* H_2SO_4 and 0.5 ml. of 4*N* HNO_3. Boil this solution 1 min., and then cool it in running water from the tap. To the cool solution add 4*N* NaOH until a precipitate remains after shaking the tube. Identify the precipitate by its appearance.[9] Now add just enough 4*N* HNO_3 to dissolve the precipitate, and then test the resulting solution for Fe^{++} and for Fe^{+++}. State the result and complete and balance the following equation: [10]

$$Fe^{++} + NO_3^- \rightarrow NO + ?$$

b. Treat 2 ml. of the ferrous test solution with several drops of 4*N* NaOH and 1 ml. of 3 per cent H_2O_2. Note the rate of change in color of the ferrous hydroxide.[11] Write the equation for the reaction.[12]

c. Acidify 2 ml. of 0.1*M* $K_2Cr_2O_7$ with 3 drops of 4*N* H_2SO_4, and add the resulting solution drop by drop to 4 ml. of the ferrous test solution. Describe the color change, and test the action of the solution with 0.1*N* KSCN.[13] Complete and balance the following equation: [14]

$$Fe^{++} + Cr_2O_7^{=} \rightarrow ?$$

(C) Reduction of Ferric Ion. 1. The Action of Metals in Acid Solution. Acidify 3 ml. of 0.1*M* $FeCl_3$ with an equal volume of 4*N* HCl. Drop a small iron nail into the solution, allow the reaction to proceed 5 min., and then filter the solution. Test the filtrate for ferrous and for ferric ion. Results? [1] Write the equation for the reaction.[2] Repeat the above procedure, using about 0.3 g. of mossy zinc in place of iron. State the results of the test for ferrous and ferric ions, and write the equation for the reaction that has taken place.[3]

2. The Action of Hydrogen. Fit a small Erlenmeyer flask with a one-holed rubber stopper and a delivery tube. Generate hydrogen in the flask by the action of 5 ml. of 4*N* HCl on about 0.5 g. of mossy zinc, and bubble the evolved gas through 3 ml. of 0.1*M* $FeCl_3$. After 3 min. test the solution for ferrous ion. Result? [4]

3. The Action of Hydrogen Sulfide. Saturate 3 ml. of 0.1*M* $FeCl_3$ with hydrogen sulfide. Tell what the precipitate is, and write the equation to account for its formation.[5]

4. The Action of Stannous Chloride. Add 2 ml. of 0.1*N* $SnCl_2$ to 2 ml. of 0.1*M* $FeCl_3$. Determine whether or not an oxidation-reduction reaction has taken place. Result? [6]

(D) Complex Cyanides of Iron. 1. The Action of Fe^{++} with an Excess of CN^-. Add 2 drops of 1*N* KCN to 3 ml. of the ferrous test solution (0.1*M* ferrous ammonium sulfate). Note the color of the precipitate, and tell what it is.[1] Now continue the dropwise addition of 1*N* KCN until the precipitate just dissolves. Drop a piece of litmus paper into the resulting solution, and add to it, drop by drop, 4*N* CH_3COOH until the solution is barely acidic in its reaction. Test the resulting solution with a drop or two of 0.1*M* $FeCl_3$. Describe the result, and tell what complex ion is thus shown to be present.[2] Write equations to show the reactions by which the complex was formed.[3]

2. The Action of Fe^{+++} with an Excess of CN^-. Repeat the foregoing procedure, but use 0.1*M* $FeCl_3$ in place of the solution containing the ferrous ion. What complex ion does the resulting solution contain? [4] Divide the solution into two equal parts, acidify each with 4*N* CH_3COOH, and then test the action of one part with 2 drops of the ferrous test solution, and the action of the other part with 2 drops of 0.1*M* $FeCl_3$. State the results, and

explain how they confirm the answer to the preceding question.[5] Write the equations for the reactions that lead to the formation of the complex.[6]

(E) Preparation of Ferric Ammonium Alum. Prepare 30 ml. of dilute sulfuric acid by adding 5 ml. of 36*N* H_2SO_4 to 25 ml. of water. Place the dilute acid in a 100-ml. beaker, and add to it 20 g. of "green vitriol" ($FeSO_4 \cdot 7H_2O$). Stir the mixture and heat it to boiling **(Hood!)**. Now add slowly, and with constant stirring, 3 ml. of 16*N* HNO_3. Continue to boil the solution 5 min. Calculate the weight of ferric sulfate in the solution just prepared.[1]

Now calculate the weight of ammonium sulfate necessary for the formation of the alum from the weight of ferric sulfate prepared.[2] Obtain the calculated weight of solid ammonium sulfate, dissolve it in 10 ml. of boiling water, and add this solution to the one containing ferric sulfate. If the solution contains undissolved material, filter the liquid into a beaker, cover the latter with a watch glass, and set it aside in the desk until the next laboratory period. At that time filter off the crystals, and dry them between filter papers.

Calculate the theoretical yield of the alum.[3] Determine the weight of the alum actually obtained,[4] and calculate the percentage yield.[5] Preserve the crystals in a stoppered vial.

(F) Properties and Reactions of Cobalt Compounds. 1. Cobaltous Hydroxide. a. Determine whether or not cobaltous hydroxide is amphiprotic by adding an excess of 4*N* NaOH to 2 ml. of 0.1*N* $Co(NO_3)_2$. Result?[1] Describe the appearance of the insoluble hydroxide.[2]

b. Precipitate cobaltous hydroxide by the addition of 1 drop of 4*N* NH_4OH to 2 ml. of 0.1*N* $Co(NO_3)_2$. Now add an excess of ammonia. Describe the result, write equations for the reactions, and name the complex ion formed.[3] Pass H_2S into the ammoniacal solution. Explain the observed result.[4]

2. Cobaltous Sulfide. a. Place separate 3-ml. portions of 0.1*N* $Co(NO_3)_2$ in two test tubes. Make one of the solutions 1*N* with respect to HCl by adding the proper volume of the 4*N* acid. Now pass H_2S through each solution. Results?[5] Quickly filter the solution containing the precipitate, and wash the latter on the filter paper with two 3-ml. portions of water. Immediately transfer a portion of the sulfide to a small evaporating dish, and there stir it with 2 ml. of 1*N* HCl (prepared from 4*N* HCl). Does the precipitate appear to dissolve?[6] The reason for the observed anomalous behavior of the sulfide is not known with certainty. The behavior is anomalous because, although CoS does not precipitate in 1*N* acid, nevertheless, once it is precipitated it fails to dissolve in 1*N* acid. After standing a short time, cobaltous sulfide changes to a form that *is* soluble in 1*N* acid.

b. Transfer the remainder of the cobaltous sulfide from the filter paper to a small evaporating dish. Now treat the sulfide with a solution made by mixing 1 ml. of 5 per cent NaClO with 3 ml. of water and 1 ml. of 6*N* HCl (prepared from 12*N* HCl). Tell what takes place, and complete and balance the following equation:[7]

$$CoS + HClO \rightarrow Co^{++} + S\downarrow + Cl^-$$

Reserve the solution of $CoCl_2$ just prepared for use in **3a.**

3. Tests for Cobaltous Ion. a. Evaporate the solution of $CoCl_2$ (from **2a**) just to dryness in a 50-ml. beaker. Add to the residue 1 ml. of water, 5 drops of 1*N* CH_3COONa and 10 drops of 1*N* CH_3COOH (prepared from the 4*N* acid). Now add to this solution 1.5 ml. of 6*N* KNO_2 and then warm the liquid. Record what takes place after a few minutes.[8] The product is $K_2Na[Co(NO_2)_6]$.

b. Make a borax bead in a loop of a platinum wire. Moisten the bead with a 0.1*N* solution of $Co(NO_3)_2$ and then heat the bead strongly in the oxidizing region of the burner flame. Record the color of the bead, and write an equation for the reaction.[9]

(G) Properties and Reactions of Nickel Compounds. 1. Nickel Hydroxide. a. Add an excess of 4*N* NaOH to 2 ml. of a 0.1*N* solution of $Ni(NO_3)_2$ in order to determine whether or not nickel hydroxide is amphiprotic. Conclusion?[1] Make a statement regarding the

behavior of the hydroxides of nickel and cobalt in this respect.[2] Describe the appearance of nickel hydroxide.[3]

b. Add an excess of 4*N* NH_4OH to 2 ml. of 0.1*N* $Ni(NO_3)_2$. Compare the behavior of Ni^{++} with that of Co^{++} for this reaction.[4] Write the equation for the reaction, and name the complex ion formed.[5] Pass H_2S through the ammoniacal solution. Compare the result with that obtained in part (F)**1b.**[6]

2. Nickel Sulfide. Repeat the experimental procedure of part (F)**2,** but use a 0.1*N* solution of $Ni(NO_3)_2$ instead of 0.1*N* $Co(NO_3)_2$. Record the action of hydrogen sulfide on neutral and on 1*N* acid solutions of $Ni(NO_3)_2$.[7] How do these results compare with those noted in the case of cobalt under the same conditions?[8] Make a statement regarding the solubility of nickel sulfide (precipitated from a neutral solution) in 1*N* HCl.[9] Compare the behavior of NiS with that of CoS in this respect.[10] State the result of the action of a mixture of hydrochloric acid and sodium hypochlorite on NiS, and compare it with the behavior of CoS with the same mixture of reagents.[11] Reserve the solution of nickel chloride prepared in this way for use in **3a.**

3. Tests for Nickel Ion. a. Carry out the experimental procedure followed in part (F)**3a** using a solution of nickel chloride (reserved from part (G)**2**) in place of cobaltous chloride. Result?[12] On the basis of this result, make a statement regarding the value of this test for cobalt in the presence of nickel.[13]

b. Make a borax bead test for nickel in the same manner in which the test was made for cobalt; use a 0.1*N* solution of nickel nitrate. Result?[14] Reheat the bead and, while it is still hot, touch it to a very small crystal of nickel nitrate. Again heat the bead in the hottest part of the burner flame. What is the color of the bead after it has cooled?[15] Now dip this bead into a 0.1*N* solution of cobaltous nitrate and heat it in the burner flame. On the basis of this result make a statement regarding the value of the bead test for nickel in the presence of cobalt.[16]

c. Add a drop of dimethylglyoxime reagent * and 2 drops of 1*N* $(NH_4)_2CO_3$ to 1 ml. of water. To this solution add 1 drop of 0.1*N* $Ni(NO_3)_2$. Shake the tube for about half a minute and then describe the precipitate that has formed.[17] Write the equation for the reaction (Text).[18]

Repeat the foregoing procedure, but use a drop of 0.1*N* $Co(NO_3)_2$ in place of nickel nitrate. Result?[19] Make a statement regarding the value of this test for Ni^{++} in the presence of Co^{++}.[20]

(H) The Preparation of Chloropentamminecobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$. Add 6*N* HCl, a little at a time, to 10 g. of cobaltous carbonate until no further action takes place. Filter the solution, if necessary, and then add to it 125 ml. of 6*N* NH_4OH (prepared by diluting 15*N* NH_4OH), followed by a solution of 25 g. of ammonium carbonate in 125 ml. of water. How many milliliters of 15*N* NH_4OH must be diluted to 125 ml. in order to prepare a 6*N* solution of this substance?[1] Add to the foregoing mixture 75 g. of ammonium chloride, and evaporate the resulting mixture on a *water bath* to a pasty mass.

Add 4*N* HCl a little at a time and with constant stirring until no more carbon dioxide is evolved. Make the solution just alkaline with 4*N* NH_4OH and then add 15 ml. more of the same reagent. Dilute this solution to a volume of 250 ml. and heat it on a water bath for an hour. Now add 150 ml. of 12*N* HCl to the solution, and continue the heating for about three quarters of an hour. At the end of this time, allow the solution to cool to room temperature. Crystals of the desired compound gradually separate during the periods of heating and cooling. Filter the mixture through a suction filter. Wash the crystals with several small amounts of 6*N* HCl, and finally several times with 95 per cent alcohol. Spread the crystals on filter paper and allow them to dry in the air. Weigh the product,[2] and then calculate the percentage yield.[3]

* A 1 per cent solution of dimethylglyoxime in 95 per cent alcohol.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV

IRON, COBALT, AND NICKEL

(A) Tests for Ferrous Ion, Fe^{++}, and Ferric Ion, Fe^{+++}. *Ferrous ion*

1.

Ferric ion

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(A) Cont'd

3.

Ion	Reagent		
	$Fe(CN)_6^{\equiv\equiv}$	$Fe(CN)_6^{\equiv}$	SCN^-
Fe^{++}			
Fe^{+++}			

4.

(B) Properties and Reactions of Ferrous Compounds. *Ferrous hydroxide*

1.

2.

3.

4.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(B) Cont'd

5.

6.

7.

Ferrous sulfide

8.

Oxidation of ferrous ion

9.

10.

11.

12.

13.

14.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(C) Reduction of Ferric Ion. *The action of metals in acid solution*

1.

2.

3.

The action of hydrogen

4.

The action of hydrogen sulfide

5.

The action of stannous chloride

6.

(D) Complex Cyanides of Iron. *The action of Fe^{++} with an excess of CN^{-}*

1.

2.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(D) Cont'd

3.

4.

5.

6.

(E) Preparation of Ferric Ammonium Alum

1. **2.**

3. **4.** **5.**

(F) Properties and Reactions of Cobalt Compounds. *Cobaltous hydroxide*

1.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(F) Cont'd

2.

3.

4.

Cobaltous sulfide

5.

6.

7.

Tests for cobaltous ion

8.

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(G) Properties and Reactions of Nickel Compounds. *Nickel hydroxide*

1.

2.

3

4.

5.

6.

Nickel sulfide

7.

8.

9.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(G) Cont'd

10.

11.

Tests for nickel ion

12.

13.

14.

16.

17.

18.

19.

Name (last name first) _____ Desk No. _____ Date _____

Experiment LV (Cont'd)

(G) Cont'd

20.

(H) The Preparation of Chloropentamminecobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$

1. **2.** **3.**

QUALITATIVE CHEMICAL ANALYSIS FOR THE CATIONS

Part I

INTRODUCTION

Purpose of Qualitative Analysis. Qualitative analysis has for its purpose the determination of the presence or absence of the elements, radicals, ions, or compounds in a sample of any material. Only an estimate is made of the relative amounts of the constituents of the material analyzed. In *quantitative* analysis, a precise determination, by weight, is made of one or more of the components or constituents of a sample. Since the procedure chosen for a quantitative analysis depends on the composition of the material, a qualitative analysis is usually made before the quantitative determination is attempted.

The study of qualitative analysis serves another purpose in that it provides a systematic survey of the reactions and properties of ions and their compounds. Furthermore, many of the fundamental principles of chemistry find application in the procedures of qualitative analysis.

Methods of Qualitative Analysis. Numerous methods are used to establish the presence or absence of certain elements, radicals, ions, and compounds. Among the methods employed are flame tests (Exps. XLV, part (E), and XLVII, part (A)), bead tests (Exps. XL, part (F)**4** and LV, parts (F)**3** and (G)**3**), blowpipe analysis, spectroscopic analysis, X-ray analysis, polarographic analysis, and microscopic analysis. However, analyses based on chemical reactions taking place in aqueous solution have proved to be the most satisfactory for general purposes.

Analysis in solution demands that the sample, if not already in solution, be dissolved in water or in an aqueous solution of an appropriate reagent. Relatively small groups of ions are then separated from one another—usually by a series of selective precipitations—and specific tests are used to identify, or confirm, each of the ions within the small groups. In Table I there are presented the members of the various groups, the reagents used to accomplish the separations, and the insoluble products formed by the reagents with solutions containing the various cations. Schematic outlines for the analysis within each group are given later.*

Laboratory Techniques of Qualitative Analysis. The special apparatus and experimental methods characteristic of qualitative analysis require the mastery of certain techniques. Some of these did not receive particular attention in the laboratory work of general chemistry, while others are entirely new. Hence, a detailed treatment of special apparatus and of a number of the commonly used experimental methods of qualitative analysis is given.

1. General Considerations. Use extreme care in following the directions given relative to such matters as concentrations and volumes of reagents used and the temperatures at which reactions are carried out. Keep all glassware scrupulously clean, and take every precaution against the contamination of the reagents used and the solutions being tested.

2. The Use of Reagents. Medicine droppers offer a convenient means of measuring the required volumes of the reagents used in the analytical procedures. A volume is usually

* The general scheme of analysis is similar to that used in *Semimicro Qualitative Analysis* by Barber and Taylor. Harper & Bros. (1942).

specified in terms of drops, and the assumption is that the volume of 1 drop is 0.05 ml. Therefore, the combined volume of 20 drops is 1 ml.

3. The Reagent Bottles. The reagent bottles both in the individual desk sets and those set out for general use should be of a type equipped with a dropper fixed into the neck of each bottle. Each dropper should be numbered to correspond with the number of its bottle in order to avoid the contamination of reagents that is certain to occur if a dropper, after use, is replaced in the wrong bottle.

TABLE I

SCHEMATIC OUTLINE OF THE GROUP SEPARATIONS

Group	Ions	Group Reagents	Precipitates Formed by the Group Reagents
I The Silver Group	Ag^+ (colorless) Pb^{++} (colorless) Hg_2^{++} (colorless)	HCl	AgCl (white) $PbCl_2$ (white) Hg_2Cl_2 (white)
II The Copper Group	Pb^{++} (colorless) Bi^{+++} (colorless) Cu^{++} (greenish blue) Cd^{++} (colorless)	H_2S in 0.3*N* acid solution	PbS (black) Bi_2S_3 (brown) CuS (black) CdS (yellow)
The Tin Group	Hg^{++} (colorless) As^{+3} (colorless) Sb^{+3} (colorless) Sn^{++} (colorless)		HgS (black) As_2S_3 (yellow) Sb_2S_3 (orange) SnS (brown)
III The Nickel Group	Ni^{++} (pale green) Co^{++} (pale red) Mn^{++} (faint pink) Zn^{++} (colorless)	NH_4OH and H_2S	NiS (black) CoS (black) MnS (flesh-colored) ZnS (white)
The Aluminum Group	Fe^{+++} (reddish brown) Cr^{+++} (dark green or blue) Al^{+++} (colorless)		$Fe(OH)_3$ (reddish-brown) FeS (black) $Cr(OH)_3$ (bluish green) $Al(OH)_3$ (white)
IV The Alkaline-Earth Group	Ba^{++} (colorless) Ca^{++} (colorless) Sr^{++} (colorless)	NH_4OH and $(NH_4)_2CO_3$	$BaCO_3$ (white) $CaCO_3$ (white) $SrCO_3$ (white)
V The Magnesium and Alkali Metals Group	Mg^{++} (colorless) K^+ (colorless) Na^+ (colorless) NH_4^+ (colorless)	No Group Reagent	$Mg(NH_4)PO_4$ (white) $K_2Na[Co(NO_2)_6]$ (yellow) $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ (yellow) .....

If reagent bottles of the type described are not available, it is emphasized that a medicine dropper must never be dipped into the bottles. Pour a few milliliters of the required solution into a beaker, and fill the dropper from this source of the reagent. Wash both the tube and the bulb of a dropper before using it to measure out a different reagent.

4. Filtration. A 3-cm. funnel, with filter paper to fit, is recommended for use in the procedures given in this scheme of analysis. If a larger size is used, such as one requiring an 11-cm. filter paper, too large a fraction of the solution is retained by the paper.*

* The directions given in the procedures are designed to maintain a volume of from 3 to 5 ml. for a solution under analysis.

The process of filtration is accelerated by suction. Figures 96 and 97 illustrate simple types of apparatus for this purpose. The degree of suction applied is regulated by constricting the rubber tubing on the suction line either with the fingers or with a pinch clamp. A disadvantage in the apparatus shown in Fig. 96 is the ease with which the filter paper is punctured if the suction is too great. To obviate this occurrence, the apparatus illustrated in

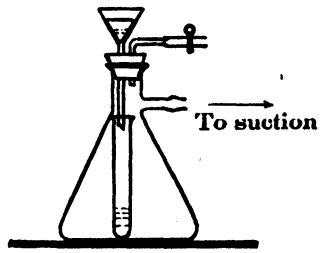


FIG. 96. A suction filter

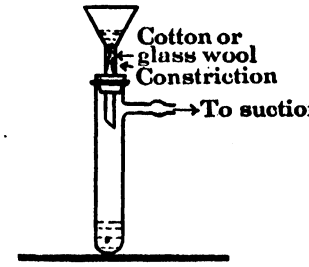


FIG. 97. A suction filter

Fig. 97 is used. The stem of the small funnel is constricted about 2 cm. below the apex, and cotton or glass wool is packed into the intervening space. A small glass rod is used to tamp the filter medium into a fairly compact layer. The medium is packed more closely for a finely divided precipitate than for a gelatinous one. The filter medium is removed by ejecting it with a wire pushed up through the stem of the funnel.

Figure 98 illustrates a type of filter designed for operation with an air-pressure line. A thistle tube (preferably Pyrex) with a constricted stem is used in place of a funnel.

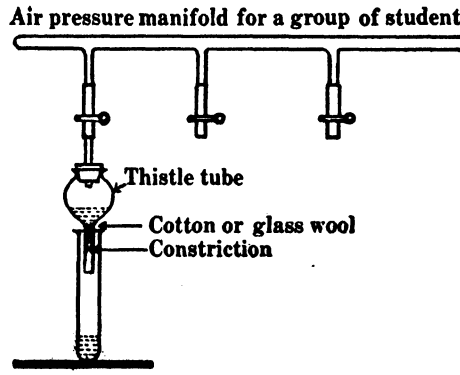


FIG. 98. A pressure filter

5. The Washing and Dissolving of Precipitates. Unless otherwise specified, precipitates are washed with water. A total of from 3 to 5 ml. of water is used. The suction is turned off and, by means of a medicine dropper, about one fourth of the wash liquid is distributed evenly over the filter medium and the precipitate. Suction is then applied until all of the liquid has been drawn through the filter medium. This entire operation is repeated several times inasmuch as a series of washings with small volumes of liquid is much more effective than washing with a single large volume of the wash liquid. If there is a comparatively large amount of a precipitate carefully stir it up, with a small glass rod, during the process of washing. A similar method is used to dissolve a precipitate.

The analytical procedures used in this manual are devised in such a manner as to make it unnecessary to use mechanical means for removing a precipitate from the filter medium. A precipitate is either observed on the medium and then discarded, or it is dissolved, and the solution is treated by whatever procedure is necessary.

Filtration, precipitation, and the dissolution of precipitates are usually more rapid at elevated temperatures. Consequently, whenever temperatures above the ordinary are not detrimental to the analysis, the test tube containing the reaction mixture is heated in a water bath. Figures 99 and 100 show the two preferred arrangements. A metal plate

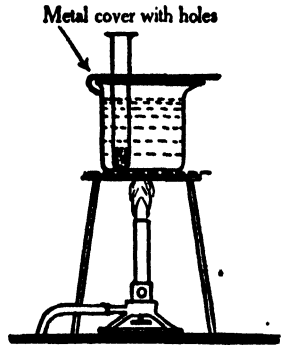


FIG. 99. A water bath for heating the contents of test tubes

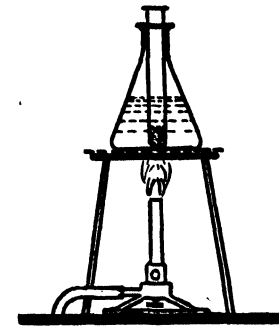


FIG. 100. A water bath for heating the contents of a test tube

(preferably Monel metal, copper or brass) with two or three holes drilled in it keeps the test tubes upright in the beaker.

6. Precipitation with Hydrogen Sulfide. If hydrogen sulfide generators are available in a ventilating hood, precipitation with hydrogen sulfide should be carried out there. The gas should be passed into a solution through a 6-mm. glass tube, drawn out at one end to form a jet. This tube should be cleaned after use by drawing an acidified solution of sodium hypochlorite into it and then rinsing it with water.

In the event that a ventilating hood is not part of the laboratory equipment, individual hydrogen sulfide generators may be used if arrangements are made to prevent the escape of the gas into the atmosphere of the laboratory. A convenient source of hydrogen sulfide is an intimate mixture of sulfur, paraffin, and asbestos,* which evolves the gas upon the application of heat. The evolution of the gas stops quickly as the mixture cools. "Aitch-tu-ess" is placed in a Pyrex test tube equipped with a delivery tube bent as shown in Fig. 101. A

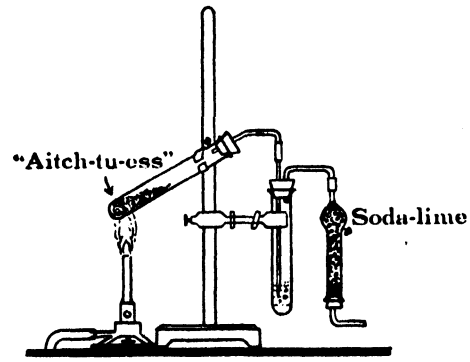


FIG. 101. Method of using an individual hydrogen sulfide generator

drying tube filled with soda lime may be used to absorb the excess hydrogen sulfide that escapes from the solution being treated with the gas. After the precipitation has been completed, the drying tube may be attached to the test-tube generator. This prevents the escape into the laboratory of the gas remaining in the generator.

* This mixture is sold commercially as "Aitch-tu-ess."

Recording the Results of Experiments and Analyses. Report sheets are not provided for recording the results of preliminary experiments or of the analyses of known and unknown solutions. However, it must be emphasized that a complete record of all the essential facts pertaining to each test is necessary for an intelligent report on the analysis. Notes should be made immediately after a test is made; they need not be detailed, but should be sufficiently complete to enable the student or the instructor to retrace the course of the analysis. This step is advisable for, in the event that the report on the analysis is incorrect, the origin of an error may be found.

It is recommended that notes dealing with the results of the preliminary experiments and the analyses, as well as the answers to the questions supplied at the end of each procedure, be kept in a notebook. Reports of analyses should be turned in on separate blanks. A recommended form is given below.

REPORT OF ANALYSIS OF UNKOWN NO.

Last Name (Print) _____ Initials _____ Lecture Instructor _____

Date Unknown Received _____ Date Reported _____

Ions Found (Valences Must Be Correctly Given) _____

Traces of Ions Found _____

Ions Missed (To Be Filled in by Instructor) _____

Laboratory Instructor's Approval to Obtain Unknown _____ Grade _____

Part II

PRELIMINARY EXPERIMENTS AND PROCEDURES FOR THE ANALYSIS OF THE GROUP I CATIONS, Ag^+, Pb^{++}, and Hg_2^{++}

(A) Preliminary Experiments. The instructor may assign any or all of the following experiments on the analytically significant reactions of the ions of this group:

1. **Silver ion, Ag^+**, Exp. XLIX, part (B)**1, 2,** and **3.**
2. **Lead ion, Pb^{++}**, Exp. LII, part (B)**1** and **4.**
3. **Mercurous ion, Hg_2^{++}**, Exp. L, part (C)**1.**

(B) Analysis of a Known.* Obtain 10 ml. of a solution known to contain the ions of Group I and analyze it by ***P.*† *1-6*** in part (F). Carry out the analysis on 5 ml. of the solution.

After the analysis is completed, study the material in parts (D) and (E), and then balance the equations and be able to answer the questions in part (G). Now report to the laboratory instructor for an oral quiz on the material studied.

(C) Analysis of a Group I Unknown. After the successful completion of the quiz, the laboratory instructor will indicate his approval on the form on which the report of analysis is to be made (p. 493). Present the approved blank to the stockroom and obtain 10 ml. of an unknown solution. Analyze 5 ml. of this solution according to ***P. 1-6,*** and reserve the other 5 ml. for a second analysis, if this should be necessary. Keep a careful record of the analysis and report the results on the blank.

(D) Discussion of the Analysis of Group I. The cations in this group (Ag^+, Pb^{++}, and Hg_2^{++}) are those whose chlorides are insoluble in acid and in neutral solutions. The oxychloride of antimony (SbOCl) and that of bismuth (BiOCl) are only slightly soluble in water, but dissolve readily in acids. Inasmuch as lead chloride is slightly soluble in water at ordinary temperatures, the Pb^{++} is not completely precipitated in this group and is therefore found in both Group I and Group II. The separation of $PbCl_2$ from AgCl and Hg_2Cl_2 is based upon the increased solubility of $PbCl_2$ in hot water and the virtual lack of an increase in the solubility of the other two salts under the same conditions.

Of the two chlorides formed by mercury (Hg_2Cl_2 and $HgCl_2$) only the mercurous compound is insoluble in water. Hence, mercury may be found in Groups I and II if Hg_2^{++} and Hg^{++} are in the original unknown.

Silver chloride is separated from Hg_2Cl_2 by the formation of the soluble complex, $[Ag(NH_3)_2]^+$. On the other hand, ammonia reacts with Hg_2Cl_2 to form the insoluble products, Hg (black, finely divided) and $HgNH_2Cl$ (white solid).

The conditions required for the precipitation or the dissolution of an insoluble substance are given in the following statements of the solubility-product principle (Text):

1. In a saturated solution of a slightly soluble salt the product of the molar concentrations of the ions—the ion product—is equal to the solubility product constant. For silver chloride this is expressed as follows:

$$[Ag^+] \times [Cl^-] = K_{AgCl} \quad (K_{AgCl} = 1.1 \times 10^{-10})$$

* Known and unknown solutions should contain about 1 mg. of each cation per milliliter of solution. It is recommended that 10-ml. samples of the known and the unknown be supplied to each student. The analyses should, in both cases, be carried out on 5-ml. samples, so as to provide a reserve of 5 ml. if the analysis needs to be repeated. The concentration of the stock solutions, from which both the known and the unknowns are prepared, may be conveniently set at 10–50 mg. of cation per milliliter of solution.

† ***P.*** = Procedure.

2. Precipitation of a substance occurs when, in a solution, the value of the ion product exceeds the solubility product constant. Thus, AgCl precipitates when

$$[Ag^+] \times [Cl^-] > K_{AgCl}$$

3. A precipitate dissolves, or is prevented from forming, if the ion product is maintained at a value lower than the solubility product constant.

Statement **1** shows that an excess of Cl^- must decrease the solubility of AgCl because of the common ion effect (Text). Hence, an excess of the reagent is added in this and in other precipitations in order to obtain as complete a removal of ions as is possible. Too great an excess of reagent is avoided because of the tendency of certain ions to form soluble complexes. Thus, high concentrations of chloride ion increase the solubility of AgCl because, when $[AgCl_2]^-$ forms, the concentration of Ag^+ becomes so small that $[Ag^+] \times [Cl^-] < K_{AgCl}$. (See Text,* pp. 466–68.)

The solubility of AgCl in ammonia is accounted for in the same way. When the diamminesilver ion $[Ag(NH_3)_2]^+$ forms, the concentration of the Ag^+ is reduced to such an extent that $[Ag^+] \times [Cl^-] < K_{AgCl}$.

In general, to dissolve a precipitate in a solution of a reagent, the concentration of the cation or the anion of the insoluble substance must be reduced so as to cause the ion product to be less than the solubility product constant. Methods by which this may be accomplished are found in the Text on pages 472–73.

(E) Schematic Outline for the Analysis of Group I

<table>
<tr><td colspan="3">1. Solution of general unknown or Group I known or unknown: Ag^+, Pb^{++}, Hg_2^{++} (also Groups II-V in the case of a general unknown). Add HCl.</td></tr>
<tr><td>7. Filtrate: Groups II-V</td><td colspan="2">2. Precipitate: AgCl, $PbCl_2$, Hg_2Cl_2
Treat with hot water</td></tr>
<tr><td rowspan="2"></td><td>3. Filtrate: Pb^{++}
Add CH_3COONH_4 and K_2CrO_4.
Yellow precipitate, $PbCrO_4$, confirms Pb^{++}</td><td>4. Residue: AgCl, Hg_2Cl_2
Add NH_4OH</td></tr>
<tr><td></td><td>5. Filtrate: $[Ag(NH_3)_2]^+ + Cl^-$
Add HNO_3
White precipitate, AgCl, confirms Ag^+</td><td>6. Residue:
Black insoluble mixture, Hg + $HgNH_2Cl$, confirms Hg_2^{++}</td></tr>
</table>

(F) Procedures for the Analysis. ***Procedure 1.*** **Known or Unknown Solution.** Add 10 drops of 6*N* HCl (from a medicine dropper) to 5 ml. of the solution to be analyzed. Shake the test tube vigorously and filter the solution. Test for complete precipitation by adding 1 drop of 6*N* HCl to the filtrate. If a precipitate forms, add from 2 to 3 additional drops of 6*N* HCl and filter the mixture through the same filter medium. Wash the precipitate with 3 ml. of cold water containing 1 drop of 6*N* HCl. (Allow this filtrate to run into the original filtrate if other groups of ions are present.) Now wash the precipitate with 2 ml. of cold

* Page references are to *General Inorganic Chemistry* by Sneed and Maynard. D. Van Nostrand (1942).

water. Treat the precipitate (AgCl, $PbCl_2$, and Hg_2Cl_2) by ***P. 2*** and the filtrate (Groups II–V) by ***P. 7.***

Procedure 2. **Precipitate from P. 1.** Pour 5 ml. of hot water onto the precipitate in the funnel. Reheat the solution, and again pour it into the funnel. Finally, wash the precipitate with an additional 2-ml. portion of hot water. Treat the aqueous solution ($PbCl_2$) by ***P. 3*** and the residue (AgCl, Hg_2Cl_2) by ***P. 4.***

Procedure 3. **Solution (from P. 2) containing $PbCl_2$.** To the hot aqueous solution add 1 drop of 4*N* CH_3COOH, 5 drops of 1*N* CH_3COONH_4, and then 2 ml. of 1*M* K_2CrO_4. A yellow precipitate of $PbCrO_4$ proves the presence of Pb^{++} in the unknown solution.

Procedure 4. **Residue from P. 2 (AgCl, Hg_2Cl_2).** Allow 1 ml. of 4*N* NH_4OH to pass through the filter medium containing the residue from ***P. 2.*** Now allow 1 ml. of water to pass through the filter and run into the ammonia solution. Treat the filtrate, which contains $[Ag(NH_3)_2]^+$ and Cl^-, according to ***P. 5.*** See ***P. 6*** with regard to the black residue on the filter paper.

Procedure 5. **Filtrate from P. 4 ($[Ag(NH_3)_2]^+$ and Cl^-).** Add 1 ml. of 4*N* HNO_3 to this filtrate. A white precipitate of AgCl proves the presence of Ag^+. If a precipitate does not form, test the solution to determine whether it is acid to litmus. AgCl does not precipitate in an ammoniacal solution.

Procedure 6. **Black residue from P. 4 ($Hg + HgNH_2Cl$).** A black residue that forms on the filter paper as a result of the action of ammonia proves the presence of Hg_2^{++}.

(G) Equations and Exercises. Balance the following equations and study the exercises before applying for an unknown.

1. Equations. Complete and balance the ionic equations for the following reactions:

a. Silver nitrate + hydrochloric acid

$$Ag^+ + Cl^- \rightarrow$$

b. Mercurous nitrate + hydrochloric acid

$$Hg_2^{++} + Cl^- \rightarrow$$

c. Lead nitrate + hydrochloric acid

$$Pb^{++} + Cl^- \rightarrow$$

d. Lead acetate + potassium chromate

$$Pb(CH_3COO)_2 + CrO_4^{=} \rightarrow$$

e. Silver chloride + ammonia

$$AgCl + NH_3 \rightarrow$$

f. Mercurous chloride + ammonia

$$Hg_2Cl_2 + NH_3 \rightarrow Hg(NH_2)Cl + Hg + NH_4^+ + Cl^-$$

g. Diamminesilver chloride + nitric acid

$$[Ag(NH_3)_2]^+ + Cl^- + H_3O^+ \rightarrow NH_4^+ + H_2O + ?$$

2. Exercises.

a. Be able to reproduce the schematic outline for the analysis of Group I.

b. Describe the confirmatory test for each ion of Group I.

c. What ion would not be detected if the precipitation of Group I was carried out in a hot solution?

d. The addition of 1 drop of 6*N* HCl to an unknown solution containing ions from all groups produced a white precipitate which dissolved in an excess of HCl. Explain.

e. What reagents other than HNO_3 might be used to precipitate AgCl from a solution of $[Ag(NH_3)_2]Cl$? Explain and formulate the reactions.

f. Name reagents that might be used to separate the substances in each of the following pairs in one operation: $Hg_2Cl_2 - PbCl_2$, $AgCl - PbCl_2$, and $HgCl_2 - AgCl$.

g. A precipitate is either AgCl, or $PbCl_2$, or Hg_2Cl_2. Explain how ammonium hydroxide might be used to determine its identity.

h. The concentration of a saturated solution of $PbCl_2$ is 0.011 g. per ml. at 25°. How many milligrams of Pb^{++} escape precipitation as the chloride from 5 ml. of a solution at 25° ?

i. Explain why mercury and lead must be tested for in Group II as well as in Group I.

j. Explain the following on the basis of the solubility product principle: (1) AgCl precipitates when HCl is added to a solution of $AgNO_3$; (2) AgCl dissolves in an excess both of HCl and of NH_3; (3) HNO_3 precipitates AgCl from solutions containing $[Ag(NH_3)_2]^+$.

Part III

PRELIMINARY EXPERIMENTS AND PROCEDURES FOR THE ANALYSIS OF THE GROUP II CATIONS, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, Hg^{++}, As^{+3} and As^{+5}, Sb^{+3} and Sb^{+5}, Sn^{++} and Sn^{+4}

(A) Preliminary Experiments. The instructor may assign any or all of the following experiments on the analytically significant reactions of the ions of this group.

1. Lead ion, Pb^{++}. Exp. LII, part (B)**1, 2, 3, 4,** and **5.** (Omit part (B)**1** and **4** if they were performed as preliminary experiments in Part II.)

2. Bismuth ion, Bi^{+++}; Arsenic, As^{+3} and As^{+5}; and Antimony, Sb^{+3} and Sb^{+5}. Exp. XLI, parts (D), (E) and (F).

3. Cupric ion, Cu^{++}. Exp. XLIX, part (A)**1b, 3,** and **5.**

4. Cadmium ion, Cd^{++}. Exp. L, part (B)**1, 2, 3,** and **4.**

5. Stannous ion, Sn^{++}, and Stannic Tin, Sn^{+4}. Exp. LII, part (A)**1, 2, 3, 4, 5,** and **6.**

(B) Analysis of a Known. Obtain 10 ml. of a solution known to contain the ions of Group II and analyze it by ***P. 7-22.*** Carry out the analysis on 5 ml. of the solution. After the analysis is completed, study the material in parts (D) and (E), and then balance the equations and be able to answer the questions in part (G). Report to the laboratory instructor for an oral quiz on the material studied.

(C) Analysis of a Group II Unknown. After the successful completion of the oral quiz, obtain 10 ml. of an unknown. Analyze 5 ml. of this solution for the ions of Group II by ***P. 7-22.***

(D) Discussion of the Analysis of Group II. The order of solubility of the sulfides of Groups II and III, as evidenced by their solubility in hydrochloric acid, is as follows: $HgS < As_2S_3 < CuS < Sb_2S_3 < Bi_2S_3 < SnS < CdS < PbS < ZnS < CoS < NiS < FeS < MnS$. When the concentration of HCl is between $0.2N$ and $0.3N$, hydrogen sulfide precipitates the sulfides of Group II, the Copper-Tin Group, whereas it does not furnish a high enough concentration of sulfide ions to precipitate the sulfides of Group III, the Nickel-Aluminum Group. Thus, a careful regulation of the concentration of the hydronium ion is necessary because this ion controls the concentration of the sulfide ion furnished by H_2S (Text). As is shown above, PbS is the most soluble sulfide of Group II and ZnS is the least soluble of Group III. When the $[H_3O^+]$ is between 0.2 and 0.3, $[Pb^{++}] \times [S^{=}] > K_{PbS}$, and $[Zn^{++}] \times [S^{=}] < K_{ZnS}$. This is the situation required to permit the precipitation of all Group II sulfides and to prevent the precipitation of the sulfides of Group III.

A solution of ammonium iodide (NH_4I) is added to any solution of Group II ions previous to the precipitation of the sulfides. This is done in order to insure the ready precipitation of arsenic. When the latter is originally present as the arsenate ion ($AsO_4^{\equiv}$) the precipitation of As_2S_5 takes place only at elevated temperatures (90°), and then only very slowly. Hydrogen iodide, formed from NH_4I in the presence of HCl, reduces the $AsO_4^{\equiv}$ to the AsO_2^{-}, with which H_2S reacts readily to precipitate As_2S_3.

Within Group II, a separation into two subgroups is effected by the use of a special reagent prepared from NaOH, Na_2S, and a small amount of sulfur (Appendix H, p. 549).

This reagent dissolves the sulfides of Hg, As, Sb, and Sn through the formation of soluble complex anions, such as the thioarsenate ion, $AsS_4^{\equiv}$; the others are $HgS_2^{=}$, $SbS_4^{\equiv}$, and $SnS_3^{=}$. The sulfides of Pb, Bi, Cu, and Cd do not form these complexes to a significant extent under the experimental conditions used and may be separated by filtration from the solution containing the thio complexes. Acidification of the solution containing the thio complexes causes the reprecipitation of the simple sulfides (***P. 15***). Thus,

$$2SbS_4^{\equiv} + 6H_3O^+ \rightarrow Sb_2S_5 \downarrow + 3H_2S \uparrow + 6H_2O$$

(E) Schematic Outlines for the Analysis of Group II.

1. Separation of the Copper Group from the Tin Group

7. Filtrate from Group I, or Group II known or unknown: Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, Hg^{++}, As^{+3}, As^{+5}, Sb^{+3}, Sb^{+5}, Sn^{++}, Sn^{+4}.

(also the ions of Groups III to V in the case of general unknown).

Adjust the acid concentration to 0.2-0.3 *N*, add NH_4I, and then pass in H_2S.

23. Filtrate: Groups III to V

8. Precipitate: PbS, Bi_2S_3, CuS, CdS, HgS, As_2S_3, Sb_2S_3, SnS. Add special NaOH—Na_2S—S reagent

9. Residue: PbS, Bi_2S_3, CuS, CdS — Copper Group

15. Solution: $HgS_2^{=}$, $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^{=}$ — Tin Group

2. The Analysis of the Copper Group

9. Residue: PbS, Bi_2S_3, CuS, CdS. Heat with HNO_3, evaporate with H_2SO_4 to fumes of SO_3, then dilute with water.

10. Residue: $PbSO_4$. Add CH_3COONH_4, CH_3COOH, and then K_2CrO_4. *Yellow precipitate,* $PbCrO_4$, confirms Pb^{++}.

11. Filtrate: Bi^{+++}, Cu^{++}, Cd^{++}. Add NH_4OH

12. Precipitate: $Bi(OH)_3$. Treat with sodium stannite. *Black precipitate,* Bi, confirms Bi^{+++}.

Filtrate: $[Cu(NH_3)_4]^{++}$, $[Cd(NH_3)_4]^{++}$. Divide into 2 equal parts.

13. 1st Part: Add CH_3COOH and $K_4Fe(CN)_6$. *Pink precipitate,* confirms Cu^{++}.

14. 2nd Part: Add KCN, pass in H_2S. *Yellow precipitate,* CdS, confirms Cd^{++}.

3. The Analysis of the Tin Group

<table>
<tr><td colspan="4">15. Solution: $HgS_2^{=}$, $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^{=}$. Add HCl.</td></tr>
<tr><td colspan="2">16. Precipitate: HgS, Sb_2S_5, As_2S_5, SnS_2, S. Add 6N HCl</td><td colspan="2">Filtrate: Discard</td></tr>
<tr><td colspan="2">17. Residue: HgS, As_2S_5. Add NH_4OH and H_2O_2.</td><td colspan="2">20. Solution: $SbCl_6^{=}$, $SnCl_6^{=}$. Boil. Add pure iron or magnesium.</td></tr>
<tr><td>18. Residue: HgS. Add HCl and NaClO. Boil. Add $SnCl_2$. White to black precipitate, Hg_2Cl_2-Hg, confirms Hg^{++}.</td><td>19. Filtrate: $AsO_4^{\equiv}$. Add magnesium nitrate mixture. White precipitate, $MgNH_4AsO_4$, indicates As. To precipitate add CH_3COOH and then $AgNO_3$. Reddish brown solid, Ag_3AsO_4, confirms As^{+3} or As^{+5}.</td><td>21. Precipitate: Sb (black) Add tartaric acid and HNO_3 Solution, $[(SbO)C_4H_4O_6]^-$. Pass in H_2S. Orange precipitate, Sb_2S_3, confirms Sb^{+3} or Sb^{+5}.</td><td>22. Filtrate: Sn^{++}. Add $HgCl_2$. White to black precipitate, Hg_2Cl_2-Hg, confirms Sn^{++} or Sn^{+4}.</td></tr>
</table>

(F) Procedures for the Analysis. ***Procedure 7.*** **Filtrate from P. 1 (Groups II to V).** To the filtrate from Group I (or to 5 ml. of Group II known or unknown) add 4*N* NH_4OH from a medicine dropper, until the solution is neutral to litmus or "Alk-acid" paper. To carry out this test, dip a small stirring rod into the solution and then touch the rod to the paper. Measure the volume of the solution and add 1 drop of 6*N* HCl to it for each milliliter of solution.*

Add 5 drops of 1*N* NH_4I to the solution. Disregard any colored iodides which may form. Place the test tube in a beaker or an Erlenmeyer flask containing hot water (Figs. 99, 100) and, when the solution itself is hot, pass H_2S into it 2 or 3 min. Now cool the solution, add 3 ml. of water to it, and pass H_2S into it 1 min.

Filter the mixture and wash the precipitate with 5 ml. of water to which a drop of 6*N* HCl has been added. Allow about 1 ml. of this wash solution to run into the filtrate and then discard the remainder. Treat the precipitate by ***P. 8*** and, in case Groups III to V are present, reserve the filtrate for treatment by ***P. 23.***

Procedure 8. **Precipitate from P. 7 (PbS, Bi_2S_3, CuS, CdS, HgS, As_2S_3, Sb_2S_3, SnS).** Pour 3 ml. of hot sodium sulfide reagent onto the precipitate from ***P. 7.*** Carefully stir the mixture in the funnel so that the reagent comes in contact with all of the precipitate. Reheat the filtrate and again pour it onto the precipitate. After all of the solution has passed through the filter, heat a fresh 2-ml. portion of the reagent and pour it over the precipitate. Now wash the residue with 5 ml. of water containing 5 drops of 1*N* NH_4NO_3. Discard the wash solution; do not allow it to flow into the sodium sulfide filtrate.

Procedure 9. **Residue from P. 8 (PbS, Bi_2S_3, CuS, and CdS).** Pour 5 ml. of hot 4*N* HNO_3 over the precipitate in the funnel. Collect the filtrate in a 50-ml. beaker. Wash the filter with 1 ml. of water and allow the wash water to flow into the solution in the beaker. Add 10 drops of 4*N* H_2SO_4 to this solution and then evaporate it until dense white fumes of SO_3 are evolved. Cool the contents of the beaker, add 3 ml. of water, and then filter the mixture. Loosen any precipitate adhering to the bottom of the beaker and use about 2 ml.

* This operation adjusts the concentration of the H_3O^+ to between 0.2 and 0.3*N* unless the acetate ion or the anion of some other weak acid is present. If this condition exists, the acidity must be adjusted in the presence of such an indicator as methyl violet. Consult the instructor with regard to the proper procedure.

of water to wash the solid into the funnel. Treat the residue according to ***P. 10*** and the filtrate (Bi^{+++}, Cu^{++}, and Cd^{++}) by ***P. 11.***

Procedure 10. **Residue from P. 9 ($PbSO_4$, white).** Mix 5 drops of 4*N* CH_3COOH with 5 ml. of 1*N* CH_3COONH_4. Pour this mixture onto the filter containing the residue from ***P. 9.*** Add 10 drops of 1*M* K_2CrO_4 to the liquid that passes through the filter. A yellow precipitate of $PbCrO_4$ confirms the presence of Pb^{++}.

Procedure 11. **Filtrate from P. 9 (Bi^{+++}, Cu^{++}, and Cd^{++}).** Add 10 drops of 15*N* NH_4OH to the filtrate from ***P. 9.*** A white or translucent precipitate ($Bi(OH)_3$) indicates the presence of Bi^{+++}. Precipitates of $Cu(OH)_2$ and $Cd(OH)_2$ may form at first, but they dissolve in an excess of ammonia to form $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$ respectively. Filter the mixture and wash the precipitate with 3 ml. of water. Treat the precipitate according to ***P. 12,*** and the filtrate by ***P. 13.***

Procedure 12. **Precipitate from P. 11 ($Bi(OH)_3$, white).** Prepare a solution of sodium stannite by adding 1 ml. of 1*N* $SnCl_2$ to 3 ml. of 4*N* NaOH. Shake the test tube vigorously. If the precipitate that first forms does not dissolve completely, add to it 1 ml. of 4*N* NaOH. Pour this solution over the precipitate on the filter. The immediate appearance of a black stain confirms the presence of Bi^{+++}.

Procedure 13. **Filtrate from P. 11 ($[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$).** The blue color of this solution indicates the presence of Cu^{++} in the original known or unknown. Divide the solution into two equal parts. To the first part add 4*N* CH_3COOH until the solution is neutral to litmus paper. Now add 10 drops of 0.1*N* $K_4Fe(CN)_6$. A pink precipitate of cupric ferrocyanide confirms the presence of Cu^{++}. A white precipitate of cadmium ferrocyanide does not interfere with the test.

Procedure 14. **Second Part of Solution from P. 13.** Add 1*N* KCN, drop by drop, until the blue color of the $[Cu(NH_3)_4]^{++}$ is discharged. (If Cu^{++} is absent, add only 1 drop of 1*N* KCN). Pass H_2S into the colorless solution. A yellow precipitate (CdS) proves the presence of Cd^{++}. If the precipitate obtained at this point is dark in color, the presence of other metals (which form black sulfides) is shown. They may be present at this point because of faulty technique in carrying out previous parts of the analysis. If the precipitate is so dark in color as not to be distinguishable as CdS, filter the mixture, and dissolve the insoluble sulfides in 2 ml. of 1*N* HCl. Treat this solution with 1 ml. of 1*N* CH_3COONH_4 and then saturate it with H_2S. A pure yellow precipitate is obtained if Cd^{++} is present.

Procedure 15. **Solution from P. 8 (Tin Group: HgS_2^-, $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, and SnS_3^-).** Add 6*N* HCl drop by drop to the solution of the Tin Group from ***P. 8*** until it is just acid to litmus paper or phenolphthalein (1 drop of its solution added directly to the solution being acidified). Shake the tube vigorously and test the solution frequently during the addition of the acid. Heat the mixture to its boiling point, then filter it, and wash the precipitate with 3 ml. of water. Discard the wash water as well as the filtrate. Treat the precipitate (HgS, As_2S_5, Sb_2S_5, and SnS_2) by ***P. 16.***

Procedure 16. **Precipitate from P. 15 (HgS, black; As_2S_5, yellow; Sb_2S_5, orange; SnS_2, yellow to brown).** Treat the precipitate from ***P. 15*** with 3 ml. of 6*N* HCl. Stir up the precipitate with the acid. After the acid solution has passed through the filter, add another 3-ml. portion of 6*N* HCl. Sb_2S_5 and SnS_2 dissolve. Treat the undissolved residue (HgS and As_2S_5) by ***P. 17,*** and the solution ($SbCl_6^{\equiv}$ and $SnCl_6^{=}$) by ***P. 20.***

Procedure 17. **Residue from P. 16 (HgS and As_2S_5).** Wash the residue with 10 ml. of water. Discard the wash water. Now pour a hot mixture of 2 ml. of 15*N* NH_4OH and 3 ml. of 3 per cent H_2O_2 onto the precipitate.* Treat the residue (HgS) by ***P. 18*** and the filtrate ($AsO_4^{\equiv}$) by ***P. 19.***

* Ammonia dissolves As_2S_5 with the formation of $AsS_4^{\equiv}$ and $AsO_3S^{\equiv}$. Hydrogen peroxide converts these ions to $AsO_4^{\equiv}$ and oxidizes $S^=$ to $SO_4^=$. This oxidation is necessary in order to prevent interference by the $S^=$ with the confirmatory test for arsenic in ***P. 19.***

Procedure 18. **Residue from P. 17 (HgS).** Treat the residue with a mixture of 10 drops of 5 per cent NaClO and 1 ml. of 6*N* HCl. Wash the filter with 2 ml. of water and allow the wash liquid to pass into the original filtrate. Boil the combined filtrate several minutes in order to decompose the HClO that it contains. Now add 2 drops of 1*N* $SnCl_2$. A white precipitate (Hg_2Cl_2) that may turn gray or black (Hg) confirms the presence of Hg^{++}.

Procedure 19. **Filtrate from P. 17 ($AsO_4^{\equiv}$).** Boil the filtrate from ***P. 17*** several minutes in a 50-ml. beaker. Now add 10 drops of magnesium nitrate mixture. A white precipitate ($MgNH_4AsO_4$) indicates arsenic. Filter off the precipitate, wash it with a 2-ml. portion of water containing 2 drops of 4*N* CH_3COOH, and then treat it with 2 or 3 drops of 0.1*N* $AgNO_3$. A change in the color of the precipitate to reddish brown (formation of Ag_3AsO_4) confirms the presence of As^{+3} or As^{+5} in the original unknown.

Procedure 20. **Solution from P. 17 ($SbCl_6^{\equiv}$ and $SnCl_6^{=}$).** Add a small quantity (about 0.1 g.) of *pure* iron or magnesium to the solution from ***P. 17.*** Place the test tube in a beaker (or an Erlenmeyer flask) containing hot water until all the metal has dissolved. A black precipitate may be antimony. Filter it off and wash it with 1 ml. of water. Treat the precipitate (Sb) by ***P. 21*** and the filtrate (Sn^{++}) by ***P. 22.***

Procedure 21. **Precipitate from P. 20 (Sb).** Treat the residue with a mixture of 1 ml. of 4*N* HNO_3 and 3 ml. of 1*N* tartaric acid.* To this solution add about 3 ml. of 6*N* CH_3COONH_4. Now pass in H_2S. An orange precipitate of Sb_2S_3 confirms the presence of Sb^{+3} or Sb^{+5} in the original unknown.

Procedure 22. **Solution from P. 20 (Sn^{++}).** Add 1 ml. of 0.1*N* $HgCl_2$. A white precipitate, changing in color to gray or black, confirms the presence of Sn^{++}.

(G) Equations and Exercises. Balance the following equations and study the exercises before applying for an unknown.

1. Equations

a. Arsenic acid + ammonium iodide

$$H_2AsO_4^- + I^- + H_3O^+ \rightarrow HAsO_2 + I_2 + H_2O$$

b. Each of the ions of Group II + hydrogen sulfide

(*Example*) $Bi^{+++} + H_2S + H_2O \rightarrow Bi_2S_3 \downarrow + H_3O^+$

c. Each of the sulfides of the Tin Group + the sodium sulfide reagent

(*Example*) $As_2S_3 + S_2^{=} + S^{=} \rightarrow AsS_4^{\equiv}$

d. Each of the sulfides of the Copper Group + nitric acid

(*Example*) $Bi_2S_3 + NO_3^- + H_3O^+ \rightarrow Bi^{+++} + S\downarrow + NO\uparrow + H_2O$

e. Lead sulfate + ammonium acetate

$$PbSO_4 + CH_3COO^- \rightarrow SO_4^{=} + ?$$

f. Lead acetate + potassium chromate

$$Pb(CH_3COO)_2 + ? \rightarrow CH_3COO^- + ?$$

g. Bismuth, copper, and cadmium nitrates + excess ammonia

(*Example*) $Cu^{++} + NH_3 + H_2O \rightarrow Cu(OH)_2\downarrow + ?$

$$Cu(OH)_2 + NH_3 \rightarrow [Cu(NH_3)_4]^{++} + ?$$

* Nitric acid oxidizes Sb to Sb_2O_3, which dissolves readily in tartaric acid to form the soluble complex, $[(SbO)C_4H_4O_6]^-$.

h. Stannous chloride + excess sodium hydroxide

$Sn^{++} + OH^- \rightarrow Sn(OH)_2$

$Sn(OH)_2 + OH^- \rightarrow ?$ (Text, p. 965)

i. Bismuth hydroxide + sodium stannite

$Bi(OH)_3 + ? \rightarrow Bi + [Sn(OH)_6]^=$

j. Tetramminecupric hydroxide + acetic acid

$[Cu(NH_3)_4]^{++} + OH^- + CH_3COOH \rightarrow Cu^{++} + CH_3COO^- + NH_4^+ + H_2O$

k. Cupric ion + potassium ferrocyanide

$Cu^{++} + K^+ + [Fe(CN)_6]^{\equiv} \rightarrow ?$ (Text, p. 1079)

l. Tetramminecupric and tetramminecadmium ions + potassium cyanide

$2[Cu(NH_3)_4]^{++} + 9CN^- + OH^- \rightarrow [Cu(CN)_4]^{\equiv} + CNO^- + NH_3 + H_2O$

$[Cd(NH_3)_4]^{++} + CN^- \rightarrow [Cd(CN)_4]^= + ?$

m. Tetracyanocadmiate ion + hydrogen sulfide

$[Cd(CN)_4]^= + H_2S \rightarrow CdS\downarrow + HCN + ?$

n. Each of the complex thio-ions of the elements of the Tin Group + hydrochloric acid

(*Example*) $SbS_4^{\equiv} + H_3O^+ \rightarrow Sb_2S_5\downarrow + H_2S + H_2O$

o. Polysulfide ion + hydrochloric acid

$S_2^= + H_3O^+ \rightarrow S\downarrow + H_2S + ?$

p. Sulfides of Sb^{+5} and Sn^{+4} + hydrochloric acid

$? + H_3O^+ + Cl^- \rightarrow SbCl_6^{\equiv} + H_2S\uparrow + H_2O + S$

$? + H_3O^+ + Cl^- \rightarrow SnCl_6^= + H_2S\uparrow + H_2O$

q. Arsenic sulfide + ammonia + hydrogen peroxide

$As_2S_5 + OH^- \rightarrow AsS_4^{\equiv} + AsO_3S^{\equiv} + 3H_2O$

$AsS_4^{\equiv} + 16H_2O_2 + 8OH^- \rightarrow AsO_4^{\equiv} + SO_4^= + H_2O$

$AsO_3^{\equiv} + 4H_2O_2 + OH^- \rightarrow AsO_4^{\equiv} + SO_4^= + H_2O$

r. Mercuric sulfide + hydrochloric acid + sodium hypochlorite

$HgS + HClO + H_3O^+ \rightarrow Hg^{++} + S + Cl^- + ?$

s. Sodium arsenate + magnesium nitrate mixture

$AsO_4^{\equiv} + Mg^{++} + NH_4^+ \rightarrow ?$

t. Magnesium ammonium arsenate + silver nitrate

$? + Ag^+ \rightarrow Ag_3AsO_4 + ? + ?$

u. Antimony + nitric acid + tartaric acid

$$Sb + NO_3^- + H_3O^+ \rightarrow Sb_2O_3 + NO\uparrow + H_2O$$

$$Sb_2O_3 + HC_4H_4O_6^- \rightarrow [(SbO)C_4H_4O_6]^- + H_2O$$

v. Antimonyl tartrate ion + hydrogen sulfide

$$[(SbO)C_4H_4O_6]^- + H_2S \rightarrow Sb_2S_3\downarrow + C_4H_4O_6^{=} + ?$$

2. Exercises

a. Be able to reproduce the schematic outlines for the analysis of Group II.

b. Describe the confirmatory test for each of the ions of Group II.

c. On the basis of the solubility product principle, explain why the concentration of the hydronium ion is set at $0.3N$ for the precipitation of the elements of Group II as their sulfides.

d. Give the general relationship between the concentration of the H_3O^+ and that of the $S^=$ in a solution containing these ions.

e. Which ion of Group II is most apt to escape precipitation if the acid concentration is too high? Which ion of Group III is most apt to precipitate with the ions of Group II if the acid concentration is below $0.2N$?

f. Explain why ammonium iodide is added previous to the precipitation of the Group II sulfides.

g. Which ions of Group II form complexes with ammonia?

h. Lead acetate is a weak salt. Explain why $PbSO_4$ dissolves in a solution of CH_3COONH_4.

i. Why is it necessary to add KCN to the solution in which the confirmatory test for Cd^{++} is to be made?

j. Give a schematic outline (any workable scheme) for the separation and identification of the ions in each of the following mixtures:

(1) Pb^{++}, Cd^{++}, Sb^{+3}
(2) Cu^{++}, As^{+3}, Sn^{++}
(3) Bi^{+++}, Hg^{++}, Sb^{+3}

k. Give a reagent which might be used to bring about a separation in each of the following pairs of compounds or ions: SnS_2–HgS, Bi^{+++}–Cu^{++}, As_2S_3–Bi_2S_3, Cd^{++}–Bi^{+++}, $PbSO_4$–$CuSO_4$, $PbSO_4$–$Cu(OH)_2$.

l. A solution of a Group II unknown yields a black precipitate with H_2S. The precipitate is partly soluble in the sodium sulfide reagent. The solution reacts with HCl to give a black precipitate that is insoluble in ammonia. The portion of the precipitate insoluble in the sulfide reagent dissolves in HNO_3, gives no precipitate with H_2SO_4, but forms a white precipitate with NH_4OH. What ions are indicated?

Part IV

PRELIMINARY EXPERIMENTS AND PROCEDURES FOR THE ANALYSIS OF THE GROUP III CATIONS, Ni^{++}, Co^{++}, Mn^{++}, Zn^{++}, Fe^{++} and Fe^{+++}, Cr^{+++}, and Al^{+++}

(A) Preliminary Experiments. The instructor may assign any or all of the following experiments on the analytically significant reactions of the ions of this group:

1. Nickel ion, Ni^{++}. Exp. LV, part (G)**1, 2,** and **3.**

2. Cobalt ion, Co^{++}. Exp. LV, part (F)**1, 2,** and **3.**

3. Manganous ion, Mn^{++}. Exp. LIV, part (A), part (B) and part (C).

4. Ferrous and ferric ions, Fe^{++} and Fe^{+++}. Exp. LV, part (A)**1, 2;** part (B)**1, 2, 3;** part (C)**1, 2, 3, 4;** part (D)**1, 2.**

5. Zinc ion, Zn^{++}. Exp. L, part (A)**1** and **2.**

6. Chromic ion, Cr^{+++}. Exp. LIII, parts B and C.

7. Aluminum ion, Al^{+++}. Exp. LI, part (A)**1, 2, 3, 4,** and **5;** part (B).

(B) Analysis of a Known. Obtain 10 ml. of a solution known to contain the ions of Group III and analyze it by ***P. 23-37.*** Carry out the analysis on 5 ml. of the solution. After the analysis is completed, study the material in parts (D) and (E), and then balance the equations and be able to answer the questions in part (G). Report to the laboratory instructor for an oral quiz.

(C) Analysis of a Group III Unknown. After the successful completion of the oral quiz, obtain 10 ml. of an unknown. Analyze 5 ml. of this solution for the ions of Group III.

(D) Discussion of the Analysis of Group III. The ions of this group precipitate as hydroxides and sulfides. After the solution from which Groups I and II have been removed is boiled to remove H_2S, there is added to it NH_4Cl and NH_4OH. The hydroxides of the trivalent ions of the Aluminum Group, Fe^{+++}, Cr^{+++}, and Al^{+++} precipitate.* Ammonium hydroxide also precipitates the hydroxides of three of the other four ions in Group II (Ni^{++}, Co^{++}, and Zn^{++}), but these precipitates dissolve in an excess of ammonia to form the complex ions $[Ni(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, and $[Zn(NH_3)_4]^{++}$. Ammonium chloride prevents the precipitation of $Mn(OH)_2$ by keeping the concentration of the OH^- so low that $[Mn^{++}] \times [OH^-]^2 < K_{Mn(OH)_2}$. For the same reason, ammonium chloride prevents the precipitation, at this point, of magnesium as its hydroxide. Magnesium is a member of Group V.

When H_2S is passed through the mixture obtained after the addition of NH_4Cl and NH_4OH, the sulfides of nickel, cobalt, manganese, and zinc are precipitated, while $Fe(OH)_3$ is changed largely to FeS. The hydroxides of chromium and aluminum are not affected because they are less soluble than the corresponding sulfides. As a matter of fact, the sulfides of these two elements are completely hydrolyzed to the hydroxides.

All the sulfides and hydroxides of this group, with the exception of NiS and CoS, are soluble in dilute HCl. No completely satisfactory explanation is known for the fact that these two sulfides do not precipitate in a weakly acidic solution yet, once they are precipitated from neutral or alkaline solution, they are insoluble in dilute HCl. One theory attributes their anomalous behavior to their transformation into less soluble allotropic modifications, while another postulates that a strong adsorption of sulfide ions brings about

* During the analysis of an unknown, the appearance or nonappearance of a precipitate at this point gives some indication of the presence or absence of these ions.

a very slow rate of dissolution of NiS and CoS. However, use is made of this peculiar behavior of these two sulfides in separating them from the other hydroxides and sulfides of this group, all of which are soluble in dilute HCl.

Zn^{++}, Cr^{+++}, and Al^{+++} are separated from Mn^{++} and Fe^{+++} by taking advantage of the amphiprotic nature of $Zn(OH)_2$, $Al(OH)_3$, and $Cr(OH)_3$. The first two hydroxides dissolve in NaOH to form the soluble anions $[Zn(OH)_4]^{=}$ and $[Al(OH)_4]^{-}$. Chromic hydroxide also reacts to form a similar anion, $[Cr(OH)_4]^{-}$, but H_2O_2 is added to oxidize it to the more stable chromate ion, $CrO_4^{=}$.

A number of procedures have been devised for the separation and identification of the ions of Group III. Difficulties are encountered in all of them because of coprecipitation, postprecipitation, and adsorption. Thus, some FeS may coprecipitate with NiS and CoS. Likewise, some $Zn(OH)_2$ and $Al(OH)_3$ may remain with the precipitate of MnO(OH) and $Fe(OH)_3$.

Other complications arise from the presence of certain ions, among which may be mentioned the phosphate, oxalate, tartrate, and citrate ions. The first of these ions causes the partial precipitation of the phosphates of Mg, Ca, Sr, and Ba with the ions of Group III; oxalates, tartrates, and citrates prevent the precipitation of Al^{+++}, Cr^{+++}, and Fe^{+++} by forming stable complexes with these ions. Thus, these interfering ions must be removed or destroyed if they are found to be present in an unknown.*

(E) Schematic Outline for the Analysis of Group III

23. Filtrate from Group II, or Group III known or unknown: Ni^{++}, Co^{++}, Mn^{++}, Zn^{++}, Fe^{++} or Fe^{+++}, Cr^{+++}, and Al^{+++} (also the ions of Groups IV and V). Boil to eliminate H_2S. Add NH_4Cl and NH_4OH.

24. Precipitate (Aluminum Group): $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$
Solution (Zinc Group): $[Ni(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, $[Zn(NH_3)_4]^{++}$, Mn^{++}. Pass H_2S into the mixture.

38. Filtrate: Groups IV and V

25. Precipitate: NiS, CoS, MnS, ZnS, FeS and Fe_2S_3, $Cr(OH)_3$, $Al(OH)_3$. Add HCl

26. Residue: NiS, CoS. Add NaClO and HCl

30. Filtrate: Mn^{++}, Zn^{++}, Fe^{++}, Cr^{+++}, Al^{+++}. Add NaOH and H_2O_2.

27. Solution: Ni^{++}, Co^{++}. Boil. Divide into 2 parts.

28. First part: Add $(NH_4)_2CO_3$ and dimethylglyoxime. *Red precipitate* confirms Ni^{++}.

29. Second part: Evaporate. Add CH_3COONa, CH_3COOH, and KNO_2. *Yellow precipitate* $K_2Na[Co(NO_2)_6]$, confirms Co^{++}.

31. Precipitate: MnO(OH), $Fe(OH)_3$. Add HNO_3 and H_2O_2. Divide into 2 parts

32. First part: Add NH_4SCN. *Deep red color* confirms Fe^{+++}.

33. Second part: Add $NaBiO_3$. *Purple color*, MnO_4^{-}, confirms Mn^{++}.

34. Filtrate: $[Zn(OH)_4]^{=}$, $CrO_4^{=}$, $[Al(OH)_4]^{-}$. Boil. Divide into 3 parts.

35. First part: Add $(NH_4)_2S$. *White precipitate*, ZnS, confirms Zn^{++}.

36. Second part: Add CH_3COOH and $Pb(CH_3COO)_2$. *Yellow precipitate*, $PbCrO_4$, confirms Cr^{+++}.

37. Third part: Add CH_3COOH, Aluminon, and $(NH_4)_2CO_3$. *Red precipitate*, confirms Al^{+++}.

(F) Procedures for the Analysis. ***Procedure 23.*** **Filtrate from P. 7 (ions of Groups III, IV, and V), or Group III Known or Unknown.** Boil the filtrate from Group II for several minutes to drive off hydrogen sulfide. To this solution, or to 5 ml. of the Group III known or unknown, add 10 drops of 6*N* NH_4Cl and 1 ml. of 15*N* NH_4OH. Brown $Fe(OH)_3$, light green $Cr(OH)_3$, and white or translucent $Al(OH)_3$ precipitate. Treat the mixture by *P. 24.*

Procedure 24. **Mixture from P. 23 ($[Ni(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, Mn^{++}, $[Zn(NH_3)_4]^{++}$, $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$).** Warm the mixture from *P. 23* to

* These ions are not to be included in the unknowns analyzed in this course.

50–60°, pass H_2S into it for about 5 minutes, and then filter the mixture. Wash the precipitate with 3 ml. of water to which has been added 1 drop of a saturated solution of NH_4Cl and 1 drop of 15*N* NH_4OH. Treat the precipitate by ***P. 25*** and the filtrate (Groups IV and V) by ***P. 38.***

Procedure 25. **Precipitate from P. 24 (NiS, black; CoS, black; MnS, flesh-colored; ZnS, white; Fe_2S_3, black; $Cr(OH)_3$, greenish; $Al(OH)_3$, white).** Add 5 ml. of 1*N* HCl to the precipitate from ***P. 24.*** Stir up the mixture in order to bring all the precipitate in contact with the acid. After the acid has passed through the filter, wash the precipitate with 3 ml. of water to which 1 drop of 6*N* HCl has been added. Allow this wash solution to flow into the acid filtrate. Only CoS and NiS remain on the filter. These sulfides should remain in contact with the acid for only the shortest possible length of time because they slowly dissolve in it. Treat the precipitate of NiS and CoS by ***P. 26*** and the filtrate by ***P. 30.***

Procedure 26. **Precipitate from P. 25 (NiS and CoS).** Treat the precipitate from ***P. 25*** with a mixture made by diluting 1 ml. of 5 per cent NaClO with 3 ml. of water and then adding 1 ml. of 6*N* HCl. Allow the solution to pass through the filter and then wash the filter with 2 ml. of water. Combine the wash liquid with the first filtrate. Treat the combined filtrate by ***P. 27.***

Procedure 27. **Filtrate from P. 26 (Ni^{++}, green; Co^{++}, pink).** Boil the filtrate from ***P. 26*** in a 50 ml. beaker for 2 or 3 min. in order to decompose HClO and to drive off the chlorine. Divide the solution into 2 equal parts and treat one of them by ***P. 28*** and the other by ***P. 29.***

Procedure 28. **First Part of Solution from P. 27.** Add 3 ml. of 2*N* $(NH_4)_2CO_3$ and 10 drops of dimethylglyoxime reagent. A scarlet precipitate of the inner complex salt of nickel dimethylglyoxime proves the presence of nickel. When Co^{++} is also present, it may be necessary to add an additional 10 drops of the reagent before the nickel precipitate will appear.

Procedure 29. **Second Part of Solution from P. 27.** Evaporate the second part of the solution from ***P. 27*** just to dryness in order to drive off HCl (use a 50-ml. beaker and do not bake the residue). Dissolve the residue in 2 ml. of water. Add to this solution 10 drops of 1*N* CH_3COONa, 1 ml. of 1*N* CH_3COOH, and 3 ml. of 6*N* KNO_2. Warm the mixture and allow it to stand for several minutes. A yellow precipitate of $K_2Na[Co(NO_2)_6]$ proves the presence of Co^{++}.

Procedure 30. **Filtrate from P. 25 (Mn^{++}, Zn^{++}, Fe^{+++}, Cr^{+++}, and Al^{+++}).** To the filtrate from ***P. 25*** add 3 ml. of 4*N* NaOH and 1 ml. of 3 per cent H_2O_2. Filter the mixture. Wash the precipitate with 2 ml. of water containing 5 drops of 4*N* NaOH, and then with 1 ml. of water. Treat the precipitate of MnO(OH) and $Fe(OH)_3$ by ***P. 31*** and the filtrate $[Zn(OH)_4]^=$, $CrO_4^=$, and $[Al(OH)_4]^-$ by ***P. 34.***

Procedure 31. **Precipitate from P. 30 (MnO(OH) and $Fe(OH)_3$).** Treat the precipitate from ***P. 30*** with a mixture of 1 ml. of 4*N* HNO_3 and 5 drops of 3 per cent H_2O_2. Wash the filter with 3 ml. of water and allow it to flow into the first filtrate. Boil the combined filtrate for several minutes in a 50-ml. beaker. This destroys the excess of H_2O_2 present and, at the same time, the nitric acid oxidizes any Fe^{++} to Fe^{+++}. Divide the solution into 2 parts for treatment by ***P. 32*** and ***P. 33.***

Procedure 32. **First Part of Solution from P. 31 (Fe^{+++} and Mn^{++}).** Add 10 drops of 0.1*N* NH_4SCN to the solution. A deep red color proves the presence of Fe^{+++}. A faint red color shows only a trace of iron which might well be present only as an impurity in the reagents.

Procedure 33. **Second Part of Solution from P. 31 (Fe^{+++} and Mn^{++}).** Add from about 20 to 30 mg. (an amount about equal in size to the head of a match) of $NaBiO_3$ to the solution. Shake the mixture for several minutes and then allow the solid to settle. A purple color, produced by the MnO_4^-, proves the presence of Mn^{++}.

Procedure 34. **Filtrate from P. 31 ($[Zn(OH)_4]^-$, CrO_4^-, $[Al(OH)_4]^-$).** Boil the filtrate from ***P. 31*** for 3 or 4 min. in a 50-ml. beaker in order to decompose excess H_2O_2. Adjust the volume of the solution to 9 ml. either by evaporation or by the addition of water. Divide the solution into 3-ml. portions for treatment by ***P. 35, P. 36,*** and ***P. 37.***

Procedure 35. **First Part of Solution from P. 34.** Add 5 drops of 1*N* $(NH_4)_2S$. A white precipitate (ZnS) proves the presence of Zn^{++}.

Procedure 36. **Second Part of Solution from P. 34.** If the solution is yellow, the presence of $CrO_4^=$ is indicated. Add 4*N* CH_3COOH, drop by drop, until the solution is acid to litmus paper. Now add 1 ml. of 0.1*N* $Pb(CH_3COO)_2$. A yellow precipitate ($PbCrO_4$) confirms the presence of Cr^{+++}.

Procedure 37. **Third Part of Solution from P. 34.** Drop 4*N* CH_3COOH into the solution until it is just acid to litmus paper. A white precipitate of $Zn(OH)_2$ and $Al(OH)_3$ forms when the solution becomes neutral, but the $Zn(OH)_2$ dissolves when the solution is made slightly acid; aluminum hydroxide remains undissolved. Treat the mixture with 5 drops of aluminon reagent and 10 drops of 2*N* $(NH_4)_2CO_3$. A red "lake" confirms the presence of Al^{+++}. Aluminon * forms lakes with other metallic hydroxides in neutral or slightly acid solutions, but these lakes are decomposed in alkaline solution while the aluminum hydroxide lake is stable. Hence, if the precipitate remains red in the presence of $(NH_4)_2CO_3$, the presence of Al^{+++} is confirmed.

(G) Equations and Exercises. Balance the following equations and study the exercises before applying for an unknown.

1. Equations

a. Ferric, chromic, and aluminum chlorides + ammonium hydroxide

(*Example*) $Fe^{+++} + NH_3 + H_2O \rightarrow Fe(OH)_3\downarrow + NH_4^+$

b. Nickel, cobalt, and zinc hydroxides + excess ammonia

(*Example*) $Ni(OH)_2 + NH_3 \rightarrow [Ni(NH_3)_6]^{++} + OH^-$

c. Ferric hydroxide + hydrogen sulfide

$Fe(OH)_3 + H_2S \rightarrow Fe_2S_3 + H_2O$

d. Ferric sulfide + hydrochloric acid

$Fe_2S_3 + H_3O^+ \rightarrow H_2S\uparrow + S\downarrow + H_2O + Fe^{++}$

i. Cobalt or nickel sulfide + hypochlorous acid

$CoS + HClO + H_3O^+ \rightarrow Co^{++} + Cl^- + S\downarrow + H_2O$

j. Nickel chloride + dimethylglyoxime

(See Text, p. 829)

k. Cobalt chloride + potassium nitrite (in the presence of acetic acid and sodium acetate)

$Co^{++} + NO_2^- + H_3O^+ \rightarrow [Co(NO_2)_6]^{\equiv} + NO\uparrow + H_2O$

$K^+ + Na^+ + [Co(NO_2)_6]^{\equiv} \rightarrow K_2Na[Co(NO_2)_6]\downarrow$

l. Zinc, chromic, and aluminum hydroxides + excess sodium hydroxide

$Zn(OH)_2 + OH^- \rightarrow [Zn(OH)_4]^=$

$Al(OH)_3 + OH^- \rightarrow ?$

$Cr(OH)_3 + OH^- \rightarrow ?$

* The ammonium salt of aurin tricarboxylic acid.

n. Sodium chromite + hydrogen peroxide in alkaline solution

$$[Cr(OH)_4]^- + H_2O_2 + OH^- \rightarrow CrO_4^= + H_2O$$

n. Manganous hydroxide + hydrogen peroxide

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO(OH) + ?$$

o. Ferrous hydroxide + hydrogen peroxide

$$Fe(OH)_2 + H_2O_2 \rightarrow Fe(OH)_3 + ?$$

p. The compound MnO(OH) + hydrogen peroxide + nitric acid

$$MnO(OH) + H_2O_2 + H_3O^+ \rightarrow Mn^{++} + O_2\uparrow + H_2O$$

q. Manganous nitrate + sodium bismuthate

$$Mn^{++} + BiO_3^- + H_3O^+ \rightarrow MnO_4^- + Bi^{+++} + H_2O$$

2. Exercises

a. Describe the confirmatory test for each ion of Group III.

b. List the following for the ions of Group III:

(1) The color of each ion
(2) The formula and color of each hydroxide precipitated by NH_4OH
(3) The hydroxides that do not react with H_2S
(4) The formulas and colors of the sulfides
(5) Those of the freshly precipitated sulfides that do not dissolve readily in dilute HCl
(6) The amphiprotic hydroxides

c. Explain the function of NH_4Cl in preventing the precipitation of $Mg(OH)_2$ with Group III and of $Mn(OH)_2$ with the hydroxides of iron, chromium, and aluminum.

d. Why does not H_2S convert $Cr(OH)_3$ and $Al(OH)_3$ to the corresponding sulfides?

e. Review the reasons advanced for the failure of freshly precipitated CoS and NiS to dissolve in dilute HCl.

f. If a white precipitate forms when NH_4Cl–NH_4OH is added to a solution containing the ions of Group III, which ions are indicated to be absent?

g. If the white precipitate obtained in **f** does not change color on the addition of H_2S, what other ions are shown to be absent?

h. A solution contains only Fe^{+++}, Al^{+++}, Zn^{++}, and Co^{++}. State the results obtained upon the addition of the following reagents:

(1) NH_4Cl and excess NH_4OH
(2) NH_4OH and H_2S
(3) Excess NaOH

i. The following observations were made during the analysis of a Group III unknown:

(1) No precipitate was formed with NH_4Cl and NH_4OH.
(2) H_2S gave a black precipitate, partially soluble in dilute HCl.
(3) When the solution obtained by the action of the black precipitate with dilute HCl was treated with NaOH, a white precipitate formed. This precipitate dissolved in an excess of NaOH.

On the basis of these observations, state which ions might be present and which must be absent.

Part V

PRELIMINARY EXPERIMENTS AND PROCEDURES FOR THE ANALYSIS OF THE GROUP IV CATIONS, Ba^{++}, Ca^{++}, and Sr^{++}

(A) Preliminary Experiments. The instructor may assign any or all of the following experiments on the analytically significant reactions of the ions of this group:

1. Barium ion, Ba^{++}, calcium ion, Ca^{++}, and strontium ion, Sr^{++}. Exp. XLVII, part (A)1, 2.

(B) Analysis of a Known. Obtain 10 ml. of a solution known to contain the ions of Group IV and analyze it by ***P. 38–44.*** Carry out the analysis on 5 ml. of the solution. After the analysis is completed, study the material in parts (D) and (E), and then balance the equations and be able to answer the questions in part (G). Report to the laboratory instructor for an oral quiz.

(C) Analysis of a Group IV Unknown. After the successful completion of the oral quiz, obtain 10 ml. of an unknown. Analyze 5 ml. of this solution for the ions of Group IV.

(D) Discussion of the Analysis of Group IV. The chlorides and sulfides of the ions of this group are not precipitated by the Cl^- and $S^=$ respectively, but their carbonates may be precipitated by $(NH_4)_2CO_3$ in a solution made alkaline with NH_4OH. When this precipitation is carried out, NH_4Cl must also be present in order to prevent the precipitation of Mg^{++} as $Mg(OH)_2$ or $MgCO_3$.

In order to precipitate the carbonates of the alkaline-earth metals and to prevent the precipitation of $MgCO_3$, the molar concentration of the $CO_3^=$ must be such that

$$[Ba^{++}] \times [CO_3^=] > 8 \times 10^{-9}$$

and

$$[Mg^{++}] \times [CO_3^=] < 4 \times 10^{-5}$$

In a solution of $(NH_4)_2CO_3$ the concentration of the $CO_3^=$ is low because of the extensive hydrolysis of the ion:

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^-$$

Indeed, the concentration of the $CO_3^=$ in a solution of $(NH_4)_2CO_3$ is too low to secure an analytically complete precipitation of all of the carbonates of the alkaline-earth metals.

The extent of the foregoing hydrolysis may be decreased by increasing the concentration of the OH^- by the addition of NH_4OH. This substance reverses, to a sufficient extent, the hydrolysis of the carbonate ion. However, if the concentration of the OH^- is too high, then $Mg(OH)_2$ or $MgCO_3$ will be precipitated. The inclusion of NH_4Cl in the group reagent brings about the desired OH^- concentration. Equal concentrations of NH_4^+ and NH_4OH usually adjust the concentration of OH^- to the proper value, and this, in turn, brings about the proper concentration of $CO_3^=$.

Differences in the solubility of various salts of Ba, Sr, and Ca in water and in other reagents are made use of in the separation of the ions of these elements. The following table of the solubilities of various salts of the elements in water is included for the purpose of providing ready reference to the solubility data of the compounds met with in this group.

TABLE II

SOLUBILITY DATA FOR COMPOUNDS OF THE ALKALINE-EARTH METALS
(GRAMS PER MILLILITER OF H_2O AT 25°) *

Hydroxides: $Ca(OH)_2$, 1.7×10^{-4}; $Sr(OH)_2$, 1.7×10^{-3}; $Ba(OH)_2$, 3.7×10^{-3}
Carbonates: $SrCO_3$, 5.9×10^{-6}; $CaCO_3$, 1.3×10^{-5}; $BaCO_3$, 2.7×10^{-5}
Sulfates: $BaSO_4$, $2\ 3 \times 10^{-6}$; $SrSO_4$, 1.0×10^{-4}; $CaSO_4$, 1.0×10^{-3}
Chromates: $BaCrO_4$, 3.7×10^{-6}; $SrCrO_4$, 1.2×10^{-3}; $CaCrO_4$, 1.6×10^{-1}
Oxalates: CaC_2O_4, 8.0×10^{-6}; SrC_2O_4, 3.8×10^{-5}; BaC_2O_4, 8.2×10^{-3}

After the precipitation of the alkaline-earth ions as their carbonates, the latter are dissolved in acetic acid. These carbonates, as well as carbonates in general, are readily soluble in an acid as weak as acetic acid because of the formation of the still weaker carbonic acid and its subsequent decomposition into CO_2 and water:

$$SrCO_3 \rightleftharpoons Sr^{++} + CO_3^{=}$$
$$+$$
$$H_3O^+ \longrightarrow HCO_3^- + H_2O$$
$$+$$
$$H_3O^+ \longrightarrow H_2CO_3 + H_2O$$
$$H_2O + CO_2\uparrow$$

To the acetic acid solution of the acetates there is added a mixture of CH_3COONH_4 and K_2CrO_4. Barium chromate alone is precipitated. If K_2CrO_4 is added to a dilute hydrochloric acid solution of the alkaline-earth ions, no precipitate is obtained. An explanation of this behavior is based on a consideration of the equilibria set up when a chromate is treated with an acid:

$$2BaCrO_4 \rightleftharpoons 2Ba^{++} + 2CrO_4^{=}$$
$$+$$
$$2H_3O^+ \rightleftharpoons 2HCrO_4^- + 2H_2O$$
$$Cr_2O_7^{=} + H_2O$$

The solubility of $BaCrO_4$ is so slight and the concentration of H_3O^+ in a solution of acetic acid is relatively so small that the concentration of the $CrO_4^{=}$ is not reduced sufficiently to bring about the dissolution of $BaCrO_4$. However, in a solution of HCl, the high concentration of the H_3O^+ shifts all the above equilibria to the right so that $[Ba^{++}] \times [CrO_4^{=}] < K_{BaCrO_4}$. Finally, a study of Table II shows $SrCrO_4$ and $CaCrO_4$ to be 400 and 10,000 times as soluble, respectively, as $BaCrO_4$. Hence, the concentration of the

* Each series of compounds is arranged in the order of the increasing solubility of its members.

$CrO_4^=$ in saturated solutions of the two more soluble salts is high enough to form an appreciable concentration of $HCrO_4^-$. The latter then changes to the $Cr_2O_7^=$ in the presence of acetic acid. As a result, the concentration of $CrO_4^=$ is not great enough to cause the precipitation of either $SrCrO_4$ or $CaCrO_4$.

In the separation of Ba^{++} from Sr^{++} and Ca^{++}, it is to be noted that acetic acid, present during the precipitation of $BaCrO_4$, is buffered with CH_3COONH_4. In this way, the concentration of the H_3O^+ is kept at such a value that the concentration of the $CrO_4^=$ is great enough to cause the precipitation of $BaCrO_4$, but is not high enough to bring about the precipitation of the other two chromates.

An organic solvent known as "Butyl Cellosolve" * has been found to display marked differences in its ability to dissolve various ionic compounds. Whereas this liquid dissolves about 240 mg. of $Ca(NO_3)_2$ per milliliter, the same volume dissolves only about 0.01 mg. of $Sr(NO_3)_2$.† These values are those for the anhydrous salts. The latter are readily formed from their hydrates at 170.6°, the boiling point of butyl cellosolve.

(E) Schematic Outline for the Analysis of Group IV

<table>
<tr><td colspan="4">38. Filtrate from Group III, or Group IV known or unknown: Ba^{++}, Sr^{++}, Ca^{++} (also the ions of Group V). Add NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$.</td></tr>
<tr><td>45. Filtrate: Group V</td><td colspan="3">39. Precipitate: $BaCO_3$, $SrCO_3$, and $CaCO_3$. Dissolve in CH_3COOH. Add CH_3COONH_4 and K_2CrO_4.</td></tr>
<tr><td rowspan="3"></td><td rowspan="3">40. Precipitate $BaCrO_4$. Dissolve in 0.1N HCl. Add saturated solution of $CaSO_4$. White precipitate, $BaSO_4$, confirms Ba^{++}.</td><td colspan="2">41. Filtrate: Ca^{++}, Sr^{++}. Add Na_2CO_3.</td></tr>
<tr><td>42. Precipitate: $CaCO_3$ and $SrCO_3$. Dissolve in HNO_3. Evaporate. Heat with boiling butyl cellosolve.</td><td>Filtrate: Discard.</td></tr>
<tr><td>43. Residue: $Sr(NO_3)_2$. Dissolve in water. Add $(NH_4)_2SO_4$. White precipitate, $SrSO_4$, confirms Sr^{++}.</td><td>44. Filtrate: $Ca(NO_3)_2$. Add $H_2C_2O_4$. White precipitate, CaC_2O_4, confirms Ca^{++}.</td></tr>
</table>

(F) Procedures for the Analysis. ***Procedure 38.*** **Filtrate from P. 24 (ions of Groups IV and V) or Group IV Known or Unknown.** To 5 ml. of a Group IV known or unknown, or to the filtrate from ***P. 24*** (evaporated to a volume of 5 ml.) add 2 drops of 6*N* NH_4Cl and 5 drops of 15*N* NH_4OH. Filter the solution if it is not clear. Now place the test tube containing the clear solution in a beaker partly filled with boiling water. When the solution is hot, add to it 1 ml. of 2*N* $(NH_4)_2CO_3$. After a few minutes, filter the solution and then wash the precipitate with 3 ml. of water to which 2 drops of 2*N* $(NH_4)_2CO_3$ have been added. Treat the white precipitate ($BaCO_3$, $CaCO_3$, and $SrCO_3$) by ***P. 39*** and the filtrate (Mg^{++}, K^+, Na^+, and NH_4^+) by ***P. 45.***

Procedure 39. **Precipitate from P. 38 ($BaCO_3$, $CaCO_3$, $SrCO_3$).** Treat the precipitate from ***P. 38*** with 3 ml. of water to which 7 drops of 4*N* CH_3COOH have been added. To the solution of the carbonates add 1 ml. of 1*N* CH_3COONH_4 and 10 drops of 1*M* K_2CrO_4.

* This is a trade name for the monobutyl ether of ethylene glycol, $C_4H_9OCH_2CH_2OH$.

† *Semimicro Qualitative Analysis*, H. H. Barber and T. I. Taylor, Harper & Bros., 1942, p. 281.

Shake the mixture and allow it to stand for several minutes. A yellow precipitate indicates the presence of Ba^{++}. Filter the mixture and then wash the precipitate with 3 ml. of water. Treat the precipitate ($BaCrO_4$) by ***P. 40*** and the filtrate (Ca^{++} and Sr^{++}) by ***P. 41***.

Procedure 40. **Precipitate from P. 39 ($BaCrO_4$).** Dissolve the precipitate in a mixture of 3 ml. of water and 3 drops of 6*N* HCl, and add to the solution 1 ml. of a saturated solution of calcium sulfate. A white precipitate ($BaSO_4$) confirms the presence of Ba^{++}. Further confirmation may be had by moistening the white precipitate with 12*N* HCl and then making a flame test on the mixture. A green flame confirms the Ba^{++}.

Procedure 41. **Filtrate from P. 39 (Ca^{++} and Sr^{++}).** To the filtrate from ***P. 39*** add 3 drops of 15*N* NH_4OH and then 1 ml. of 2*N* Na_2CO_3. Place the test tube containing the mixture in a beaker partially filled with hot water. Filter the hot mixture and then wash the precipitate with 3 ml. of water to which a drop of 2*N* Na_2CO_3 has been added. Discard the filtrate and treat the precipitate by ***P. 42***.

Procedure 42. **Precipitate from P. 41 ($CaCO_3$, $SrCO_3$).** To the precipitate from ***P. 41*** add 5 ml. of water which has been acidified with 5 drops of 4*N* HNO_3. Allow the solution to pass through the filter and then evaporate the filtrate in a 50-ml. beaker until the residue is *almost but not quite dry*. Add 1 ml. of butyl cellosolve to the residue and evaporate the liquid until only a drop or two remains. Do not evaporate to complete dryness! Now treat the residue with 3 ml. of butyl cellosolve, heat the mixture until the liquid boils, and then pour it onto a *dry* filter. Add an additional 1 ml. of butyl cellosolve to the residue in the beaker, heat the liquid to its boiling point, and pour it through the same filter. Reserve the filtrate ($Ca(NO_3)_2$) for ***P. 44*** and treat the residue (the $Sr(NO_3)_2$ remaining in the beaker and on the filter) by ***P. 43***.

Procedure 43. **Residue from P. 42 ($Sr(NO_3)_2$).** Dissolve the residue from ***P. 42*** in 3 ml. of water. Pour this solution through the filter containing the remainder of the solid found to be insoluble in butyl cellosolve. Wash the beaker and the filter with 1 ml. of water and combine this with the original 3 ml. of solution. Add 10 drops of 1*N* $(NH_4)_2SO_4$ to the combined solution and then heat it for a few minutes in a test tube placed in hot water. A white precipitate ($SrSO_4$) confirms the presence of Sr^{++}. Further confirmation may be obtained by filtering off the precipitate, moistening it with 1 drop of 12*N* HCl, and making a flame test. A crimson flame confirms Sr^{++}.

Procedure 44. **Filtrate from P. 42 ($Ca(NO_3)_2$).** Add 5 drops of 1*M* $H_2C_2O_4$ * to the butyl cellosolve solution from ***P. 42***. A white precipitate (CaC_2O_4) proves the presence of Ca^{++}. To obtain further confirmation, filter off the precipitate, moisten it with a drop of 12*N* HCl, and make a flame test. A brick red flame confirms Ca^{++}.

(G) Equations and Exercises. Balance the following equations and work out these exercises dealing with the analysis of Group IV.

1. Equations

a. Potassium chromate + an acid

$$CrO_4^{=} + H_3O^+ \rightleftharpoons HCrO_4^- + ? \rightleftharpoons Cr_2O_7^{=} + ?$$

b. Barium chromate + hydrochloric acid

$$BaCrO_4 + H_3O^+ \rightarrow Cr_2O_7^{=} + ? + ?$$

2. Exercises

a. Give the confirmatory tests for the ions of Group IV.

b. On the basis of the solubility product principle, the common ion effect, and the hydrolysis of ions, explain why both NH_4Cl and NH_4OH must be present when the ions of Group IV are precipitated by $(NH_4)_2CO_3$.

* A solution of $(NH_4)_2C_2O_4$ must not be used because the insolubility of this salt in butyl cellosolve brings about the precipitation of solid $(NH_4)_2C_2O_4$.

c. What difficulties would arise in the precipitation of the carbonates if no NH_4OH were added? if no NH_4Cl were present?

d. Explain why $BaCrO_4$ precipitates from an acetic acid solution while $CaCrO_4$ and $SrCrO_4$ do not.

e. Why is Na_2CO_3 more effective than $(NH_4)_2CO_3$ in precipitating Ca^{++} and Sr^{++}?

f. Refer to Table II (p. 511) and suggest a scheme for the separation of Ca^{++} and Sr^{++} which would not involve the use of an organic solvent.

g. $SrSO_4$ is not readily soluble in acids. With what reagent could it be converted to a salt readily soluble in acids? Explain.

Part VI

PRELIMINARY EXPERIMENTS AND PROCEDURES FOR THE ANALYSIS OF THE GROUP V CATIONS. Mg^{++}, K^+, Na^+, and NH_4^+

(A) Preliminary Experiments. The instructor may assign any or all of the followin experiments on the analytically significant reactions of the ions of this group:

1. **Magnesium ion, Mg^{++}.** Exp. XLVIII, part (A).
2. **Potassium ion, K^+, and sodium ion, Na^+.** Exp. XLV, part (E)**1, 2.**
3. **Ammonium ion, NH_4^+.** Exp. XXXVIII, part (E)**2, 3.**

(B) Analysis of a Known. Obtain 10 ml. of a solution known to contain the ions c Group V and analyze it by ***P. 45–50.*** Carry out the analysis on 5 ml. of the solution. · Afte the analysis is completed, study the material in parts (D) and (E), and then balance th equations and be able to answer the questions in part (G). Report to the laboratory in structor for an oral quiz.

(C) Analysis of a Group V Unknown. After the successful completion of the oral quiz obtain 10 ml. of an unknown. Analyze 5 ml. of the solution for the ions of Group V.

(D) Discussion of the Analysis of Group V. The ions of this group do not form insol uble compounds with any of the group reagents used to precipitate the ions of the four pre ceding groups. Furthermore, no group reagent is available for the simultaneous precipita tion of the ions of Group V. However, Mg^{++} is readily separable from the other three ion

In the detection of the NH_4^+ there is a marked divergence from the usual procedure for analysis in that the test for this ion is carried out on the original solution, regardless c whatever other ions may be present. This unusual procedure is made necessary by the fac that quantities of ammonium salts are added throughout the analysis of the precedin groups. Therefore, the test for the NH_4^+ is always carried out on a small separate sampl of the original known or unknown.

(E) Schematic Outline for the Analysis of Group V

<table>
<tr><td colspan="3">45. Filtrate from Group IV, or Group V known or unknown: Mg^{++}, K^+, Na^+, NH_4^+. Add $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$. Filter. Discard the precipitate. Use two thirds of the filtrate for 46 and one third for 49.</td></tr>
<tr><td colspan="2">46. Filtrate (larger portion). Add $(NH_4)_2HPO_4$.</td><td rowspan="2">49. Filtrate: (smaller portion). Evaporate nearly to dryness. Add CH_3COOH and uranyl zinc acetate. Yellow precipitate, $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$, confirms Na^+.</td></tr>
<tr><td>47. Precipitate: $MgNH_4PO_4$. Dissolve in HCl. Add p-nitrobenzeneazo-α-naphthol and NaOH. Blue precipitate confirms Mg^{++}.</td><td>48. Filtrate: K^+, Na^+, NH_4^+. Evaporate to dryness. Ignite residue. Add $Na_3[Co(NO_2)_6]$. Yellow precipitate, $K_2Na[Co(NO_2)_6]$, confirms K^+.</td></tr>
<tr><td colspan="3">50. Original known or unknown. Add NaOH. Heat. Vapors change red litmus to blue. Confirms NH_4^+.</td></tr>
</table>

(F) Procedures for the Analysis. ***Procedure 45.*** **Filtrate from P. 38, or Group V Known or Unknown (Mg^{++}, K^+, Na^+, NH_4^+).** To the filtrate from ***P. 38*** add 5 drops of 1*N* $(NH_4)_2SO_4$ and 5 drops of 0.1*M* $(NH_4)_2C_2O_4$. These reagents precipitate any Ba^{++}, Ca^{++}, and Sr^{++} not removed by $(NH_4)_2CO_3$ in ***P. 38.*** Filter the mixture and discard the precipitate. Use two thirds of the total volume of the filtrate in ***P. 46*** and one third of it in ***P. 49.*** If the solution is a Group V known or unknown, add to it 5 drops of a saturated solution of NH_4Cl and then 5 drops of 15*N* NH_4OH. Make the same division of the volume as directed above.

Procedure 46. **Larger Volume of Solution from P. 45 (Mg^{++}, K^+, Na^+, NH_4^+).** Add 10 drops of 1*M* $(NH_4)_2HPO_4$ to the solution. Heat the mixture for several minutes in a hot-water bath. Remove the tube occasionally and shake it. A flocculent white precipitate ($MgNH_4PO_4$) indicates the presence of Mg^{++}. Filter the mixture and wash the precipitate with 3 ml. of water containing 1 drop of 4*N* NH_4OH. Treat the precipitate by ***P. 47*** and the solution by ***P. 48.***

Procedure 47.* **Precipitate from P. 46 ($MgNH_4PO_4$).** The white precipitate obtained in ***P. 46*** is usually sufficient evidence for the presence of Mg^{++}, but further confirmation is possible. Dissolve the precipitate in a solution of 3 drops of 6*N* HCl in 3 ml. of water. Add 5 drops of *p*-nitrobenzeneazo-α-naphthol reagent and 10 drops of 4*N* NaOH. A blue lake confirms the presence of Mg^{++}.

Procedure 48. **Filtrate from P. 46 (K^+, Na^+, NH_4^+).** Place the filtrate from ***P. 46*** in a porcelain crucible or a small evaporating dish. Carefully evaporate the solution to dryness. Ignite (heat very strongly) the residue until all the ammonium salts have been volatilized. This has been accomplished when white fumes cease to be evolved during the heating of the residue. Finally, heat the crucible or evaporating dish around the edges to drive off any ammonium salts that may have collected there. Allow the crucible to cool and then dissolve the residue in 3 ml. of water. Filter the solution and treat the filtrate with 1 ml. of 1*M* $NaNO_2$ and 10 drops of 4*N* CH_3COOH. Heat the filtrate for 5 min. in a boiling water bath. This treatment destroys traces of NH_4^+ which may not have been volatilized during the ignition. Now cool the solution and add to it 1 ml. of the sodium cobaltinitrite reagent. A yellow precipitate of $K_2Na[Co(NO_2)_6]$ confirms the presence of K^+.

Further confirmation may be had by filtering off the precipitate and subjecting it to a flame test. The flame must be viewed through a plate of cobalt glass or through a solution of chrome alum [Exp. XLV, part (E)]. The glass or the solution absorbs the yellow light of the sodium flame which would otherwise mask the violet-colored flame given by a potassium compound.

Procedure 49. **Smaller Volume of Solution from P. 45 (Mg^{++}, K^+, Na^+, NH_4^+).** Evaporate the solution almost to dryness. Dissolve the residue in 5 drops of water and 2 drops of 4*N* CH_3COOH, and then add 1 ml. of the uranyl zinc acetate reagent. Shake the mixture and allow it to stand from 3 to 5 min. A yellow precipitate of sodium uranyl zinc acetate,

$$NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O,$$

confirms the presence of Na^+. This ion may also be confirmed by making a flame test on the original known or unknown. The yellow flame produced by the ion must be persistent because traces of sodium are always present as an impurity. Very small amounts of sodium give only a transitory yellow color to the flame.

Procedure 50. **Original Known or Unknown (Test for NH_4^+).** To 1 ml. of the solution, placed in a 50-ml. beaker, add 10 drops of 4*N* NaOH. Now cause a piece of wet red litmus paper to adhere to the under side of a small watch glass, and use this to cover the

* This procedure may be omitted if the *p*-nitrobenzeneazo-α-naphthol reagent is not available.

HNO_3 and 3 volumes of 12*N* HCl). A residue formed by this treatment may be AgCl, $PbCl_2$, or certain hydrated oxides of Sn and Sb.

Hydrochloric acid, when used alone, dissolves only those metals standing above hydrogen in the activity series. Furthermore, in the absence of an oxidizing agent, this acid permits the loss of As and Sb through the formation of gaseous hydrides of arsenic and antimony; these are arsine, AsH_3, and stibine, SbH_3. Therefore, the use of HCl alone is not recommended as a means of bringing alloys into solution.

3. Preparation and Analysis of the Solution of an Alloy. a. Use of HNO_3. If the test in 2 shows the alloy is attacked by HNO_3, treat from 25 to 50 mg. of the alloy with 3 ml. of 1 : 1 HNO_3. Heat the mixture in a water bath until the reaction is complete. Shake or stir the mixture frequently if a white solid covers the metallic particles during the course of the reaction. This treatment hastens the process of solution; the addition of more acid is unnecessary.

Transfer the mixture or the clear solution to a 50-ml. beaker and evaporate *almost* to dryness. Add 5 ml. of water to dissolve the residue. If the solution is clear, analyze it by ***P. 1–47.**** In case the solution is cloudy, or if a residue is observed, carefully decant the solution into a filter. Analyze the filtrate by ***P. 1–47.*** Wash the residue twice with 1-ml. portions of water and treat the solid along with the filtrate from Group I (***P. 7–47***).

b. Use of Aqua Regia. If the test in **2** shows the use of aqua regia is necessary to dissolve the alloy, dissolve from 25 to 50 mg. of the latter in 4 ml. of the reagent. Heat the mixture in a water bath until the reaction is complete. Transfer the clear solution or the mixture to a 50-ml. beaker and evaporate to a volume of about 1 ml. Dilute this solution with 4 ml. of water and 4 drops of 6*N* HCl. Treat the filtrate by ***P. 7–47*** and the precipitate by ***P. 2–6.*** The precipitate is probably AgCl and/or $PbCl_2$, but it may also contain oxycompounds of antimony, bismuth, and tin. These oxycompounds remain on the filter after treatment by ***P. 6*** (mercurous mercury cannot possibly be present). Use this same filter for the filtration of the Group II sulfides and, in this way, convert the oxycompounds into sulfides by the action of the H_2S present in the mixture. Thus, Sb, Bi, and Sn which would otherwise be lost are again included in the analysis.

4. Report of Analysis. Report the results of the analysis on the same type of form used for the other unknowns.

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* It is assumed that the alloy does not contain Ba, Sr, or the alkali metals. A few alloys contain Ca.

APPENDIX

A. PRECISION AND ERRORS

Whenever the value of a physical property, such as density, specific heat, melting point, etc., is determined, certain measurements and observations are required. Such measurements must be made with the apparatus and instruments available in the laboratory. Every measurement with this apparatus is subject to a certain amount of error. The error may be greater for certain methods and types of apparatus than for others.

It is always important to know the reliability of a given experimental result. This can be determined only through careful consideration of all the possible errors involved in the use of the apparatus. An estimate of the number of significant figures which should be used in expressing the final result may also be made from such considerations. For example, the result on density obtained in part (A) of Exp. IV should not be reported to five places—0.99782 g./ml. The method described and the apparatus used give results which are reliable only to the first three places—0.998 g./ml. The following elementary discussion on precision and errors shows how this conclusion may be reached.

Mistakes and Errors. Mistakes should not be confused with errors. Mistakes are blunders resulting from carelessness on the part of the observer. The following are a few common mistakes: mistakes in arithmetic; mistakes in recording data; misreading scales by one or more divisions on apparatus such as graduated cylinders, burettes, thermometers, etc.; adding up weights incorrectly; using the wrong units for measured quantities. Such inaccuracies are eliminated by careful observation and by carefully calculating and recording the numerical values. The observations and the recorded values should be checked to make certain that no mistakes have been made.

When an observer measures a quantity with the greatest care and skill possible, it is found that successive trials will differ slightly from one another. Different observers using the same apparatus with great care and skill may also obtain slightly variant results. Furthermore, slight differences may appear if a different method or a different apparatus is used. The small differences between these experimental measurements and the true value or "accepted value" are referred to as *errors*. The magnitude of the error gives a measure of the accuracy of the result. The *accuracy* of a result, then, is the concordance between the experimentally determined one and its *true value*.

Measurement and a Count. The fundamental difference between a measurement and a count is that a measurement always has an error or uncertainty associated with it. A count gives the correct result. For example, six test tubes would never be counted as 5.9 or 6.1. The correct number is six and it is not possible to make an error. It is possible, however, to make a *mistake* or blunder and count seven. On the other hand, if the volume of one of the test tubes was measured with a graduated cylinder, the results for successive trials would vary somewhat as follows: 22.2 ml., 22.5 ml., 22.1 ml., etc. If the "true" or accepted value was known to be 22.30 ml., the *absolute errors* for the measurements would be respectively -0.1 ml., $+0.2$ ml., -0.2 ml., etc. These values give the accuracy of each of the determinations. The *relative* or *percentage* error in the first determination would be $\frac{0.1}{22.30} \times 100 = 0.45$ per cent, or 0.45 parts per 100. The average or *arithmetical mean* of the three measurements is 22.27. It has an absolute error of only 0.03 ml. or a percentage error of $\frac{0.03}{22.30} \times 100 = 0.13$ per cent.

Accuracy and Precision. If the correct value for a quantity is not known, it is impossible to calculate the absolute error of an experimental result. This is the situation most commonly met in measuring an unknown length or volume; in establishing the density of an unknown liquid or solid; or in analyzing a substance of unknown composition, etc. In such cases, the *arithmetical average or mean* of a series of measurements is taken as the most reliable or *best value* for that particular set of observations or measurements. The *deviations* of the individual measurements from this average value are called *residuals.* The average of these deviations, called the *average deviation of a single observation* from the mean (a.d.), represents the accidental error that, on the average, attaches to a single observation. It gives the average difference between the observed values and the arithmetical mean. (See **Precision Measures.**)

The average deviation of a single observation or measurement is often used in chemistry as an approximate measure of the precision of the determination. This is true especially when only two or three observations are made. When several observations are made, the average deviation is used to calculate *average deviation of the mean* (A.D.), which in turn is used as a more reliable precision measure of the arithmetical mean. (See **Precision Measures.**)

Precision, therefore, expresses the degree of concordance or consistency within a set of observed or measured values. In other words, it gives a measure of the reproducibility or the uncertainty of the measurement. The *precision measure* or simply the precision gives the consistency or, in other words, the reliability of the measurements by indicating the numerical values between which there is a certain probability that the observed values will fall.

The magnitude of the precision measure is determined by the difference between the arithmetical mean and these limiting values. Thus if the precision measure of the weight of an object is written as 42.52 g. $\pm$ 0.02 g., it means that there is a fairly high probability that the observed weight of the object measured under these same conditions will be between 42.50 g. and 42.54 g. These limits give a measure of the uncertainty or, in other words, the reliability of the average weight. The narrower the limits set by the precision measure, the more precise and the more reliable is the arithmetical mean.

In addition to the accidental and indeterminate errors of observation, there may be constant and systematic operative errors associated with the use of the apparatus and with the method of measurement. Because these constant and systematic operative errors may shift the whole set of observations in one direction or another, the arithmetical mean is usually not the true value of the measured quantity. Likewise, the average deviation, or any other precision measure used, does not necessarily give the limits between which the true value lies. Only by correcting the arithmetical mean for all known sources of error can the *most probable value* of the measurement be ascertained. The precision measure of this most probable value is determined from the *average deviation of the mean* and the *uncertainty or precision measures of the correcting factors.* This procedure is described later.

Summary of Definitions. As a summary, it may be concluded that *accuracy* gives the correctness of a result, while the *precision* gives a measure of the consistency or reproducibility of a set of observations. A *deviation or residual* is the difference between an observed value and the arithmetical mean, while an *absolute error* is the difference between an observed value and the true value, or the difference between the arithmetical mean and the true value. Since the *true value* is seldom known, the *precision measure* of the *most probable value* is taken as a measure of the reliability of the result. The various methods of calculating precision measures for a small number of measurements are discussed under **Precision Measures.**

Sources of Error. 1. Constant and Systematic Operative Errors. Constant and systematic errors arise from operative factors that are known to influence the results. Often they may be determined, corrected for, or eliminated by use of proper care and skill. Con-

stant or systematic operative errors may be classed as (*a*) errors in the instruments or apparatus, (*b*) errors due to the method or conditions, (*c*) personal errors due to constitutional inability or prejudice.

(*a*) *Errors in the Instruments or Apparatus.* A few examples are as follows: Unequal arm lengths on a balance; discrepancies between the actual and indicated values of weights; inaccuracies of the graduations on volumetric apparatus or thermometers; impurities in chemicals.

(*b*) *Errors Due to Method or Conditions.* Unfavorable conditions and operative errors generally may be corrected for or eliminated by the proper precautions and care. Examples of these errors are: air motion during weighing on an uncovered balance, temperature differences, failure to allow temperature equilibrium to be reached, weighing crucibles before drying, absorption of moisture from the air, failure to clean burettes and pipettes, and allowing water to evaporate before it is weighed. Finally, there are those errors which are inherent in the particular method used, for example, the failure of a reaction or precipitation to proceed to completion.

(*c*) *Personal Errors Due to Constitutional Inability or Prejudice.* Errors from these sources arise from such conditions as color blindness, slowness in time of personal reaction, and prejudice in favor of a previous observation.

In more advanced courses, considerable care is used to eliminate or to minimize the constant and systematic operative errors by calibration of weights, balances, thermometers, and volumetric apparatus, and by the use of as refined technique and skill as is possible in carrying out the determinations.

2. Accidental or Indeterminate Errors. Slight differences in successive observations made by the same observer on the same apparatus, and under as nearly the same conditions as possible, are attributed to accidental or indeterminate errors. They arise from the inability of the observer to read graduations exactly and from other indeterminate causes. Usually these errors cannot be ascertained or corrected for readily. Errors resulting from causes over which the observer has no control are also classed as accidental errors. The methods of evaluating accidental or indeterminate errors are discussed in the following sections.

Precision Measures. In order to obtain a measure of the uncertainty of a measurement arising from accidental or indeterminate errors, it is necessary to repeat the measurement several times under as nearly the same conditions as possible. If time is not available to repeat the measurement several times, the uncertainty may be deduced from previous experience of other observers with the same type of apparatus. This latter method is, of course, only a rough approximation.

The method of calculating the precision measure depends, among other factors, on the number of measurements made. If only two or three measurements have been made, the *average deviation of a single observation* is used as a precision measure. However, if a larger number of measurements have been made, the *average deviation of the mean* is a more reliable precision measure. Other precision measures are used when still larger numbers of measurements have been made.

1. Uncertainty of an Observation Known from Previous Use of a Piece of Apparatus. From previous experience, it is possible to estimate the probable uncertainty or precision of an observation made with certain types of apparatus. This assumes that the observation is to be made as carefully and as correctly as possible, and that the apparatus or its graduations are not faulty. The following rules may be made regarding the precision with which apparatus in general chemistry is generally used. Volumetric apparatus, such as graduated cylinders, burettes, or any graduated instrument, may be read accurately to a value indicated by the smallest graduated divisions. Readings may then be estimated usually to tenths of the *next division* with a precision of ± 0.2 of the value represented by the division

marks. For instance, a 100-*ml. graduate* is graduated in milliliters. The volume may, therefore, be read to the nearest milliliter and estimated to tenths of the next milliliter with an uncertainty of ±0.2 ml. Thus, if it is estimated that the bottom of the meniscus is at a point two tenths of the distance between the 47-ml. mark and the 48-ml. mark, the volume is read 47.2 ml. ±0.2 ml.

The precision in reading a *burette* is ordinarily ±0.02 ml. Similarly, with *thermometers* of the type used in general chemistry, the precision in reading the temperature is generally ±0.2° C. *Verniers* (Fig. 23) may be used to read *scales* in order to increase the precision of estimating the position between two marks on the scale.

The precision in *weighing* on a *laboratory trip balance* is generally ±0.1 g.; on a *hornpan* or *small beam balance* it is ±0.01 g. (10 mg.) or, by careful weighing, the precision measure may be as low as ±0.005 g. (5 mg.); on an *analytical balance* the precision may be made at least ±0.0002 g. (0.2 mg.). These are only approximate precision measures, and if the procedure for weighing outlined in Exp. III is not followed carefully, the precision will not be within the uncertainty values listed above.

The preceding uncertainty values are taken as precision measures and not as the accuracy of the weighing. By calibrating the weights and balances, and by eliminating or correcting for all known errors, such as buoyancy of the air, adsorption of moisture, etc., the most probable value of the weight could be obtained along with its precision measure.

2. Average Deviation of a Single Observation as a Precision Measure. It is much more satisfactory to obtain the precision measure from experimental values than to take a single observation and attach to it the uncertainty values listed in the last section. The precision measure is determined experimentally by making several independent, unbiased observations as carefully and correctly as possible. The average of these values (the arithmetical mean) is chosen as the best representative value of the set of observations. The deviation or residual of each observation is noted. The average of these deviations, obtained by dividing their sum by the number of determinations, gives the average deviation of a single observation (a.d.). Thus, a student measured the volume of a test tube and found the following values:

	Observation	Deviation from the Mean
	22.2 ml.	+0.1 ml.
	22.5 ml.	+0.2 ml.
	22.1 ml.	−0.2 ml.
Average	22.3 ml.	±0.17 ml. (±0.2 ml.) average deviation

The result of the measurement should be quoted as 22.3 ml. ± 0.2 ml. The average deviation in this case is used as a precision measure. It gives a measure of the consistency within the set of measurements. Whenever only two or three measurements are made, this approximation is about as reliable as any other precision measure.

3. Average Deviation of the Mean as a Precision Measure. It can be shown that the arithmetical mean is more reliable than any given determination by the square root of the number of determinations. Thus the uncertainty of the mean is equal to the uncertainty of a single determination divided by the square root of the number of determinations (n). As previously explained, the average deviation is taken as a measure of the uncertainty of a single determination. It follows that the uncertainty of the mean, or the *average deviation of the mean* (A.D.) is given by the equation, $\text{A.D.} = \frac{\text{a.d.}}{\sqrt{n}}$, in which a.d. is the average deviation. The value of A.D. is a better measure of the precision than is a.d. when several determinations have been made. It is seen from the above equation that the greater the number of determinations made, the more precise is the arithmetical mean.

4. Precision Measure of the Most Probable Value. Because of the constant and systematic errors present in most determinations, the arithmetical mean must be corrected for the known or estimated value of these errors. This corrected arithmetical mean will give the most probable value of the measurement. The correction terms are not absolute errors because they are not known exactly. Their magnitude could be determined only within certain limits. That is, each calibration or correction term has associated with it an uncertainty or precision measure itself. The uncertainties of the correction terms are sometimes called *residual deviations or residual errors.* They cause the result to be in doubt by more than the average deviation of the mean (A.D.). Therefore, these residual deviations should be included in the calculation of the precision measure of the most probable value. Sometimes the sum of all the residual deviations (uncertainties of the correcting terms) and the average deviation of the mean (A.D.) is taken as an approximate precision measure. A more reliable precision measure, however, is the square root of the sum of the squares of the average deviation of the mean and the residual deviations of the correcting terms ($e_1, e_2, \cdots$), that is,

$$\text{p.m.} = \sqrt{\text{A.D.}^2 + e_1^2 + e_2^2 \cdots}$$

in which p.m. is the precision measure of the most probable value (the corrected arithmetical mean). If the constant and systematic errors are small, or if the residual deviations are small, the precision measure is simply equal to the average deviation of the arithmetical mean (A.D.).

An illustration of the above calculations is given in the following example. Suppose the following weights were obtained for 100 ml. of water at 20°:

	Weighings	Deviations
	99.718 g.	−0.003 g.
	99.723	+0.002
	99.720	−0.001
	99.725	+0.004
	99.719	−0.002
Average	99.721 g.	±0.012 ÷ 5 = ±0.0024 g. average deviation (a.d.)

$$\text{Average deviation of the mean (A.D.)} = \frac{\pm 0.0024}{\sqrt{5}} = \pm 0.001 \text{ g.}$$

Corrections and calibrations:

Buoyancy of the air = +0.105 g. ±0.002 g.
Corrections for weights = −0.0044 ±0.0002 g.

The most probable weight is therefore

$$99.721 \text{ g.} + 0.105 \text{ g.} - 0.004 \text{ g.} = 99.822 \text{ g.}$$

The precision measure of this value may be taken as the sum of the A.D. and the precision measures of the correcting terms,

$$\begin{aligned} \text{A.D.} &= \pm 0.001 \\ e_1 &= \pm 0.002 \\ e_2 &= \pm 0.0002 \\ \text{p.m.} &= \pm 0.0032\ (\pm 0.003) \end{aligned}$$

or better, as the square root of the sum of their squares,

$$\text{p.m.} = \sqrt{0.001^2 + 0.002^2 + 0.0002^2} = \pm 0.0026\ (\pm 0.003 \text{ g.})$$

It is seen that either of the calculations gives approximately the same precision measure. In some cases, however, there is a greater difference between the two. The latter calculation

gives a better precision measure. Hence, the result of the above measurement is 99.822 g. ±0.003 g.

5. Percentage Precision. The relative or percentage precision is more useful for purposes of comparison than is the precision measure in units of the measurement. The percentage precision is given by the expression:

$$\text{Percentage precision} = \frac{\text{precision measure}}{\text{arithmetical mean}} \times 100 = \frac{\text{p.m.}}{\text{a}} \times 100$$

The percentage precision of the measurement 22.3 ml. ± 0.2 ml. is

$$\frac{0.2}{22.3} \times 100 = \pm 0.9\%$$

The result of the measurement is therefore stated as 22.3 ml. ± 0.9 per cent. This is 0.9 part per 100 or 9 parts per 1000. The percentage precision must always be calculated when it is desired to determine the precision of a quantity calculated from two or more measurements by multiplication or division.

Indirect Measurements and the Calculation of Results. In most experimental work the desired quantity cannot be measured directly. It is generally calculated from two or more different measurements. Thus, the determination of the density of a substance requires the measurement of the volume and the weight of a given quantity of a substance. The density is then calculated by dividing the weight by the volume. It is important to know how the precision or uncertainty of each of these measurements influences the final result. The precision of each measurement is determined by one of the methods described above. When the arithmetical mean of the series of measurements is calculated, it is important to know how many figures to carry in the result, and how many figures to carry when the result is used in another calculation. In more advanced courses where a larger number of observations are made, the number of significant figures is determined in a formal way from the precision measure of each measurement. For a course in general chemistry, however, the following generalizations and approximations are sufficient.

1. Significant Figures. Recording of Data. The significant figures of a number representing a measurement are taken as those figures which are definitely known, and the first uncertain figure. Thus if an object with a weight of 80.3 g. is weighed on a laboratory trip balance to the nearest 0.1 g., the 0.3 is uncertain by ±0.1 g. The 0.3 is considered a significant figure. If the object is weighed to the nearest 10 mg. (0.01 g.) on a beam balance, the weight is found to be 80.34 g. In this case the 0.3 is definite and the 0.04 is uncertain by ±0.01 g. All four figures are therefore significant. However, if the weight had been reported as 80.342 g. to the nearest 0.01 g., both the 4 and the 2 are uncertain. Only the first uncertain figure is retained. The 2 is therefore not a significant figure and is dropped.

Zeros are not considered significant when they occur between the decimal point and the first larger digit. Thus the number 0.00251 has only three significant figures. Zeros are significant if they occur within a number or at the end of a number. In the latter case the zero is significant only when it indicates that the value is nearer zero than any other digit. Thus, all three zeros in the number 1070.0 are significant. In the number 96,500 the zeros are not significant unless the precision is specified as ±1 to ±9. If the precision is ±10, or greater, then only the first zero is significant.

Unless otherwise specified, the uncertain figure is assumed to be the last one in the number, and it is assumed to be in doubt by at least plus or minus 1 (1070.0 ± 0.1). Therefore, it is important to use the correct number of significant figures in recorded data. Too many figures give a false impression of the precision, and too few do not give credit to the precision actually attained.

In calculating the average of measurements, the sum of the values is divided by the number of measurements. When only two or three measurements are made, the division should be carried out only to as many figures as occur in the values of the measurements. Thus, three weighings of the object mentioned in the preceding paragraph gave the following values: 80.34 g., 80.32 g., and 80.35 g. The calculated average is 80.336667 g. Obviously the answer should not contain this many figures, but it should be stated as 80.34 g., with an average deviation of ±0.01 g.

Sometimes the precision measure warrants one more figure in the result than is found in the measurements. This may be the case when values for a larger number of measurements have been taken. If eight weighings of the above object had been made with an average deviation (a.d.) of ±0.01 g., the average deviation of the mean (A.D.) may be taken as the precision measure. Thus

$$\text{A.D.} = \frac{\pm 0.01}{\sqrt{8}} = \frac{\pm 0.01}{2.84} = \pm 0.0037 \text{ g.}$$

This means that the third decimal place is uncertain, and hence the result is 80.337 g. ±0.004 g.

When extra figures are rejected, the uncertain figure is increased by 1 if the rejected figure is 5 or greater. If the average of the measurements is to be used for further calculations, it is advisable to retain one more figure than the first uncertain one. In this instance the precision measure is used to determine the number of figures which should be retained in the calculated result. The general rules are described in the following sections.

2. Precision of a Calculated Result. Addition or Subtraction. When addition or subtraction of a number of measurements is made, *the result cannot be reliable beyond the last significant figure in any one of the terms.* Thus,

0.0157 g.	± 0.0001 g.		0.0 g.
20.5	± 0.1	or	20.5
18.12	± 0.01	preferably	18.1
38.6 g.	± 0.1 g.		38.6 g. ± 0.1 g.

In other words, the result will not be more precise than the precision of the least reliable measurement.

If the measurements have about the same precision measure, then the precision measure of their sum or of their difference is taken as the square root of the sum of the squares of the precision measures or errors of each measurement.

$$\text{P.M.} = \sqrt{(\text{p.m.})_1^2 + (\text{p.m.})_2^2 + \cdots}$$

For addition or subtraction all of the precision measures or errors must be in terms of the final result, *not* in terms of percentage precision or percentage error.

In general chemistry, where the precision or uncertainty of each measurement will in general be estimated, the precision measure or the uncertainty of the result will be taken as the *sum* of the precision measures of the terms added or subtracted instead of the square root of the sum of their squares. For example,

Measurement	Precision	Percentage Precision
20.5 g.	±0.1 g.	±0.48%
5.3 g.	±0.1 g.	±1.9%
25.8 g.	±0.2 g.	±0.78%

In accordance with the convention adopted, the precision of the sum is the sum of the precision measures of the two terms, namely, ±0.2 g. Notice also that the percentage precision of the sum is *not* the sum of the percentage precisions of the two terms. The percentage precision of the sum lies between the percentage precisions of the two terms. If the precision had been calculated as the square root of the sum of the squares of the precision measures of the two terms [$\sqrt{(0.1)^2 + (0.1)^2}$], the result would have been 25.8 g. ± 0.14 g. This method of calculating the precision measure of the result is not necessary for experiments in general chemistry.

Whenever two measurements are subtracted, the uncertainty or precision of the result will be taken as the sum of the precisions of the two terms in the same way as described for addition. The precision measure *must be in units of the final result.* Thus

Measurement	Precision Measure	Percentage Precision
43.4 ml.	±0.1 ml.	±0.23%
38.2 ml.	±0.1 ml.	±0.26%
5.2 ml.	±0.2 ml.	±3.8%

If the difference between the two terms is small the percentage precision is much larger than the percentage precision of either of the terms. Note also that the number of significant figures is no greater than the number of figures in either term. In the above case there are fewer.

3. Precision of Calculated Results. Multiplication and Division. When multiplication or division is used to calculate a final result from two or more measurements, the percentage precision of each factor must first be determined. If the percentage precisions of the two factors are of a *different order*, then the percentage precision of the result is equal to the percentage precision of the least precise factor. This is generally the factor with the least number of significant figures. The following general rule with regard to significant figures is deduced: *Retain as many significant figures in each factor and in the final result as are contained in the measurement with the poorest percentage precision or*, in other words, *the measurement with the greatest uncertainty.* It follows that the percentage precision of the result cannot be better than that of the least precise factor.

The following example illustrates these principles:

Measurement	Precision Measure	Percentage Precision
12.5 ml.	±0.2 ml.	±1.7%
22.18 g.	±0.01 g.	±0.05%

Suppose it is desired to calculate the density from these measurements. First it will be noted that the percentage precision of these two measurements is of a different order. The percentage precision of the quotient is taken to be equal to that of the least precise factor, namely, ±1.7 per cent. Since the volume measurement has only three significant figures, only three figures need to be used to express the weight of the substance. Similarly the quotient (or product) should contain only three significant figures. Thus

$$22.2 \div 12.5 = 1.77 \text{ g./ml.} \pm 1.7\% = 1.77 \text{ g./ml.} \pm 0.03 \text{ g./ml.}$$

If the precision of the result is to be increased, a more precise method must be used to measure the volume. More precise weighing will not increase the precision of the above result.

If the percentage precisions of the two measurements *are of about the same magnitude*, then the percentage precision of the product or quotient may be taken as the sum of the percentage precisions of the factors. A more reliable measure of the precision of the result

is the square root of the sum of the squares of the percentage precisions of the factors. Suppose the volume in the above example had been measured with a burette instead of a graduated cylinder. The measurements would be:

Measurement	Precision Measure	Percentage Precision
12.51 ml.	±0.02 ml.	±0.17%
22.18 g.	±0.01 g.	±0.05%

Density = 22.18 ÷ 12.51 = 1.773 g./ml. ± 0.22%

The precision, according to the method most commonly employed in general chemistry, is the sum of the percentage precisions of the two factors, 0.22 per cent.

The percentage precision of the quotient on the basis of the second method of calculation would be:

$$\sqrt{0.17^2 + 0.05^2} = \pm 0.18\%$$

4. The Number of Significant Figures in a Result. It will be noted that there are four significant figures in each factor, and also in the final result of the last example in the previous section. This is in accordance with the general rule quoted above. The use of four significant figures, and no more, may be justified as follows:

$$(1.773) \times (\pm 0.23\%) = \pm 0.0041 \text{ g./ml.}$$

This shows that the fourth figure (3) is in doubt. According to the definition of significant figures, only the first doubtful figure is retained. The 3 is therefore retained.

In the first example cited above, the result was given as 1.77 g./ml. ± 1.7% or 1.77 g./ml. ± 0.03 g./ml. This shows that the third figure, that is, the second decimal place in the figure 1.77 is in doubt. Therefore no more than three figures should be used to express the result.

The Percentage Error. It must be understood that, in a philosophical sense, the accurate or correct value of a measured property will never be known *exactly*. Consequently the *absolute error* cannot be calculated exactly. However, by use of refined methods, pure substances, and by elimination of or correction for all possible errors, the most probable value of a property may be determined rather precisely. For all practical purposes this value may be taken as a standard for determining the accuracy of subsequent determinations. This most probable value will be designated as the "accepted value." The percentage error will then be the difference (Δq) between the measured value and this accepted value divided by the accepted value (Q) times 100:

$$\text{Percentage error} = \frac{\Delta q}{Q} \times 100$$

It may be pointed out again that the precision of a measurement is often a better measure of the skill and technique of the operator than is the percentage error. The discrepancy from the accepted value may be associated with faulty apparatus or with constant and systematic errors. If, however, the apparatus is not faulty, or if it has been calibrated, a large percentage error may show that the operator is not using the proper diligence in eliminating operative errors and errors due to improper conditions.

Analysis of Experiment IV. 1. Estimation of the Precision Attainable in Experiment IV, Part (A). The precision attained in an experiment on the determination of the density of a liquid depends upon the apparatus used. In part (A) of Exp. IV the weight of the water is determined by difference on a laboratory trip balance, and the volume of the water is determined by means of a 100-ml. graduated cylinder. It was previously pointed out that the uncertainty in reading the volume on a 100-ml. graduated cylinder is ordinarily ±0.2 ml.

The weight of an object may be determined with an uncertainty of ±0.1 g. on a trip balance that is in satisfactory operating order. These uncertainty values may be used as an approximate precision measure.

The precision measure which should be attained in the determination of density may be estimated as illustrated by the following example:

	Weight	Precision Measure
Weight of graduate + water	156.7 g.	±0.1 g.
Weight of graduate	104.6 g.	±0.1 g.
Weight of water	52.1 g.	±0.2 g.
Percentage precision = (0.2 ÷ 52.1) × 100 = ±0.4%		
Volume of water	52.5 ml.	±0.2 ml.
Percentage precision = (0.2 ÷ 52.5) × 100 = ±0.4%		

The density is obtained by dividing the weight by the volume, 52.1 g. ÷ 52.5 ml. = 0.994 g./ml. The precision measure is taken as the sum of the precision measures of the two measurements, (±0.4%) + (±0.4%) = ±0.8%. Therefore the measured density is 0.994 g./ml. ±0.8% = 0.994 ± 0.007 g./ml. The third figure is uncertain by ±7. It follows that no more than the three figures should be used to report the density.

The above estimated precision measure—0.994 g./ml. ± 0.007 g./ml.—shows it to be highly probable that the measured value of the density will fall between the limits 0.987 g./ml. and 1.001 g./ml., that is, the reproducibility of the results on the apparatus described should be within at least ±0.007 g./ml. of their average value. The average deviation of two different determinations should, therefore, not be greater than ±0.007 g./ml. If the average deviation is greater, it means that the student is not using sufficient care and skill in reading the volumes and in making the weighings.

The accepted value of the density determined at 25° in a glass vessel and with brass weights (Appendix E) is 0.9962 g./ml. If this be taken as the correct value, then the percentage error of the mean value of the measured density is:

$$0.996 - 0.994 = 0.002 \text{ g./ml.} \quad \text{or} \quad \frac{0.002}{0.996} \times 100 = 0.2\%$$

2. Precision Attainable in Experiment IV, Part (C). A similar analysis of the method used in part (C) is made as follows: Readings of the volume on a burette may be made with a precision of ±0.02 ml. Weighings on a small beam balance may be made to the nearest 10 mg. This means the precision is approximately ±0.01 g. (10 mg.). The results of a typical experiment are:

Final reading	35.32 ml.	± 0.02 ml.	
Initial reading	0.88 ml.	± 0.02 ml.	
Volume	34.44 ml.	± 0.04 ml.	= 34.44 ml. ± 0.11%
Flask counterbalanced	———	± 0.01 g.	
Flask + water	36.48 g.	± 0.01 g.	
Weight of water	36.48 g.	± 0.02 g.	= 36.48 g. ± 0.05%

$$\text{Density} = \frac{M}{V} = \frac{36.48 \pm 0.05\%}{34.44 \pm 0.11\%} = 1.058 \text{ g./ml.} \pm 0.16\%$$

In this example, the sum of the percentage precisions of the two measurements has been taken as the percentage precision of the result. If more reliable precision measures of the two measurements had been determined experimentally, then the square root of the sum of the squares of the two percentage precisions would have given a better measure of the precision.

The density times the estimated percentage precision (1.058 × 0.0016 = 0.0017 or 0.002 g./ml.) gives the precision which should be attained by the correct use of the apparatus described. Therefore, the average deviation taken as a precision measure of the two determinations made in part (C), should not be greater than ±0.002 g./ml. If the average deviation is larger than this, greater care must be used in carrying out the experiment.

According to the convention on significant figures, the result should not be reported with more than one doubtful figure. In the above determination the 8 is in doubt by ±2, and is, therefore, the last figure retained. If the division had been carried out further, the answer would have been 1.05782 g./ml. ± 0.16%. In order to determine the number of figures to be left in the answer, multiply 1.05782 by ±0.0016 (0.16%). The result is ±0.0017 g./ml. This shows that the third decimal is in doubt by one or more. The figure in the third decimal place is, therefore, the last one retained. The 2 is dropped, and because 8 is greater than 5, the 7 is changed to 8, thereby giving 1.058 g./ml. ± 0.002 g./ml. It would be incorrect to retain a greater number of figures. If the density had been reported as 1.05782 g./ml., it would indicate that the determination had been carried out with a precision given by 1.05782 g./ml. ± 0.00001 g./ml. This is far from being true. If fewer figures had been used to report the result, the precision actually attained would not be indicated.

More precise determinations of the density of liquids involve refinements in the methods of determining the volume and weight of the liquid. Special pycnometers (Fig. 30) have been designed for this purpose.

3. Comparison with Experiments. Experiment IV, parts (A) and (C), requires two determinations to be made. As pointed out in the last two sections, the average deviation of the two measurements should not exceed a certain value. A comparison of the precision actually attained with the above estimates will give a measure of the consistency, or of the care and skill used by the observer. The comparison should be made in a manner similar to that used in the following example:

	Trial 1	Trial 2
Weight of graduate + water	149.0 g.	164.3 g.
Weight of the graduate	104.6 g.	104.7 g.
Weight of water	44.4 g.	59.6 g.
Volume of water	44.6 ml.	59.6 ml.
Temperature	30°	30°
Density	0.995 g./ml.	1.000 g./ml.
Average density	0.998 g./ml.	
Deviations	0.003 g./ml.	0.002 g./ml.
Average deviation	±0.0025 or ±0.003	
Percentage precision	±0.26%	
Accepted apparent density at 30°	0.9949 g./ml.	
Percentage error	0.3%	

The average deviation of the two determinations is taken as the precision measure. The density is, therefore, reported as 0.998 g./ml. ± 0.003 g./ml. The analysis of this method made in the previous section showed that the precision should be at least as good as ±0.007 g./ml. The experiment reported in the example is, then, sufficiently precise.

The percentage error is calculated as follows:

$$\frac{\text{Determined value} - \text{accepted value}}{\text{Accepted value}} \times 100 = \text{percentage error}$$

or

$$\frac{0.998 - 0.995}{0.995} \times 100 = \frac{0.003}{0.995} \times 100 = 0.3 \text{ per cent}$$

B. EXPONENTS AND LOGARITHMS

Exponents

Exponential System of Notation for Large and Small Numbers. The value of a very large quantity, such as Avogadro's number

602,000,000,000,000,000,000,000

is cumbersome to express and unwieldy to use in calculations. It may be much more simply expressed by the exponential notation 6.02×10^{23}. This means that the number is 10^{23} times as large as 6.02, and therefore the decimal point of the nonexponential number is 23 places to the right of its position in 6.02. The economy in space is at once obvious. Examples are given to further illustrate the exponential system of expressing numbers:

$$1 = 10^0 \qquad 192 = 1.92 \times 10^2$$

$$10 = 10^1 \qquad 354.5 = 3.545 \times 10^2$$

$$100 = 10 \times 10 = 10^2 \qquad 1{,}091 = 1.091 \times 10^3$$

$$1{,}000 = 10 \times 10 \times 10 = 10^3 \qquad 6{,}900{,}000 = 6.9 \times 10^6$$

$$10{,}000 = 10 \times 10 \times 10 \times 10 = 10^4 \qquad 82{,}500{,}000 = 8.25 \times 10^7$$

As is seen from the above examples, a number greater than 1 is expressed in the exponential system by moving the decimal point of the number to the left and placing it after the first significant figure. The result is then multiplied by 10 raised to the power equal to the number of places the decimal point has been moved. Conversely, the number corresponding to the notation 6.9×10^6 is obtained by moving the decimal point 6 places to the right to give 6,900,000.

Numbers less than 1 may be expressed in the following manner:

$$0.1 = \frac{1}{10} = 10^{-1} \qquad 0.25 = 2.5 \times 10^{-1}$$

$$0.01 = \frac{1}{10^2} = 10^{-2} \qquad 0.0653 = 6.53 \times 10^{-2}$$

$$0.001 = \frac{1}{10^3} = 10^{-3} \qquad 0.00809 = 8.09 \times 10^{-3}$$

$$0.0001 = \frac{1}{10^4} = 10^{-4} \qquad 0.00006 = 6.0 \times 10^{-5}$$

Thus, a number less than 1 is expressed in the exponential form by moving the decimal point to the right, placing it after the first significant figure, and then multiplying the value by 10 raised to the negative power equal to the number of places the decimal point has been moved to the right. Conversely, the number corresponding to 5.8×10^{-4} is obtained by moving the decimal point 4 places to the left to give 0.00058.

Calculations Involving Exponents. The following statements and examples illustrate the use of exponents in mathematical operations:

1. Multiplication with exponential numbers is carried out by adding the exponents algebraically. Thus,

a. $10^4 \times 10^2 = 10^6$

and

b. $(3 \times 10^7) \times (2 \times 10^{-4}) = 6 \times 10^3$

2. Division with exponential numbers is accomplished by subtracting algebraically the exponent of the divisor from the exponent of the dividend. Thus,

a. $10^8 \div 10^6 = 10^2$

b. $10^6 \div 10^{-2} = 10^8$

c. $10^{-7} \div 10^4 = 10^{-11}$

d. $4.6 \times 10^8 \div 2 \times 10^3 = 2.3 \times 10^5$

3. A power of an exponential number is obtained by multiplying the exponent by the indicated power. Thus,

a. $(10^3)^3 = 10^9$

b. $(10^{-2})^4 = 10^{-8}$

c. $(2 \times 10^3)^2 = (2)^2 \times (10^3)^2 = 4 \times 10^6$

4. The root of an exponential number is found by dividing the exponent by the index of the root. Thus,

a. $\sqrt[3]{10^{12}} = 10^4$

b. $\sqrt{10^{-6}} = 10^{-3}$

c. $\sqrt{2.25 \times 10^4} = 1.5 \times 10^2$

d. $\sqrt{1.6 \times 10^5} = \sqrt{16 \times 10^4} = 4 \times 10^2$

The additional step in d is necessary because the exponent 5 is not evenly divisible by 2. Hence, 10^5 is divided by 10, and 1.6 is multiplied by 10. These operations do not change the value of the number, but they give an exponent evenly divisible by the index of the root.

5. The following examples further illustrate the use of exponential numbers:

a. $$\frac{6.02 \times 10^{23}}{22{,}400} = \frac{6.02 \times 10^{23}}{2.24 \times 10^4} = 2.7 \times 10^{19}$$

b. $$\frac{500 \times 0.06 \times 90{,}000}{300{,}000 \times 0.003} = \frac{5 \times 10^2 \times 6 \times 10^{-2} \times 9 \times 10^4}{3 \times 10^5 \times 3 \times 10^{-3}} =$$

$$\frac{270}{9} \times \frac{10^4}{10^2} = 30 \times 10^2 = 3.0 \times 10^3 = 3000$$

Common Logarithms

Introduction. Logarithms, like exponential numbers, are used to facilitate mathematical calculations. Any number may be expressed as a power of 10, and *a common logarithm is the power to which 10 must be raised to equal any given number.* Another system of logarithms, convenient in higher mathematics, employs 2.718 as a base. These logarithms, known as *natural* or *Naperian* logarithms, are not discussed in this section.

The relationship between numbers expressed as powers of 10 and their logarithms is shown below.

Number	The Number as a Power of 10	The Logarithm of the Number
1,000.00	$1.0 \times 10^3 = 10^{3.0000}$	3.0000
525.50	$5.255 \times 10^2 = 10^{2.7206}$	2.7206
100.00	$1.0 \times 10^2 = 10^2$	2.0000
52.55	$5.255 \times 10^1 = 10^{1.7206}$	1.7206
10.00	$1.0 \times 10^1 = 10^{1.0000}$	1.0000
5.255	$5.255 \times 10^0 = 10^{0.7206}$	0.7206
1.00	$1.0 \times 10^0 = 10^{0.0000}$	0.0000
0.5255	$5.255 \times 10^{-1} = 10^{\bar{1}.7206}$	$\bar{1}$.7206
0.10	$1.0 \times 10^{-1} = 10^{\bar{1}.0000}$	$\bar{1}$.0000
0.05255	$5.255 \times 10^{-2} = 10^{\bar{2}.7206}$	$\bar{2}$.7206
0.01	$1.0 \times 10^{-2} = 10^{\bar{2}.0000}$	$\bar{2}$.0000

The integral part of a logarithm is its *characteristic* and the fractional part is its *mantissa*. A characteristic is determined by the inspection of a number, while the mantissa is read from a table of mantissae. A table of these values is actually called a table of logarithms despite the fact that characteristics are usually omitted from these tables.

Procedure for Finding the Logarithm of a Number. Directions are given for determining the characteristic and for finding the mantissa.

1. Rules for Determining the Characteristic. For a number greater than 1, the characteristic is positive in sign and one less numerically than the number of figures to the left of the decimal point. The following examples illustrate this rule:

Number	Characteristic
760.5	2.
85.18	1.
4.867	0.

For a number less than 1, the characteristic is negative in sign and is one more numerically than the number of zeros between the decimal point and the first significant figure. The following examples illustrate this rule:

Number	Characteristic
0.0058	$\bar{3}$. (−3)
0.0106	$\bar{2}$.
0.2851	$\bar{1}$.

2. Procedure for Finding the Mantissa in a Four-Place Table of Logarithms. Two illustrations of the procedure are given:

Numbers:	525.5	0.005255
Find 52 in column of natural numbers, follow across this row to column 5, and find the mantissa:	.7202	.7202
Under 5, in proportional parts, and in same row with 52, find	4	4
Add to obtain the mantissa	.7206	.7206

The two numbers have the same mantissa but their characteristics are different.

3. The Logarithm of a Number. As determined according to the rules given in the two preceding sections, the logarithms of 525.5 and 0.005255 are 2.7206 and $\bar{3}.7206$ respectively.

Sometimes it is desirable to convert a *mixed* logarithm, such as $\bar{3}.7206$, to a completely negative logarithm. In this case,

$$\bar{3}.7206 = (-3 + 0.7206) = -2.1794$$

Procedure for Finding the Number Corresponding to a Given Logarithm. The number corresponding to a given logarithm is called an *antilogarithm.*

1. The Antilogarithm from a Table of Antilogarithms. If a table of antilogarithms is available, apply the method illustrated by the following examples. The characteristic is disregarded in the first steps because it is needed only to fix the position of the decimal point.

It is desired to find the antilogarithms of 2.7206 and $\bar{3}.7206$:

Opposite .72 in column 0 is 5248.
In the same row, under column 6 in proportional parts, is 7.
Add the two numbers and obtain 5255.

The location of the decimal point in the antilogarithm is determined by applying one of the following rules:

a. If the characteristic is positive, place the decimal point so that the number of figures preceding the point is one greater than the numerical value of the characteristic.

b. If the characteristic is negative, immediately follow the decimal point with a number of zeros, one less than the numerical value of the characteristic.

The application of rule **a** to the antilogarithm of 2.7206 gives 525.5, while rule **b** gives 0.005255 as the antilogarithm of $\bar{3}.7206$.

2. The Antilogarithm Obtained Without the Use of a Table of Antilogarithms. The number corresponding to a given logarithm may be obtained from a table of logarithms. As an illustration of the procedure used, the directions for finding the antilogarithm of 1.7206 are given.

Look through the logarithm table for the two mantissae between which :7206 occurs. These two mantissae are .7202 and .7210 respectively. Since the characteristic is 1, the numbers are 52.5 and 52.6. The fourth figure, obtained by interpolation, will place the antilogarithm between 52.50 and 52.60. The method of interpolating follows:

log 52.6 =	1.7210	log of given number =	1.7206
log 52.5 =	1.7202	log 52.5 =	1.7202
Difference =	8	Difference =	4

Then, $\frac{4}{8} = 0.5$, and therefore the number is 52.55.

Mathematical Operations with Logarithms. Multiplication, division, and a number of other fundamental calculations are carried out in the following sections.

1. Multiplication: $\log ab = \log a + \log b$. To multiply two or more numbers, add the logarithms of the numbers and then find the antilogarithm of the sum. The following examples serve as illustrations:

a. $760 \times 22.4 \times 273 = ?$

log 760 =	2.8808
log 22.4 =	1.3505
log 273 =	2.4362
Sum =	6.6772

Answer = antilog 6.6772 = 4,647,000

b. $15.45 \times 0.0095 = ?$

Method 1	Method 2
$\log 15.45 = 1.1889$	1.1889
$\log 0.0095 = \bar{3}.9777$	$7.9777 - 10$
$\text{Sum} = \bar{1}.1666$	$9.1666 - 10 = \bar{1}.1666$

$$\textit{Answer} = \text{antilog } 1.1666 = 0.1468$$

It must be remembered that mantissae are always positive, and therefore any number carried over to be added with the characteristics is also positive. Characteristics are added algebraically. Thus in method 1, when $+1$ is carried over to be added to $+1$ and -3, the total is -1.

In method 2 the negative characteristic is converted to a positive one by adding 10 to it: $+10 - 3 = +7$. Once the addition has been made, 10 is subtracted from the sum.

2. Division: $\log \frac{a}{b} = \log a - \log b$. To divide by means of logarithms, subtract the logarithm of the divisor from the logarithm of the dividend. The antilogarithm of the difference is the desired quotient. Subtract the characteristics algebraically, that is, change the sign of the subtrahend and add algebraically. The following are examples:

a. $683.1 \div 25.40 = ?$

$\log 683.1$	$= 2.8345$
$\log 25.40$	$= 1.4048$
Difference	$= 1.4297$

$$\textit{Answer} = \text{antilog } 1.4297 = 26.98$$

b. $0.01545 \div 0.0893 = ?$

Method 1	Method 2
$\log 0.01545 = \bar{2}.1889$	$18.1889 - 20$
$\log 0.08930 = \bar{2}.9509$	$8.9509 - 10$
$\text{Difference} = \bar{1}.2380$	$9.2380 - 10 = \bar{1}.2380$

$$\textit{Answer} = \text{antilog } \bar{1}.2380 = 0.1730$$

Before .9509 can be subtracted from .1889, one (1) must be borrowed from the characteristic of the minuend. The latter then becomes $\bar{3}$. Then, to subtract $\bar{2}$ from $\bar{3}$ algebraically, change the sign of $\bar{2}$ and add it to $\bar{3}$. Thus

$$\bar{3} - (\bar{2}) = \bar{3} + 2 = \bar{1}$$

In method 2, both negative characteristics are converted to positive ones.

3. A Series of Consecutive Multiplications and Divisions:

$$\log \frac{a \times b \times c}{d \times e} = (\log a + \log b + \log c) - (\log d + \log e)$$

To make a series of consecutive multiplications and divisions, subtract the sum of the logarithms of the divisors from the sum of the logarithms of the dividends. An example follows:

$$98.3 \times \frac{285}{279.1} \times \frac{810}{795} = ?$$

log 98.3 = 1.9926	log 279.1 = 2.4458
log 285 = 2.4548	log 795 = 2.9004
log 810 = 2.9085	Sum = 5.3462
Sum = 7.3559	

Sum of logs of dividends = 7.3559
Sum of logs of divisors = 5.3462
Difference = 2.0097

Answer = antilog 2.0097 = 102.2

4. Involution (Raising a Number to a Power): $\log a^n = n \log a$. To raise a number to a power, multiply the logarithm of the number by the power to which the number is to be raised. The antilogarithm of the product is the answer. Two illustrations follow:

a. $(154.5)^3 = ?$

$$\log 154.5 = 2.1889$$
$$\underline{\qquad\qquad 3}$$
$$6.5667$$

Answer = antilog 6.5667 = 3,687,000

b. $(0.0393)^3 = ?$

$$\log 0.0393 = \bar{2}.4904$$
$$\underline{\qquad\qquad 3}$$
$$\bar{6} + 1.2712 = \bar{5}.4712$$

Answer = antilog $\bar{5}$.4712 = 0.00002959 = 2.959×10^{-5}

When the mantissa in example **b** is multiplied by 3, then +1 must be carried over to the left of the decimal point and added to $\bar{6}$ to give $\bar{5}$.

5. Evolution (Extracting a Root of a Number): $\log \sqrt[n]{a} = \frac{\log a}{n}$. To extract a root of a number, divide the logarithm of the number by the index of the root. If the characteristic is negative and not evenly divisible by the index, the form of the logarithm must be changed so that the characteristic is either evenly divisible or is made positive. Three examples follow:

a. $\sqrt{163.5} = ?$

$\log 163.5 = 2.2135$, and $2.2135 \div 2 = 1.1068$

Answer = antilog 1.1068 = 12.78

b. $\sqrt{16.35} = ?$

$\log 16.35 = 1.2135$, and $1.2135 \div 2 = 0.6068$

Answer = antilog 0.6068 = 4.043

c. $\sqrt[3]{0.03093} = ?$

$$\log 0.03093 = \bar{2}.4904$$

Method 1	Method 2
$\bar{2}.4904 = (\bar{3} + 1.4904)$	$\bar{2}.4904 = 28.4904 - 30$
$(\bar{3} + 1.4904) \div 3 = \bar{1}.4968$	$(28.4904 - 30) \div 3 = 9.4968 - 10$
	$= \bar{1}.4968$

$$Answer = \text{antilog } \bar{1}.4968 = 0.3139$$

6. The Logarithm of a Reciprocal: $\log \frac{1}{a} = \log 1 - \log a$. To determine the logarithm of a reciprocal, subtract the logarithm of the number from the logarithm of 1. This operation finds direct application in calculating a pH value from the concentration of the hydronium ion inasmuch as $\text{pH} = \log \frac{1}{[H_3O^+]}$.

The logarithm of the reciprocal of a number is the *cologarithm* of the number. As an illustration of the process, the following problem is solved:

Calculate the pH of a solution in which $[H_3O^+] = 0.0045$.

$$\log \frac{1}{0.0045} = ?$$

$$\log 1 = 0.0000$$
$$\log 0.0045 = \bar{3}.6532$$
$$\text{Difference} = 2.3468 = \text{pH}$$

In order to subtract 0.6532 from 0.0000, borrow 1 from the zero characteristic (add -1 to it) to make the latter $= \bar{1}$. Then $\bar{1} - \bar{3} = \bar{1} + 3 = 2$.

7. The Number Corresponding to the Logarithm of a Reciprocal: $\log a = \log 1 - \log \frac{1}{a}$. This operation is carried out in calculating the concentration of the hydronium ion from the pH. The antilogarithm of the difference between the log of 1 and the pH is the $[H_3O^+]$. An example follows:

$$\text{pH} = \log \frac{1}{a} = 4.513$$
$$\log a = \log 1 - \text{pH}$$
$$\log 1 = 0.0000$$
$$\text{pH} = 4.5130$$
$$\log a = \bar{5}.4870$$
$$\text{antilog } \bar{5}.4870 = 0.00003069 = 3.069 \times 10^{-5}$$

Hence, the concentration of H_3O^+ is 3.069×10^{-5} moles/liter.

FOUR-PLACE LOGARITHMS

Natural Numbers	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

FOUR-PLACE LOGARITHMS

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
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	9026	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	3	4

C. VAPOR PRESSURE OF WATER

Temperature		Pressure, Mm.	Temperature		Pressure, Mm.
°F	°C		°F	°C	
32.0	0	4.6	78.8	26	25.1
41.0	5	6.5	80.6	27	26.5
46.4	8	8.0	82.4	28	28.1
48.2	9	8.6	84.2	29	29.8
50.0	10	9.2	86.0	30	31.5
51.8	11	9.8	87.8	31	33.4
53.6	12	10.5	89.6	32	35.4
55.4	13	11.2	91.4	33	37.4
57.2	14	11.9	93.2	34	39.6
59.0	15	12.7	95.0	35	41.8
60.8	16	13.6	104.0	40	55.0
62.6	17	14.5	122.0	50	92.2
64.4	18	15.4	140.0	60	149.2
66.2	19	16.3	158.0	70	233.8
68.0	20	17.4	176.0	80	355.5
69.8	21	18.5	194.0	90	526.0
71.6	22	19.7	212.0	100	760.0
73.4	23	20.9			
75.2	24	22.2			
77.0	25	23.6			

D. CORRECTION OF BAROMETRIC READINGS FOR THE EXPANSION OF MERCURY (WOODEN SCALE)

A column of mercury expands with rising temperature and hence a correction must be made. The values recorded in the table below are to be subtracted from the observed reading to obtain the barometric pressure in millimeters of mercury at 0°.

Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.
15°	2.0	19°	2.5	23°	3.0	27°	3.5
16°	2.1	20°	2.6	24°	3.1	28°	3.6
17°	2.2	21°	2.7	25°	3.2	29°	3.7
18°	2.3	22°	2.8	26°	3.4	30°	3.9

E. THE DENSITY OF WATER

The values recorded in the following table give the density of water in grams per milliliter at the temperature indicated. The absolute density in grams per cubic centimeter may be obtained by dividing the values listed in the table by 1.000027.

Temperature °C	Density g./ml.	Temperature °C	Density g./ml.
15	0.9991	26	0.9968
16	0.9990	27	0.9965
17	0.9988	28	0.9963
18	0.9986	29	0.9960
19	0.9984	30	0.9957
20	0.9982	31	0.9954
21	0.9980	32	0.9951
22	0.9978	33	0.9947
23	0.9976	34	0.9944
24	0.9973	35	0.9940
25	0.9971	36	0.9937

Note. When it is desired to calculate the volume of a given weight of water, the mass of the water must be known. Since the buoyancy effect of the air on brass weights and on water is different, the weight obtained by weighing on a balance should be corrected to the weight in a vacuum. Instead of using the above procedure, the corrections may be applied to the density in such a way that the volume of a glass vessel delivering a given quantity of water may be obtained by dividing the observed weight by the "apparent density." The apparent density of water when weighed in air with brass weights and at a pressure of 760 mm. of mercury is given in the table below. These values have been determined from a consideration of the following: the change in the density of water with change in temperature; the difference in the buoyancy of the air on the water and the brass weights; and the difference in the volume of the glass vessel from its volume at 20° C. (Volumetric apparatus is generally marked "to deliver" or "to contain" a stated volume at 20°). The values listed in the table below should also be used to determine the percentage error of the density determined experimentally in the laboratory. The previous table is used only when the weights have been reduced to "vacuo."

APPARENT DENSITY OF WATER WHEN WEIGHED IN AIR WITH BRASS WEIGHTS AT 760-MM. PRESSURE

Temperature °C	Apparent Density g./ml.	Temperature °C	Apparent Density g./ml.
15	0.9980	26	0.9959
16	0.9978	27	0.9957
17	0.9977	28	0.9955
18	0.9975	29	0.9952
19	0.9973	30	0.9949
20	0.9972	31	0.9946
21	0.9970	32	0.9944
22	0.9968	33	0.9941
23	0.9966	34	0.9938
24	0.9964	35	0.9935
25	0.9962	36	0.9932

F. A UNIVERSAL INDICATOR

Dissolve the following in 500 ml. of 95 per cent ethyl alcohol:

0.1 g. phenolphthalein
0.3 g. dimethylaminoazobenzene
0.2 g. methyl red
0.4 g. bromthymol blue
0.5 g. thymol blue

The colors of the indicator at different pH values are as follows:

pH	Color
2	red
4	orange
6	yellow
8	green
10	blue

Other universal indicators are obtainable from chemical supply houses.

G. STANDARD BUFFER SOLUTIONS (CLARK AND LUBS)

Primary solutions: 0.1*M* HCl; 0.2*M* HCl; 0.2*M* KCl; 0.1*M* potassium hydrogen phthalate ($KHC_8H_4O_4$); 0.1*M* NaOH; 0.1*M* KH_2PO_4; 0.1*M* H_3BO_3.

Composition	pH
48.5 ml. 0.2*M* HCl + 25 ml. 0.2*M* KCl diluted to 100 ml.	1.0
20.75 ml. 0.2*M* HCl + 25 ml. 0.2*M* KCl diluted to 100 ml.	1.4
5.30 ml. 0.2*M* HCl + 25 ml. 0.2*M* KCl diluted to 100 ml.	2.0
39.6 ml. 0.1*M* HCl + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	2.4
20.32 ml. 0.1*M* HCl + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	3.0
9.90 ml. 0.1*M* HCl + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	3.4
0.40 ml. 0.1*M* NaOH + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	4.0
7.50 ml. 0.1*M* NaOH + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	4.4
23.85 ml. 0.1*M* NaOH + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	5.0
35.45 ml. 0.1*M* NaOH + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	5.4
45.45 ml. 0.1*M* NaOH + 50 ml. 0.1*M* $KHC_8H_4O_4$ dil. to 100 ml.	6.0
12.60 ml. 0.1*M* NaOH + 50 ml. 0.1*M* KH_2PO_4 dil. to 100 ml.	6.4
23.65 ml. 0.1*M* NaOH + 50 ml. 0.1*M* KH_2PO_4 dil. to 100 ml.	7.0
39.50 ml. 0.1*M* NaOH + 50 ml. 0.1*M* KH_2PO_4 dil. to 100 ml.	7.4
46.80 ml. 0.1*M* NaOH + 50 ml. 0.1*M* KH_2PO_4 dil. to 100 ml.	8.0
8.50 ml. 0.1*M* NaOH + 50 ml. 0.1*M* H_3BO_3 dil. to 100 ml.	8.4
21.30 ml. 0.1*M* NaOH + 50 ml. 0.1*M* H_3BO_3 dil. to 100 ml.	9.0
32.00 ml. 0.1*M* NaOH + 50 ml. 0.1*M* H_3BO_3 dil. to 100 ml.	9.4
43.90 ml. 0.1*M* NaOH + 50 ml. 0.1*M* H_3BO_3 dil. to 100 ml.	10.0

H. APPARATUS AND MATERIALS

I. Recommended Desk Equipment

1. Returnable

5 Beakers, Pyrex, 50, 100, 150, 250, 400 ml.
1 Boat, combustion
8 Bottles, reagent, 125 ml. g. s. and Block
1 Bottle, vial-mouthed, 90 ml.
2 Bottles, wide-mouthed, 125 ml.
2 Bottles, wide-mouthed, 250 ml.
2 Crucibles, porcelain, 15 ml.
2 Crucible covers
1 Evaporating dish, porcelain, 7.5 cm.
1 Evaporating dish, porcelain, 10 cm.
1 Evaporating dish, porcelain, 12 cm.
2 Flasks, Erlenmeyer, Pyrex, 50 ml.
1 Flask, Erlenmeyer, Pyrex, 250 ml.
1 Flask, Florence, Pyrex, 150 ml.
1 Flask, Florence, Pyrex, 500 ml.
2 Funnels, 6.5 cm., long stem
4 Glass plates, 10 × 10 cm.
2 Graduates, 5 ml., 100 ml.
1 Mortar, 8.5 cm., and Pestle
1 Spatula, stainless steel blade
10 Test tubes, Pyrex, 6 × $\frac{3}{4}$ in.
1 Thermometer
1 Tube, combustion, Pyrex, 25 cm. × 20 mm.
1 Tube, thistle top
1 Tube, drying
3 Watch glasses, 5, 7, and 10 cm.
2 Burners, Tirril, or Bunsen
2 Clamps, burette, single
1 Clamp, Hoffman's screw type
1 Clamp, Mohr's pinch type
1 Crucible tongs, iron, nickel-plated
1 Deflagration spoon
1 Forceps, iron
1 Funnel arm
2 Ring stands, medium
2 Rings, iron, 4 in. and 5 in.
1 Test-tube holder, wooden
1 Test-tube rack
1 Tripod, 5 in.
1 Triangle, clay, 2 in.
1 Wing top

2. Nonreturnable

1 Brush, test tube
3 Corks, to fit test tubes
1 File, triangular
1 Gauze, wire, 5″ × 5″
10 Labels, No. 219 Dennison
1 box Matches
50 sheets Paper, filter, 11 cm.
1 tube Paper, litmus, blue
1 tube Paper, litmus, red
2 Rods, glass, $\frac{3}{16}$″ × 8″
1 Sponge, cellulose
6 Splints, wood
1 Stopper, rubber, No. 5, two-hole
1 Towel
1 length Tubing, glass, 4–6 mm. × 5′
1 burner Tubing, rubber, 2′
1 Tubing, rubber, 1′, $\frac{3}{16}$″ × $\frac{3}{64}$″

II. Additional Apparatus for Qualitative Analysis

1 Flask, suction, Pyrex, 250 ml.
2 Funnels, 25 mm., with constriction (Fig. 97)
6 Medicine droppers
50 sheets Paper, filter, $4\frac{1}{4} - 5\frac{1}{2}$ cm.
1 Plate, metal (Fig. 99)
6 Test tubes, Pyrex, 100 × 13 mm.
1 Test tube, Pyrex, with side tube, 125 × 15 mm.
1 Thistle tube, Pyrex, with constriction (optional), Fig. 98

III. Equipment Issued on Loan from the Stockroom

Anodes, copper, nickel, and carbon (see Exp. XXXIII)
Balance, beam, and set of analytical weights
Bridge, metal (Exp. V (C))
Burettes, 50-ml. Mohr and Geissler type
Condenser, water-jacketed (Liebig)
Conductivity cell (Fig. 79)
Copper, wire, No. 14, No. 18
Crucibles, iron and nickel
Flasks, distilling, 150 ml., 250 ml.
Funnel, separatory
Graphite electrodes
Lead, wire, shot, rods (100 to 150 g.) and strips, $\frac{1}{2}'' \times 2''$
Nichrome, wire, No. 18
Pipettes, 5 ml. and 10 ml.
Platinum, wire and electrodes
Pneumatic trough
Stop watch
Voltmeter (0 to 10 volts)

IV. List of Chemicals

1. Liquids and Solutions

All solutions are aqueous and 0.1 normal except as otherwise noted. Because of infrequent use, and because of a number of other considerations, it is suggested that starred items (*) be issued only at the stockroom.

Acetic acid (4*N* and glacial)
Acetic anhydride *
Acetone *
Albumen, egg (0.1%) *
Alcohol (95% and absolute) *
Aluminum chloride
Aluminum nitrate
Ammonium acetate (0.1*N*, 1*N*, and 6*N*)
Ammonium carbonate (2*N*)
Ammonium chloride (0.1*N* and 1*N*)
Ammonium hydroxide (15*N*)
Ammonium nitrate
Ammonium oxalate
Ammonium phosphate, secondary (1*M*)
Ammonium sulfate
Ammonium sulfide (1*N*)
Ammonium thiocyanate
Antimony trichloride
Arsenic trichloride
Arsenic trioxide (saturated solution) *
Barium acetate
Barium chloride
Barium hydroxide (saturated solution)
Barium nitrate
Benzene *
Bismuth chloride
Bismuth nitrate
Bromine water (saturated)
iso-Butyl alcohol *
n-Butyl alcohol *
sec-Butyl alcohol *
tert-Butyl alcohol *
Cadmium nitrate
Calcium chloride
Calcium hydroxide (saturated)
Calcium sulfate (saturated)
Carbon disulfide
Carbon tetrachloride
Chlorine water (saturated)
Chloroform
Chrome alum (0.1*M*)
Chromic chloride (0.1*M*)
Chromic nitrate (0.1*M*)
Cobalt chloride
Cobalt nitrate
Cupric chloride
Cupric nitrate
Cupric sulfate (0.1*N* and 1*M* *)
Disodium hydrogen phosphate (1*M*)
Ether
Ferric chloride (0.1*M*)
Ferric nitrate (0.1*M*)
Ferrous ammonium sulfate (0.1*M*)
Formaldehyde (2% solution) *
Gelatin (0.1%) *
Hydriodic acid
Hydrobromic acid (1*N*)
Hydrochloric acid (in toluene) *
Hydrochloric acid, standard, 1*N* *
Hydrogen peroxide (3%) *
Iodine water (saturated)
Kerosene *

Lead acetate
Lead nitrate
Magnesium chloride
Manganous nitrate (0.1*M*)
Manganous sulfate
Mercuric chloride
Mercuric nitrate
Mercurous nitrate
Methanol (methyl alcohol) *
Nickel ammonium sulfate *
Nickel nitrate
Nickel sulfate
Oil, lubricating (light) or transformer *
Oil, pine *
Oxalic acid
Phenolphthalein (1% in 90% alcohol)
Phosphoric acid (85%)
Phosphorus trichloride *
Potassium bromate (0.1*M*)
Potassium bromide (0.1*N* and 1*N* *)
Potassium chloride (0.1*N* and 1*N* *)
Potassium chromate (0.05*M* * and 0.1*M*)
Potassium cyanide (1*N*)
Potassium dichromate (0.1*M*)
Potassium ferricyanide
Potassium ferrocyanide
Potassium hydroxide (1*N*) *
Potassium iodate (0.1*M*)
Potassium iodide
Potassium nitrite (6*N*) *
Potassium permanganate (0.1*M*)
Potassium pyroantimonate (saturated) *
Potassium thiocyanate
Silver nitrate
Soap solution (castile, 1%) *
Sodium acetate (1*N*)
Sodium arsenate (0.1*M*)
Sodium arsenite (0.1*M*)
Sodium bicarbonate (1*M*) *
Sodium carbonate (0.1*N* and 2*N* *)
Sodium chloride (0.1*N* and 1*N* *)
Sodium dihydrogen phosphate (1*M*)
Sodium fluoride
Sodium hydrogen sulfide
Sodium hypochlorite (5%) *
Sodium iodide
Sodium nitrate (0.1*N* and 10% *)
Sodium nitrite (0.1*M*)
Sodium oxalate (0.1*M* and standard 0.05*M* *)
Sodium potassium tartrate (1*M*)
Sodium silicate (36% — water glass) *
Sodium sulfate
Sodium sulfide (0.1*M*)
Sodium sulfite (0.1 *M*)
Stannic chloride (0.1*M*)
Stannous chloride (0.1*N* and 1*N*)
Strontium chloride
Strontium sulfate (saturated)
Sugar (1*M*) *
Tartaric acid (1*N*) *
Tragacanth (0.1%) *
Trisodium phosphate (0.1*N* * and 1*M*)
Xylene *
Zinc acetate
Zinc nitrate
Zinc sulfate (0.1*N* and 1*M* *)

2. Solids

Acetamide *
Alum, $KAl(SO_4)_2 \cdot 12H_2O$
Aluminum (turnings and high purity wire *)
Aluminum oxide
Aluminum stearate *
Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ *
Ammonium carbonate
Ammonium chloride
Ammonium nitrate
Ammonium sulfate
Antimony (powdered) *
Antimony trioxide *
Arsenic (powdered) *
Arsenic pentoxide *
Arsenic trioxide *
Barium carbonate
Barium chloride, $BaCl_2 \cdot 2H_2O$
Barium peroxide
Barium sulfate
Bismuth (powdered) *
Bismuth trioxide *
Bone black
Borax, $Na_2B_4O_7 \cdot 10H_2O$
Boric acid
Calcium *
Calcium carbonate (powdered)
Calcium chloride (anhydrous)
Calcium cyanamide *

Calcium fluoride
Calcium hydroxide
Calcium oxide
Calcium phosphate (primary) *
Calcium phosphide *
Calcium sulfate
Cellophane (untreated), 8″ squares *
Charcoal (wood and animal, powdered)
Chromic chloride, $CrCl_3 \cdot 6H_2O$
Clay plate, porous *
Coal, bituminous *
Cobalt carbonate *
Cobalt chloride, $CoCl_2 \cdot 6H_2O$
Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$
Copper (wool and turnings)
Cotton
Cupric chloride, $CuCl_2 \cdot 2H_2O$
Cupric nitrate, $Cu(NO_3)_2 \cdot 6H_2O$
Cupric oxide (powdered and wire)
Cupric sulfate, $CuSO_4 \cdot 5H_2O$
p-Dichlorobenzene *
3,5-Dinitrobenzoyl chloride *
or
3,5-Dinitrobenzoic acid *
Diphenyl *
Eosin *
Ferric oxide
Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
Ferrous sulfate, $FeSO_4 \cdot 7H_2O$ *
Ferrous sulfide
Graphite (flake) *
Iodine *
Iron (filings and pure wire *)
Iron pyrites
Lead (granulated)
Lead dioxide
Lead monoxide
Lead nitrate
Lead sulfide (galena)
Magnesium (ribbon * and turnings)
Magnesium carbonate
Magnesium stearate *
Magnesium sulfate, $MgSO_4 \cdot 7H_2O$
Manganese dioxide
Manganous sulfate, $MnSO_4 \cdot 4H_2O$
Marble (chips)
Mercuric oxide
Mercury *
Nails (iron, 1.5 cm.)
Naphthalene *
Nickel chloride, $NiCl_2 \cdot 6H_2O$
Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$
Palmitic acid *
Paraffin
Petroleum jelly *
Phosphorus (red)
Phosphorus pentachloride *
Phosphorus pentoxide *
Plaster of Paris *
Portland cement *
Potassium acid tartrate *
Potassium bromide
Potassium chlorate *
Potassium chloride
Potassium dichromate
Potassium hydroxide (pellets or flakes) *
Potassium iodide
Potassium nitrate
Potassium perchlorate *
Potassium permanganate
Potassium sulfate
Salicylic acid *
Silica gel (commercial) *
Silicon (powdered) *
Silicon dioxide (sand)
Soap (castile) *
Sodium *
Sodium acetate, $CH_3COONa \cdot 3H_2O$
Sodium aluminum sulfate, $NaAl(SO_4)_2$ *
Sodium ammonium hydrogen phosphate, microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$
Sodium bicarbonate
Sodium bismuthate *
Sodium bromide
Sodium carbonate (anhydrous)
Sodium carbonate, $Na_2CO_3 \cdot 10H_2O$ *
Sodium chloride
Sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_2O$
Sodium hexametaphosphate *
Sodium hydrogen sulfite (bisulfite)
Sodium hydroxide (pellets or flakes) *
Sodium iodide
Sodium metaphosphate
Sodium nitrate
Sodium nitrite
Sodium peroxide *
Sodium pyrophosphate
Sodium sulfate, $Na_2SO_4 \cdot 10H_2O$
Sodium sulfite
Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$

Stearic acid *
Strontium chloride, $SrCl_2 \cdot 6H_2O$ *
Sugar
Sulfur (powdered and roll)
Tartaric acid *
Thymol *
Tin (mossy and foil *)
Tricalcium phosphate
Triphenylmethane *
Turmeric paper *
Vaseline *
Wire, picture (5-in. lengths)
Wool (glass * and steel)
Yarn, woolen, white *
Zeolite (Permutit)
Zinc, wire or strips *
Zinc (mossy and powdered)
Zinc sulfate, $ZnSO_4 \cdot 7H_2O$

3. Individual Set of Reagents

a. General Chemistry

Ammonium hydroxide (4*N*)
Hydrochloric acid (4*N* and 12*N*)
Nitric acid (4*N* and 16*N*)
Sodium hydroxide (4*N*)
Sulfuric acid (4*N* and 36*N*)

b. Qualitative Analysis

The preceding reagents are all supplied in small dropping bottles; 6*N* HCl is used instead of the 4*N* acid specified for general chemistry.

4. Reagents for Qualitative Analysis

(*All liquids to be in dropping bottles*)

Acetic acid (1*N* and 4*N*)
Aluminon (see Special Reagents)
Aluminum, wire (pure)
Ammonium acetate (1*N* and 6*N*)
Ammonium carbonate (2*N*)
Ammonium chloride (6*N*)
Ammonium hydroxide (15*N*)
Ammonium iodide (1*N*)
Ammonium nitrate (1*N*)
Ammonium phosphate, secondary (1*M*)
Ammonium sulfate (1*N*)
Ammonium sulfide (1*N*)
Ammonium thiocyanate (0.1*N*)
Butyl cellosolve
Dimethylglyoxime (see Special Reagents)
Hydrogen peroxide (3%)
Iron, wire (pure)
Lead acetate (0.1*N*)
Magnesium nitrate mixture (see Special Reagents)
p-Nitrobenzeneazo-*a*-naphthol (see Special Reagents)
Phenolphthalein (see Special Reagents)
Potassium chromate (1*M*)
Potassium cyanide (1*N*)
Potassium ferrocyanide (0.1*N*)
Potassium nitrite (6*N*)
Silver nitrate (0.1*N*)
Sodium acetate (1*N*)
Sodium bismuthate
Sodium cobaltinitrite (see Special Reagents)
Sodium hydroxide—sodium sulfide—sulfur reagent (see Special Reagents)
Sodium hypochlorite (5%)
Sodium nitrite (1*M*)
Stannous chloride (1*N*)
Tartaric acid (1*N*)
Uranyl zinc acetate (see page 395)

5. Special Reagents

Alizarin. Suspend 50 g. of 20% alizarin paste in 1 liter of water.

Aluminon. A 0.1% solution of the ammonium salt of aurin tricarboxylic acid.

Ammonium molybdate reagent. Dissolve 20 g. of MoO_3 in 100 ml. of 6*N* NH_4OH. Stir in 375 ml. of 6*N* HNO_3 and then dilute the solution to a volume of 500 ml.

Dimethylglyoxime. A 0.1% solution in 95% alcohol.

Hydrochloric acid. A standard 1*N* solution.

Iodic acid. Each liter of solution contains 4.86 g. of KIO_3 and 9 ml. of 4*N* H_2SO_4. This solution should be freshly prepared on the day it is to be used.

Magnesium nitrate mixture. Dissolve 25 g. of $Mg(NO_3)_2 \cdot 6H_2O$ and 75 g. of NH_4NO_3 in 175 ml. of water. To this solution add 45 ml. of 15*N* NH_4OH and enough water to make 250 ml. of solution.

Methyl orange. A 0.2% solution (in dropping bottle).

Methyl violet. A 0.1% solution (in dropping bottle).

Nickel Plating Solution. Dissolve 90 g. of $NiSO_4 \cdot 6H_2O$, 30 g. of $NiCl_2 \cdot 6H_2O$, and 15 g. of H_3BO_3 in enough water to make a liter of solution.

***p*-Nitrobenzeneazo-α-naphthol.** A 0.1% solution in 95% alcohol (in dropping bottle).

Orange IV. A 0.1% solution (in dropping bottle).

Phenolphthalein. A 1% solution in 95% alcohol (in dropping bottle).

Phenol red. Dissolve 0.1 g. of the indicator in 3 ml. of 0.1*N* NaOH and dilute the solution to 100 ml. (in dropping bottle).

Potassium chlorate. A saturated aqueous solution. For use in Exp. XXXIV.

Soap solution. The standard solution. Dissolve 100 g. of dry castile soap in 1 liter of 80% alcohol.

Sodium chlorate. A saturated aqueous solution. For use in Exp. XXXIV.

Sodium chloride. A saturated aqueous solution. For use in Exp. XXXIV.

Sodium cobaltinitrite. Dissolve 250 g. of $NaNO_2$ in 500 ml. of water, and add to the solution 150 ml. of 6*N* CH_3COOH and 25 g. of $Co(NO_3)_2 \cdot 6H_2O$. Let the mixture stand overnight, then filter it and dilute the filtrate to 1 liter.

Sodium hydroxide—sodium sulfide—sulfur reagent. Dissolve 120 g. of NaOH, 80 g. of $Na_2S \cdot H_2O$, and 0.1 g. of S in enough water to make 1 liter of solution.

Sodium indigodisulfonate. A 0.1% solution (in dropping bottle).

Sodium thiosulfate. Freshly prepared 0.05*M* and 0.1*M* solutions.

Starch solution. Stir 10 g. of soluble starch with enough water to make a thin paste and then pour the mixture into 500 ml. of boiling water. Stir the liquid vigorously during the addition of the starch paste. Allow the mixture to stand 12 hrs. Decant the clear liquid and add to it 2 ml. of chloroform or toluene.

Sulfurous acid. Dissolve 3.33 g. of Na_2SO_3 and 30 ml. of 4*N* H_2SO_4 in enough water to make 5 liters of solution. This solution should be freshly prepared on the day it is to be used. For use in Exp. XXXII.

Sulfurous acid. A freshly prepared saturated solution of SO_2. For use in Exp. XXVIII.

Universal Indicator. See **Appendix F.**

Uranyl zinc acetate solution. See page 395.

Zimmerman—Reinhardt solution. See page 296.

Zinc chloride—Hydrochloric acid. Dissolve 136 g. of anhydrous zinc chloride in 88 ml. of 12*N* HCl.

INTERNATIONAL ATOMIC WEIGHTS

1943

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22