GENERAL CHEMISTRY LABORATORY MANUAL

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GENERAL CHEMISTRY LABORATORY MANUAL

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PREFACE

The exercises in this manual are complementary to the author's "General Chemistry, Theoretical and Applied." The numbering of the chapters and sections follows that of the textbook exactly, as it is expected that students will study both simultaneously. In fact, the exercises can often advantageously precede the corresponding lectures; although in such cases the instructor will find it necessary to give more extended oral instructions at the beginning of the laboratory period than would otherwise be required. Such preliminary instructions must be given in any event during the early part of the course in order to familiarize the student with the ordinary pieces of apparatus and their manipulation, the regulations and routine of the laboratories and storerooms, and the prescribed system of recording results and submitting them to the instructor for inspection and approval. Oral and written quizzes based on the laboratory work, but involving knowledge of both the laboratory work and the lectures, will be found helpful.

The pseudo-quantitative experiments included in the course are best performed by the members of large classes by means of triple-beam balances, made as noncorrodible as possible. Such balances have the double advantage of quick weighing and irremovable weights. Chemical balances, however, should be used with some of the later experiments.

Students intending to *specialize* in chemistry are expected to perform such additional or different experiments as the professor in charge may indicate, and to do much collateral reading.

It is thought that this course cannot be taken by students in an absent-minded, mechanical way. It is also thought that the tests given under the head of Applied Chemistry may readily be connected with the environment in such a way as to make this part of the work of unusual interest.

J. C. BLAKE.

College Station, Texas,
March 1, 1913.

NOTE TO THE STUDENT

KEEP your desk looking as neat as you can. Do not throw any solids into the sinks or on the floor. Throw them into the earthenware slop jar nearest your desk. Other substances may be thrown into the sinks, *provided a moderate amount of water is simultaneously run in.* Do not allow a *single drop* of concentrated acids, alkalies, or other corrosive liquids to get on your desk, clothing, or person; in case this happens accidentally, however, immediately flood the affected spot with water. Keep a sponge or dirty towel to mop with and a clean towel for *drying objects which have been washed clean*, including your hands. Any broken glass which accidentally gets to the floor should immediately be brushed to one side, or, preferably, brushed up and put in a slop jar, so that it will not be trampled on.

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GENERAL CHEMISTRY LABORATORY MANUAL

PART I

HYDROGEN AND THE ACID-FORMING ELEMENTS

(*The sections are numbered to conform with those of the Text.*)

CHAPTER I

INTRODUCTORY

2. The Combustion of Wood and Coal. — *a. Test for Water.*—Ignite a splint of wood or a fragment of lignite or cannel coal and hold a few inches above the flame a dry inverted funnel the stem of which has been sprinkled with a mixture of powdered anhydrous ferrous sulfate and potassium ferricyanide. If this green material turns dark blue more readily than it does in the air of the laboratory, water was formed by the burning of the wood or coal. The blue substance is Turnbull's blue.

b. Hold a drop of **limewater** on a stirring rod just above the flame of the burning fragment. If the drop turns milky before it is evaporated to dryness and sooner than it would turn milky in the air of the laboratory, carbon dioxide has been formed by the burning of the wood or coal. The milkiness is due to "limestone" formed by the interaction of the limewater and the carbon dioxide.

3 and 4. The Combustion of Metals. — *a.* Try to burn samples of all metals available, and arrange them in

the order of their chemical activity, remembering that the finer a solid is divided, the faster it will burn. (Why?)

Determine the chemically equivalent weight of magnesium by burning a weighed portion of it (about half a gram) in a closed crucible of which the weight is also known. Do not make the third weighing, which gives the weight of the oxide formed by the combustion, until after the crucible has cooled to the temperature of the room.

Add a drop of pure water to the oxide thus formed and test the resulting liquid with **litmus paper**. Alkalies turn litmus blue; acids turn it red.

6. Differentiating between Pure Substances some of whose Properties are nearly Identical.— Determine the boiling-point of water and of formic acid by immersing the bulb of the same thermometer successively in each of these liquids when boiling. Could you distinguish between them by their appearance or by their boiling-points? Can you distinguish between them in any other way? The test with formic acid is best made in a flask with a long neck and narrow opening. Why?

10. Chemically Equivalent Weights of the Metals determined by Displacement. — Determine the chemically equivalent weights of copper and of silver by ascertaining what weight of each of these metals is displaced from any of their soluble salts by a weighed amount (about 0.2 gram) of zinc. Carry out this reaction in a weighed test tube. The precipitated metal must be washed free from dissolved salts and then dried at a low temperature before its weight can be ascertained. The metal is best washed by **decantation,** great care being taken to see that none of it is carried away by the water. To dry the metal, immerse the test tube containing it in a

beaker of boiling water. Many other experiments of this kind can be made if time permits.

14. Percentage Composition of Substances derived from their Formulæ. — Calculate the percentage of each element in the substances whose formulæ are as follows: anhydrous ferrous sulfate, $FeSO_4$; green vitriol, $FeSO_4 \cdot 7\,H_2O$; anhydrous copper sulfate, $CuSO_4$; blue vitriol, $CuSO_4 \cdot 5\,H_2O$; limestone, $CaCO_3$; magnesia, MgO; formic acid, $H \cdot HCO_2$. Note the chemical use of the period in the formula of blue vitriol. **It signifies, in such cases, an unknown method of union of the parts of the compound whose formula it divides.** The period in the formula of formic acid **separates the basic from the acid** radical (Text 29*c*, 3).

16. Chemical Equations. — Balance the following equations:

$$C + O_2 \rightarrow CO_2$$

$$H_2 + O_2 \rightarrow H_2O$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

$$Mg + O_2 \rightarrow MgO$$

$$Zn + \underset{\substack{\text{Cupric}\\ \text{chloride}}}{CuCl_2} \rightarrow Cu \downarrow + \underset{\substack{\text{Zinc}\\ \text{chloride}}}{ZnCl_2}$$

$$Al + CuCl_2 \rightarrow Cu \downarrow + \underset{\substack{\text{Aluminium}\\ \text{chloride}}}{AlCl_3}$$

Notice the use of the **parentheses** around the OH group in calcium hydroxide, $Ca(OH)_2$, indicating that the subnumber modifies both of these symbols; also the use of the arrow pointing downward in the case of the formation from solution of "limestone" and the free metals. This phenomenon is called **precipitation.** In case any gas is formed from solution, this is also called precipitation, but

the arrow is pointed upward to indicate that the gas ordinarily escapes.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$$

Using the data obtained in Lab. Exp. 10, write the equations involved as true mathematical expressions of the relation by weight of the reacting substances.

CHAPTER II

OXYGEN

21b. Heat a little mercuric oxide in a test tube and test for oxygen by a glowing splint. Notice the formation of a mirror or globules of metallic mercury.

23. **Preparation of Oxygen.** — *c and d.* Prepare oxygen by heating small portions of lead dioxide, manganese dioxide, barium peroxide, potassium chlorate, and potassium nitrate separately in test tubes. Note the relative temperatures at which the oxygen comes off. Test for the oxygen by a glowing splint. Note that the glass of the test tube is badly attacked in the experiment in which barium peroxide was used. The barium oxide formed, which is an alkaline oxide (can you prove it?), has **fluxed** the glass to form a more fusible **slag** (Text, 80*b*, 4).

e. Carefully melt a little potassium chlorate and then, while keeping it barely hot enough to prevent its resolidification, drop in a small pinch of manganese dioxide. What happens? Prepare four jars of oxygen by gently heating a mixture of potassium chlorate and manganese dioxide, collecting the oxygen by means of the pneumatic trough. Save this oxygen for Exp. 25*b*.

f. Prepare one jar of oxygen by placing a small piece of " oxone " beneath the mouth of a jar of pure water standing in a separate trough. Save this oxygen for Exp. 25*b* (Fe). Test the water with litmus. What alkali is present?

25. Chemistry of Free Oxygen. — *b.* Ignite small pieces of carbon (charcoal), sulfur, phosphorus, and magnesium ribbon in the air and then immediately plunge each into one of the jars of oxygen prepared in Exp. 23*e*. Does the material burn faster in air or in oxygen? Why? Allow these jars to stand, covered with a piece of glass. Burn a piece of iron wire in the jar of oxygen prepared in Exp. 23*f*. In order to heat the iron to the kindling temperature, even in pure oxygen, it will be necessary to wrap a little thread or cotton around the end of the wire, rub the end of the wire thus treated in flowers of sulfur, ignite the sulfur in the air, and immediately plunge the wire into the jar of oxygen. Don't mistake the odor of the burning sulfur for a combustion product of iron. Remove the globules of magnetite from the bottom of the jar. Wash them thoroughly with pure water and test them for alkalinity and acidity by placing them on pieces of moist litmus paper. Also test them with a magnet.

c. Test with litmus the water which has drained from the sides of the four jars left standing in Exp. 25*b*. Classify the five elements used for these combustions as to their metallic or non-metallic character. If the carbonic acid formed does not give a satisfactory test with litmus, we may nevertheless classify carbon among the non-metals because both carbonic acid and carbonic anhydride **react with alkalies to form salts** (Exp. 2), and are therefore acidic. This new conception of acids and alkalies should be carefully borne in mind until it is met with again (Text, 44*i*).

CHAPTER III

HYDROGEN

28. Preparation of Hydrogen. — *b. From Acids and Metals.* — Determine as closely as possible the relative rates at which hydrogen is liberated by the action of magnesium and various ambiguous elements on hydrochloric, HCl, acetic, $H \cdot CH_3CO_2$, and sulfuric acids, H_2SO_4. To make the tests comparable the acids must be of the same concentration (about 4 normal), the metals must each present the same surface of contact to the acid (why?), and the temperature at the start must be the same. Further, most of the metals will be found to be coated with a thin film of their oxides. Since these oxides are often much less active toward acids than the free metal is, they should be scraped off just before the experiment is made. If a gas readily explodes when ignited in the presence of the air and is not known to be any other gas, it is assumed to be hydrogen. In case a gas is liberated very slowly from a liquid, the vessel holding the liquid should be inverted so that the gas will accumulate above the liquid.

Arrange the metals in the order of their activity as determined by one and the same acid. Also, arrange the acids in the order of their activity as determined by one and the same metal. Does nitric acid, HNO_3, liberate hydrogen on contact with metals?

From Alkalies and Ambiguous Elements. — Treat some powdered aluminium with a solution of caustic soda or caustic potash and test the resulting gas for hydrogen.

c. From Active Metals and Cold Water. — Determine whether sodium, potassium and freshly scraped magnesium liberate hydrogen from cold water. What character of substance is left in solution? Test with litmus. Determine whether any other of the common metals liberate hydrogen from cold water. Try calcium, if available.

31. **Reduction.** — Generate a considerable amount of hydrogen in a flask or in a Kipp's apparatus, and pass it over some heated cupric oxide contained in a (hard) glass tube. The hydrogen should be dried before passing it over the cupric oxide in order that any water formed by the reduction of the cupric oxide may be detected in the gases after they have passed over the oxide. This is conveniently done by passing it over fused calcium chloride. The water formed by the reaction can then be detected by the mixture used in Lab. Exp. 2 or by anhydrous copper sulfate. If the hydrogen is not liberated fast enough, add to the generating flask a few drops of a solution of copper sulfate.

The hydrogen should be allowed to run through the apparatus for about two minutes before applying a match to the escaping gas or heating the tube containing the cupric oxide in order to remove all of the air which the apparatus originally contained. Otherwise an explosion may occur. Still further to insure safety, place a towel over the apparatus just before applying a match to the escaping gas, stand as far away as possible, and warn your neighbors. After the reduction seems to have taken place, turn off the heat from the tube, put out the lighted gas jet at the end of the tube, and then take the apparatus apart and examine for copper and water produced by the reduction. Write the reactions involved.

CHAPTER IV

WATER

AND HYDROGEN PEROXIDE

35*b*. Plot the vapor tensions of water at various temperatures from −75° to 360°, plotting the tensions in millimeters at low temperatures and in atmospheres at high temperatures. Connect the points plotted by a smooth curve. What form does the curve seem to have?

36*d*. **Hydrolysis.**—Test all available acids and alkalies with litmus. Test all available salt solutions with litmus. Divide the salt solutions into three classes: (1) those which are neutral to litmus; (2) those which are acid to litmus; (3) those which are alkaline to litmus. How do you account for these different reactions? Can you tell which are the active metals by hydrolysis? Can you tell which are the active acids by hydrolysis? Try to write the reactions showing the hydrolyses observed and submit them to the instructor for inspection.

36*e and g*. **Solubility.**—Grind up in a mortar a small piece of alum and put it in a test tube with about five times its volume of water. Shake vigorously until no more seems to dissolve. The solution is now saturated. Gently warm the test tube and note whether any more of the alum dissolves. If it does, the temperature coefficient of solubility of alum is positive. After all of the alum has dissolved, set the test tube aside till it has cooled to the ordi-

nary temperature. Does the excess of alum, that is, the part which would not dissolve at the ordinary temperature, crystallize out as the solution cools? Why not? Add a *little* powdered alum to the cool supersaturated solution. What happens?

37. Add a few drops of **hydrogen peroxide** to a very dilute solution of dichromic acid, $H_2Cr_2O_7$, formed by the interaction of potassium dichromate, $K_2Cr_2O_7$, and sulfuric acid. The blue color produced is supposed to be due to perchromic acid, $H_2Cr_2O_8$, formed as a result of the oxidizing properties of the hydrogen peroxide. It is much more soluble in ether than in water. On shaking the water solution of perchromic acid with a little ether, the perchromic acid distributes itself between the water and the ether according to its independent solubility in each of the two solvents. Try the same experiment, in so far as its distribution between these two solvents is concerned, with iodine. The ratio of the independent solubilities in cases of distribution between two solvents is called the partition coefficient.

Is ether soluble in water or water in ether? Is alcohol soluble in water? in ether? Do gases dissolve in liquids? Test the latter by heating some tap water in a V-shaped tube closed at one end.

CHAPTER V

SULFUR,

SELENIUM AND TELLURIUM

41. Physical Properties. — *a. Preparation of Orthorhombic Sulfur.* — Powder some roll sulfur (brimstone) in a mortar, put it in a test tube and add about five times its volume of carbon disulfide (inflammable, keep away from flames). Does all the sulfur dissolve? Pour the solution into a vessel which can be loosely stoppered, insert the stopper, and set aside till next time. Then examine the crystals left in the vessel.

Repeat the same experiment, using flowers of sulfur, which is the part formed by the sudden cooling of the gas in the distillation of sulfur. Does all of this sulfur dissolve? Why not?

b. Allotropy of Liquid Sulfur. — Gently heat some powdered roll sulfur in a test tube and note the color and mobility of the molten sulfur (shake the test tube). Pour a little of this sulfur into a beaker of water and compare it with that to be obtained in a similar manner later on. Continue the gentle heating of the remainder of the liquid sulfur in the test tube, with gentle shaking, until the sulfur seems to solidify. What color is the sulfur now? Will it run out of the test tube if inverted? If it is allowed to cool in the air, it will change back to mobile sulfur. Finally continue the heating until the sulfur fumes strongly, then

pour it into another beaker of cold water. Does the sulfur solidify? Is it soluble in carbon disulfide? Determine whether it has become crystalline sulfur by the time you next return to the laboratory (try carbon disulfide).

42*b and c.* *Crystal Forms.* — Examine various crystal models and crystals and determine to which system each belongs.

d. Physical Evidences of Orientation in Crystals. — Examine a crystal of calcite. To what system does it belong? Strike it gently on one side. The resulting fragments are called **rhombohedrons** and the cleavage of calcite is said to be rhombohedral. How does this show a relation between the forces of the crystal and its internal structure? Show that the rhombohedrons belong to the hexagonal system. Put a clear rhombohedron about a fourth of an inch thick over a narrow printed line and observe the line as you slowly rotate the rhombohedron around a vertical axis. Does this experiment reveal any further evidence of relation between the forces in the crystal and its crystal form? What kind of cleavage has galena? fluorspar? mica? gypsum?

43. **Chemistry of Sulphur.** — *c. Ways in which Sulfur resembles Oxygen.* — Mix some powdered iron with some powdered sulfur in about equal proportions by volume and heat the mixture in a test tube. Is there any combustion? After the combustion starts take the test tube out of the flame and notice whether it continues. Don't confuse the ignition taking place in the interior of the test tube with the burning of the sulfur at the mouth of the test tube, which occurs when the combustion is nearly ended. Examine the product left in the test tube after the combustion is

over and ascertain whether it is iron or sulfur, or contains either of these substances in appreciable amount. Treat a small piece of it in a test tube with dilute hydrochloric acid and observe the odor of any gas given off. Compare this odor with that of hydrogen sulfide. Write the reaction by which the iron burned in the sulfur, also the reaction which took place when the product of combustion was treated with hydrochloric acid.

Heat some pyrite in a test tube and then suddenly pour it out on to an iron plate. Is there any sign of combustion? What gas is formed? Smell of the gases given off from the glowing coals after the material has been poured out of the test tube. Would iron oxide burn as the sulfide does? Does the chemistry of sulfur as exhibited in this experiment resemble or differ from that of oxygen? Write the reaction for this last combustion.

Pass some hydrogen sulfide into a solution of a chromate, such as potassium chromate, K_2CrO_4, acidified with sulfuric acid. All chromates are yellow, of various shades. Does the solution change color? What color does it become? Wait till the sulfur thrown out by the reaction has settled out or filter it out. All **chromium salts** have the same color as the resulting solution, of various shades. Chromium salts are derived from the oxide Cr_2O_3; chromates and the chromic acids (Text, 36*a*; 155) are derived from the acid anhydride CrO_3. What was the nature of the action of the hydrogen sulfide on the chromate?

Pass some hydrogen sulfide (under the hood) into a dilute solution of blue litmus. What happens? Does sulfur in hydrogen sulfide resemble oxygen very closely?

d. Ways in which Sulfur is wholly different from Oxygen. — What compounds of oxygen correspond to the sul-

fides? to the sulfites? to the sulfates? to sulfurous anhydride? to sulfuric anhydride? to sulfuric acid?

Prepare a solution of **sulfurous acid** by passing sulfurous anhydride through cold water. Smell of this solution, test it with litmus, and save it in a stoppered bottle for further use. Prepare the sulfurous anhydride called for in this experiment either by treating a sulfite with sulfuric acid or by acting on sulfuric acid with copper (Text, 43*d*, 2). Write the reactions involved.

Boil a small piece of undyed silk or wool in a soap solution; rinse in water, and immerse in part of the solution of sulfurous acid which you prepared. What happens?

Heat some ferric sulfate in a test tube and determine by the odor, by the color, and by litmus paper the nature of the gases evolved. Why could not sulfuric acid be made on the large scale by leading these gases into water?

Examine a bottle of concentrated sulfuric acid (very corrosive to cloth and flesh). Could you distinguish a bottle of this acid from a bottle of water by merely examining the bottle? Carefully remove the stopper and touch the acid clinging to it to a splint of wood. The black substance formed where the acid touched the wood is pure carbon. Where did it come from, and how? Try the same experiment with a little sugar in a test tube, pouring the acid on the sugar. **Never look into the mouth of a loaded test tube!** Carefully pour a few drops of concentrated sulfuric acid into as much water, remembering the caution just given. What happens? Feel of the test tube.

Determine by the method used in Exp. 28*a* whether concentrated or dilute (1 part acid to 5 parts water, previously mixed and cooled; **ordinarily represented thus — 1 : 5**) sulfuric acid is the more active as an acid. How

do you account for the difference in activity, remembering (try it) that sulfuric acid one to five is much more active than sulfuric acid one to twenty-five?

Determine from among a number of available salt solutions and solutions of acids which ones contain the sulfate radical by using a solution of barium chloride acidified with nitric acid. Is barium sulfate soluble in water? Is it soluble in nitric acid? in hydrochloric acid?

Treat a small piece of potassium or sodium nitrite, KNO_2 or $NaNO_2$, with a few drops of dilute sulfuric acid, The gases given off come from the decomposition of the nitrous acid, (HNO_2), liberated by the double decomposition (write the reaction), and, although in equilibrium with two other oxides of nitrogen, as indicated below, correspond to the nitrous anhydride used in the lead-chamber process of making sulfuric acid. The equilibrium referred to is as follows:

$$N_2O_3 \rightleftarrows NO + NO_2$$

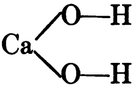
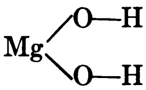
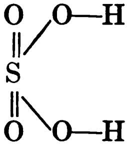
NO_2 is a brown gas; NO is colorless. Does any change seem to take place around the mouth of the test tube? (See nitrogen.) Hold the test tube at an angle of 45° in front of a piece of white paper. The bluish color which appears in the liquid when the reaction is the most vigorous is due to nitrous anhydride in solution.

Heat a few drops of sulfuric acid in a test tube and explain what takes place.

Determine the "**reaction**" of solutions of potassium sulfate, K_2SO_4, of potassium bisulfate, $KHSO_4$, and of ferrous sulfate, $FeSO_4$. Explain.

Carefully mix moderately dilute solutions of the following substances and determine the heat effects with a

thermometer: sodium chloride and potassium sulfate; hydrochloric acid and sulfuric acid; sodium hydroxide and potassium hydroxide; sodium hydroxide and potassium sulfate; sodium chloride and sulfuric acid; sodium hydroxide and sulfuric acid; potassium hydroxide and hydrochloric acid. Explain the results.

The structural formulæ of various alkalies are as follows: sodium hydroxide, Na—O—H; potassium hydroxide, K—O—H; calcium hydroxide,  magnesium hydroxide,  That of sulfuric acid is 

Why is not sulfuric acid ordinarily called a hydroxide? What is the structural formula of potassium sulfate? of calcium sulfate? of nitrosylsulfuric acid? of sulfurous acid?

48. Selenium and Tellurium.—Examine some "metallic" selenium. Treat a small piece with concentrated nitric acid (**very corrosive**) in a test tube and evaporate to dryness by immersing in a beaker of boiling water or on the sand bath. **Take up** with a few cubic centimeters of pure water and test the resulting solution with litmus. Is selenium a metal or a non-metal? Add a little of your solution of sulfurous acid to the rest of your solution of selenious acid. Notice the orange precipitate which soon forms. What is it?

CHAPTER VI

CHLORINE,

FLUORINE, BROMINE, AND IODINE

50. Natural Occurrence of Chlorides. — *b. Purification of Rock Salt by Recrystallization.* — Dissolve some rock salt in hot water, filter, and set aside till next time. Then examine the salt crystallized out as to its apparent purity compared with the original supply and as to its crystalline form.

51. Preparation of Chlorine. — *c.* Prepare small amounts of chlorine by the action of concentrated hydrochloric acid on manganese dioxide and on lead dioxide. Test for the chlorine by the odor (do not allow much chlorine to escape into the room, as it is very annoying and injurious; when you are through with any particular experiment in which chlorine is made, add a large excess of water to the containing vessel: by diluting the acids present this prevents any further liberation of chlorine); by the color; and with a piece of filter paper dipped in a mixture of potassium iodide and starch. Explain this last test (consult the Text).

Repeat this experiment, using a mixture of common salt and sulfuric acid in place of the hydrochloric acid.

d. Prepare several jars of chlorine as needed for the experiments mentioned in 53*b* by allowing hydrochloric acid (1 : 1) to drop from a separatory funnel into a flask containing a layer of potassium permanganate about one fourth of an inch deep.

53. Chemical Properties. — *b.* Fill a tall jar nearly full of chlorine (color) by upward displacement of the air it contains, having the jar closed with a perforated cardboard while the chlorine is being collected. Then immediately transfer the delivery tube of the generating apparatus (Exp. 51*d*) to another empty jar and sprinkle a pinch of finely powdered antimony into the jar just filled with chlorine. Is there any sign of combustion? Cover the jar with a piece of glass to keep the unused chlorine from entering the room until you are ready to leave it.

Using the same precautions as to the source of hydrogen that were emphasized in Exp. 31, plunge a lighted jet of hydrogen into a jar of chlorine and explain the results.

Heat a sand bath for a few minutes with the Bunsen burner. Turn off the gas and place on the sand bath a small evaporating dish half full of turpentine. Immerse a piece of cloth in the turpentine thus gently warmed, squeeze out the excess of turpentine, and then immediately hang the cloth in a jar of chlorine, allowing the cover glass to rest on the cloth to hold it up. Is there any sign of combustion? Is any acid produced (litmus and odor)? What acid? Where did the soot come from?

e. Shake some water with a jar of chlorine, and determine whether the resulting chlorine-water will bleach organic coloring matter (dyed cloth or yarn or colored flowers). The bleaching is due to hypochlorous acid. Where does this acid come from?

Pass some chlorine into a solution of potassium hydroxide. After the experiment has run for some time, dip a colored rag into the resulting solution, and then dip it in a dilute solution of sulfuric acid. Is it bleached? Which of

the two methods bleaches the better? Which liquid absorbs chlorine the better?

Prepare a solution of bleaching powder. Filter it and try to bleach as in the last experiment. How do the results compare? The odor of bleaching powder is due to hypochlorous acid.

Grind up a small crystal of potassium chlorate, mix it with an equal volume of flowers of sulfur, place the mixture in small amounts on an anvil, and hit it sharply with a hammer. What happens? What are some of the chemical changes which have taken place (notice the odor of the gases formed by the explosion)?

54. **Fluorine.**—*b. Properties.*—Examine some hydrofluoric acid. Why isn't it kept in a glass bottle? If any of it gets on the hands, wash it off at once. What does it smell like?

Cover the bottom of a lead dish with powdered fluorspar, cover this with concentrated sulfuric acid, and, finally, cover the dish with a piece of glass coated with paraffin, having previously traced a design in the paraffin coating with a pointed stick or lead pencil. Examine this design the next time you return to the laboratory and explain results.

55. **Bromine and Iodine.** — Prepare some bromine and some iodine by gently heating a mixture of manganese dioxide, concentrated sulfuric acid, and some bromide or iodide. Test for the iodine with starch paper, letting some of the heavy vapor **flow** out of the test tube on to the paper while you are heating the test tube. How else could iodine be detected in this experiment? Test for the bromine in the same way you tested for chlorine. How else could it be detected in this experiment, more especially

as the first test applied would not distinguish it from chlorine?

b. Properties. — 1. Pour a few drops of liquid bromine (**extreme care, as liquid bromine instantly cooks the flesh on contact with it**) into a test tube and drop into the tube a pinch of finely powdered antimony. Does any combustion take place? The product formed is antimony tribromide, $SbBr_3$.

2. Mix some powdered iodine with some powdered antimony. Does any combustion take place? Mix some powdered iodine with some powdered zinc. Does any combustion take place? Pour the mixture into a **dry** test tube and cautiously add a few drops of water. Does any combustion take place (is any heat liberated)? The residue contains zinc iodide, ZnI_2. How did the water facilitate the reaction for its formation? Most substances interact only when one or both of them are in solution or in the gaseous state (Text, 36*e*; also Exp. 2*a*).

Drop a small piece of dry yellow phosphorus into a test tube containing some powdered iodine. Phosphorus triiodide, PI_3, is formed. Is antimony or phosphorus the more active? Iodine or bromine?

CHAPTER VII

NITROGEN, PHOSPHORUS, AND ARSENIC

NITROGEN

63. Preparation. — *a. From the Air.* — Dry a small piece of "yellow" phosphorus on a piece of filter paper, and then put it in a small crucible floating on water. Ignite the phosphorus by touching it with a hot piece of metal, and then gently lower an "empty" wide-mouthed jar over it. Notice the fumes of phosphoric anhydride. Is there any evidence of the liberation of heat? Why do some bubbles come out from the mouth of the jar, especially just after it has been lowered over the burning phosphorus? After the combustion is over and the water has ceased to rise in the jar, slip a piece of glass under the mouth of the jar, remove it from the vessel in which the crucible was floating, invert it, letting the water it contains run down to the bottom without releasing the glass plate closing the jar. Now remove the glass plate and immediately plunge a flaming brand into the residual gas (not the water in the jar). What happens to the flame? Many gases besides nitrogen will extinguish flames, such, for example, as carbon dioxide. How could you distinguish nitrogen from carbon dioxide? If you used a large enough piece of phosphorus for the combustion, some of it will be left in the (submerged) crucible after this experiment is over. Recover the crucible, dry the residual phosphorus with

filter paper, and then see if this phosphorus will burn in the air. Could the inactivity of nitrogen be inferred from this latter observation?

How high did the water rise in the jar? How high would it have risen if the jar had contained pure oxygen at the moment it made a hydraulic seal with the water in the larger vessel, providing an **excess** of phosphorus had been present?

65. Chemical Properties. — *c. Ammonia.* — 2. Heat a little hide powder or dried albumin in a test tube and notice the **empyreumatic** odor. Can you detect ammonia in the gases evolved? Try a piece of moist litmus paper.

1. Examine a bottle of ammonium hydroxide, (NH_4OH). Could you distinguish it from water by a superficial examination? Don't taste of any substances in the chemical laboratory except when you know what they are and that they are not particularly poisonous; then, as soon as you have observed the taste, spit the material out (into the sink). Don't smell of any bottle in the laboratory without approaching it gradually, as the odor of its contents may not be agreeable. Hold pieces of litmus, moist and dry, about five inches above the bottle of ammonium hydroxide (**usually called " ammonia "**) and determine which is the more sensitive to ammonia. Explain your observation. " Ammonia " is the only common volatile " alkali." Is ammonia, NH_3, an alkali (Text, 44)?

3. Treat a number of solutions of metallic salts with " ammonia." The hydroxides of those which are precipitated are insoluble in water. The hydroxides of some of those not precipitated are also insoluble in water, but they do not precipitate because **complex salts** are formed with

the ammonia. Is there any resemblance between ferric hydroxide and iron rust? Write the reactions involved in these experiments, **considering them all to be double decompositions where a precipitate forms unless you are informed to the contrary.** As a general rule **bases precipitate bases** (that is, soluble bases, which are the alkalies, precipitate the insoluble bases from solutions of their salts).

4. Are the ammonium salts of active acids hydrolyzed by cold water? Is ammonium, (NH_4), an active or ambiguous basic radical?

d. 1. Digest some sulfur with concentrated nitric acid. Dilute, filter off the unchanged sulfur, and test the filtrate for the sulfate radical. Write the reactions involved.

2. Pass some hydrogen sulfide into dilute nitric acid. What is the white turbidity due to? Boil the mixture, filter out the precipitate, dry it, and see if it will burn.

3. Cautiously heat a **little** powdered charcoal and powdered potassium nitrate in a test tube. Compare gunpowder (Text, 208*b*).

4. Heat some copper nitrate in a test tube and describe what happens. Is copper nitrate soluble in water? Is all of the copper nitrate decomposed by the heating? (Treat the residue with water.)

5. Prepare some nitrous oxide by gently heating some ammonium nitrate in a flask. Collect the gas over a small amount of water, as it is fairly soluble. Test the first jar with a glowing splint. Invert the second jar over a piece of burning phosphorus as in the experiment for the preparation of (impure) nitrogen. How high does the water rise in the jar after the combustion is over and the residual gas has cooled off? If no bubbles had escaped at the be-

ginning of the combustion, the water would not rise at all, showing that in the reaction —

$$N_2O \rightarrow N_2 + O_{\text{nascent}}$$

the nitrogen occupies just as much space as the nitrous oxide from which it was evolved, the oxygen having all been removed by union with the phosphorus and solution of the resulting phosphoric anhydride in water. Could you modify this experiment in such a way that the peculiarity here pointed out, with regard to the relative volumes of these gases, would be apparent?

PHOSPHORUS

69. Chemical Properties. — *a.* 1. Pour a little phosphoric anhydride (phosphorus pentoxide) in a pile on a piece of white paper. Cautiously place a few drops of water near it, so that finally they make contact with it. Is there any evidence of liberation of heat? The gelatinous mass left on the paper is metaphosphoric acid, HPO_3. Is it active toward indicators? If this experiment is performed on glass instead of on paper, pure metaphosphoric acid will be obtained.

2. When sodium metaphosphate and secondary sodium orthophosphate ("**sodium phosphate**") interact with silver salts in solution, the reactions are as follows:

$$NaPO_3 + AgNO_3 \rightarrow AgPO_3 \downarrow + NaNO_3$$
$$Na_2HPO_4 + 3\,AgNO_3 \rightarrow Ag_3PO_4 \downarrow + 2\,NaNO_3 + HNO_3$$

Could you distinguish between meta- and orthophosphoric acids by means of these reactions? Try it.

c. 1. Examine some phosphate rock. Does it contain any **water-soluble** phosphate? The orthophosphate radi-

cal is tested for by a solution of ammonium molybdate, $(NH_4)_2MoO_4$, acidified with about five per cent of its volume of concentrated nitric acid. The yellow precipitate which forms under these conditions, especially when the solution is gently warmed (60°), has the composition represented by the formula $(NH_4)_3PO_4 \cdot 12MoO_3$. Phosphorus is usually separated from impurities contained in its compounds by means of this substance, which is also often used for its quantitative determination. Its formation in strong nitric acid solution shows that it has acidic properties, since **acids precipitate acids** (that is, acids drive other acids from solution; compare preparation of HCl, HNO_3, and other acids). **Bases dissolve acids** (that is, soluble bases, the alkalies, form soluble salts with substances having acidic properties). See if this yellow precipitate is acidic in its nature by this last test.

2. Heat a little powdered phosphate rock with a drop or two of concentrated sulfuric acid and determine whether any water-soluble phosphates are then present.

3. Test several samples of commercial "superphosphate," to which a little water has been added, with litmus paper.

4. Fuse a little sodium metaphosphate on a piece of porcelain and then sprinkle over it a minute amount of cobaltous oxide, CoO, or any compound of cobalt, and heat again. Repeat, using first microcosmic salt, and then borax. Compounds of manganese and of some other metals also give beautiful tests with these reagents.

ARSENIC

71. Preparation. — 1. Heat a **little** powdered mispickel (arsenopyrite, FeAsS) in a loosely stoppered test tube.

The existence of at least two allotropic modifications of arsenic may thus be observed. Write the reaction which takes place.

2. Heat in the same way a small amount of white arsenic, As_2O_3, mixed with powdered charcoal. Write the reaction which takes place.

73. Chemical Properties. — *a.* Which is the more active acid anhydride, arsenious anhydride, As_2O_3, or arsenic anhydride, As_2O_5? Treat with water and test with litmus. How do you account for the difference?

c. 1. Test for the orthoarsenate radical in the same way that you tested for the orthophosphate radical. Could you distinguish between these two radicals by this test? Treat a solution of sodium phosphate and one of sodium arsenate with hydrogen sulfide and then acidify the solution (use any common acid except nitric for this purpose). Could you distinguish between these two radicals by this test? Could you test for them both in the same solution?

2. Digest the precipitate obtained in the last experiment with a solution of ammonium sulfide. What salt is present in the solution? Filter it off from any residue which may be present and acidify the filtrate. What precipitate is formed? What gas escapes (odor or lead nitrate paper — lead sulfide is black)? How does sulfur in ammonium sulfoarsenite resemble oxygen?

CHAPTER VIII

CARBON, SILICON, AND BORON

CARBON

75. Physical Properties. — *a.* Mark on paper with some crystallized graphite. See if you can burn graphite in the Bunsen flame. Notice its **unctuous** feel. What kind of cleavage does it have?

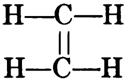
b. Adsorption. — Shake some bone-black or powdered charcoal with a solution of iodine in water. Filter off the carbon and test the filtrate for iodine. Repeat this experiment with solutions of various dyestuffs and with a solution of potassium permanganate, determining the degree of adsorption by the color of the filtrate.

76. Chemical Properties. — *c.* 2. *Preparation and Properties of Carbonic Acid and Carbonic Anhydride.* — Treat a number of carbonates with any of the acids of the laboratory and notice the liberation of carbon dioxide (effervescence). Try some of the same carbonates with various salt solutions which have been found (Exp. 36*d*) to react acidic. Some such salts, for example, alum and potassium bitartrate, $KH\overline{C_4H_4O_6}$ (cream of tartar), are used with cooking soda, $NaHCO_3$, to make baking powder. A common substitute for baking powder is a mixture of cooking soda and sour milk, which contains lactic acid,

$$H \cdot \overline{CH_3 \cdot CHOH \cdot CO_2}$$

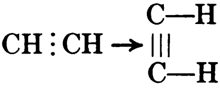
Baking powders containing alum and other salts of common heavy metals are considered unwholesome.

The **periods used in the formula** of lactic acid indicate that the **carbon atoms** separated by them **are connected** with each other by one bond or valence. A colon indicates that the carbon atoms which it separates are connected by two bonds, as in ethylene, $CH_2 : CH_2$, which, in extended form, gives the graphic formula —



$$\begin{array}{c} H\text{—}C\text{—}H \\ \| \\ H\text{—}C\text{—}H \end{array}$$

Similarly three dots indicate that two adjacent carbon atoms are connected by three bonds, as in acetylene:



$$CH \vdots CH \rightarrow \begin{array}{c} C\text{—}H \\ ||| \\ C\text{—}H \end{array}$$

3. Generate some carbonic anhydride in a flask and pass it into a dilute solution of blue litmus. It should first be passed through a **wash bottle** to remove all of the acid used in its generation unless this acid was sulfuric, which has no vapor tension at the ordinary temperature. Is there any evidence of the formation of carbonic acid? Does carbonic acid seem to be active or inactive? After the carbonic anhydride has run into the solution until there seems to be no further change of color, divide the solution into two portions and add a drop of hydrochloric acid to one of the portions. Explain what takes place. This feature of this experiment is still more striking if congo red, a dyestuff, is substituted for the litmus.

4. Test all available soluble carbonates with litmus or other indicators. How do they react? Why?

Test limestone with indicators in the presence of pure water. How does it react? See if it will neutralize acids. Heat some of it in the Bunsen flame, holding it with the

nippers, and then see how it reacts toward indicators. Limestone is a typical **alkaline earth**. Can you describe what an alkaline earth is in scientific terms?

Invert a jar of carbonic anhydride over a dish of clear limewater and describe what takes place. How high does the water rise in the jar?

5. *Bicarbonates.* — Put the calcium carbonate precipitated in the last experiment in a test tube with some pure water, and pass carbonic anhydride into the mixture until no further change is apparent. Write the reaction which takes place. Heat the solution of calcium bicarbonate thus formed very gently and notice the escape of carbonic anhydride long before the solution boils or any calcium carbonate is reprecipitated. This comes from the decomposition of free carbonic acid in solution. Finally boil the solution. Write the reaction by which the precipitate is formed. How does it compare in bulk with that started with?

Prepare a solution of cooking soda and taste it. Heat it to boiling, cool it in running water, and taste again. Is the taste the same? If not, what caused the difference?

d. 2. *Carbon Monoxide.*— Put enough oxalic acid, $H_2C_2O_4$ (see if this is an active acid by dissolving a little of it and testing in the ordinary way), in a flask to cover the bottom. Cover it over with concentrated sulfuric acid. Heat it cautiously on a sand bath, collecting all the escaping gases in different jars over water, and test each jar full of gas thus collected to see if it will burn. After a jar of gas has thus been collected which will burn, take the jar of gas next collected and invert it over limewater. What part of the gas (**by volume** — the results in **gas analysis** are nearly always expressed in per cent by volume) is absorbed?

The addition of sodium hydroxide greatly facilitates the absorption. What is left? What does this experiment show about the chemistry of the residual gas? Reinvert the jar, letting the liquid run to the bottom. Now see if the residual gas will burn. If one desires to prove that this gas burns to carbon dioxide, the carbon dioxide which the mixture of gases originally contained must be removed by passing them through a wash bottle containing an excess of limewater (Text, 170*c*, 3), or some other alkali. The product of the combustion of the gas not thus absorbed can then be tested with more limewater.

Has carbon monoxide any odor? How would knowledge of this fact affect the care with which it should be handled, since it is undoubtedly poisonous if inhaled in quantity?

c. What per cent of the calorific value of pure carbon would be lost up chimney as unburned carbon monoxide if the supply of air were sufficient to burn completely only four-fifths as much carbon as that actually used? Assume that all the carbon first burns to carbon monoxide and then part of this gas burns to the dioxide.

SILICON

80. Chemical Properties. — *b.* Treat a concentrated and a dilute solution of **water-glass** each with an equal volume of concentrated and dilute hydrochloric acid. Set the mixtures aside till next time, and then examine the different mixtures of silicic acids thus produced. One of the mixtures will retain its silicic acid in colloidal solution. Could pure silicic acid be obtained from this solution? If so, how? Another of the mixtures will exhibit a beautiful crystallization. What substance crystallizes out? Don't

fail to distinguish between these crystals and the amorphous **silicious sinter** also present.

c. 1. Examine some hand specimens of so-called "granite" rocks, and determine approximately the per cent of each of the **phenocrysts** (well-crystallized minerals) present. The clear glass or pure white granules are generally quartz; the largest crystals present, of a dull, vitreous luster, usually pale cream-colored or pink, are feldspars; the bright shiny **plates** are mica; the black **prismatic** crystals are usually hornblende.

4. *Fluxing.* — Put a little sodium hydroxide or sodium carbonate in a test tube, hold the tube in a horizontal position, and heat it below the alkali. The alkali will flux the silicates in the glass (170*b*, 4), forming a slag which fuses much more readily than the original glass. Try it, by heating the other side of the test tube.

BORON

84. Chemical Properties. — *b.* Examine some **boric acid**, H_3BO_3. Notice its unctuous feel and pearly luster. Determine by means of litmus or congo red, or both, whether boric acid is an active or weak acid. Put a little powdered borax in an evaporating dish, cover it over with sulfuric acid (1 : 1), then cover the mixture with alcohol and ignite the alcohol. Why does borax react alkaline?

CHAPTER IX

MOLECULAR AND ATOMIC WEIGHTS

88. Boyle's Law.— How much denser is the air during a period of high barometric pressure than during a period of low barometric pressure, assuming the barometric reading of the " high " to be 30.6 inches and that of the " low " 29.6 inches?

Assuming that the differences in the air noted in the last problem are due entirely to difference of temperature (which is not entirely true), what would be the surface temperature of the "high" when the surface temperature of the " low " is 20°?

89. Gay-Lussac's Law of Temperatures (Charles' Law). — How much lighter is the air at the equator (mean temperature assumed to be 0°) than that at the poles (mean temperature assumed to be −50°), providing both have the same composition and that the barometric reading at both places is the same?

91. The General Gas Law. — A liter of gas at 0° and under a pressure of one atmosphere is heated to 200° at a pressure of 800 millimeters. What is its final volume?

92. Gay-Lussac's Law of Combining Volumes. — What volume of steam at 110° and under a pressure of one atmosphere would be formed by burning five grams of hydrogen in oxygen, the weight of a liter of steam at 100° at atmospheric pressure being 0.60577 gram?

How many cubic feet of air are required to burn a pound of petroleum to water and carbon dioxide, assuming

the average composition of the petroleum to agree with that of hexadecane, $C_{16}H_{34}$, and assuming that the air is one-fourth oxygen by weight?

93. Avogadro's Deduction; also **95. Gram Molecular Volume.** — From a consideration of the fact that the molecular weight of any gaseous substance expressed in grams occupies 22.39 liters under standard conditions, we are able readily to calculate not only the proportions by weight (Ex. 16*b*) in which such substances react, but also the proportions by volume. Thus

	C	+	O_2	$\rightarrow$	CO_2
(By weight)	12 grams		32 grams		44 grams
(By volume)	0 cc.		22.39 liters		22.39 liters

The volume of the carbon is placed at zero cubic centimeters because the volume of all solid and liquid substances is negligible compared to that of the chemically equivalent weight of any gas at atmospheric pressure.

How many cubic centimeters of oxygen under standard conditions can be obtained from 216 grams of mercuric oxide? How many from 10 grams of mercuric oxide?

What volume of gas passes up the stack in burning one (short) ton of anthracite coal (considered to be pure carbon), provided 100 per cent in excess of the theoretical amount of air at 20° enters the grate, and provided the temperature of the gases in the stack is 300°? The air may be regarded (Text, 215) as four-fifths nitrogen and one-fifth oxygen by volume.

97. Methods of Determining Molecular Weights of Substances in Solution. — *a.* Weigh out a tenth of a gram molecule of cane sugar, dissolve it in 50 cc. of pure water, and then add to this solution 50 grams of finely cracked ice (preferably passed through an ice-

shaving machine or meat grinder). Stir rapidly with a thermometer until all of the ice has melted except enough to form a single layer of ice particles over the surface of the liquid. Read the temperature at this time, which will be approximately the true freezing-point of the solution; for although the solution is now a little more than molal concentration, so that the temperature should be a little lower than the freezing-point of a molal solution, the influx of heat from the surrounding air virtually offsets this error. Determine the temperature of cracked ice on the same thermometer. The difference between these two readings is the molecular freezing-point lowering of water. Compare the value you get with that given in the Text.

b. When 0.6878 gram of pure sugar is dissolved in 100 grams of water, the resulting solution freezes at −0.0378°. What is the molecular weight of sugar as indicated by this one experiment?

98. Empirical Formulæ. — The percentage composition of sugar is as follows: carbon, 42.08 per cent; hydrogen, 6.47 per cent; oxygen, 51.46 per cent. What is the empirical formula of sugar and what is the **lower limit** of its molecular weight (assuming its true molecular weight to be unknown)?

What are the empirical formulæ of the substances having the following compositions:

Sodium	27.05	Potassium	40.27	Potassium	26.59	Potassium	7.00
Nitrogen	16.48	Chromium	26.77	Chromium	35.39	Aluminium	4.86
Oxygen	56.46	Oxygen	32.95	Oxygen	38.02	Silicon	15.21
						Oxygen	22.93

99. Relations existing between the Atomic Weights of the Elements. — *a. Law of Dulong and Petit.* — Put 50 cc. of water in a beaker, and place a thermometer in it.

Weigh out about 20 grams of several different metals in massive form. Heat each piece of metal for about five minutes in boiling water, then quickly take it out, shake off most of the adhering water, and put it in the beaker containing the thermometer, having read the temperature indicated by this thermometer just before transferring the metal. Gently stir the metal around in the beaker until the temperature becomes constant. Calculate the specific heat of the metals used. From the specific heats so obtained calculate the atomic weights of the metals.

b. Law of Mitscherlich. — To a hot saturated solution of the first member of the following pairs of salts add a small amount of a hot concentrated solution of the second member and let the solution cool. After the solution has cooled nearly to room temperature, **decant** off the **supernatant** liquid and try to determine whether the pure colorless salt (the first member of each pair) has crystallized out, or whether the two salts have crystallized out together. If in doubt, wash the crop of crystals with a few cubic centimeters of cold water, pouring off the water as soon as the crystals have been stirred up with it. If still in doubt, wash the crystals again. If any of the color still persists, redissolve the crystals in a small amount of hot water and again let the solution cool. If this crop of crystals are colored, they are isomorphous mixtures. Assuming the valences of all of the elements in the colorless salts to be those indicated in their formulæ, write, by means of the law of isomorphism, the valences of any other elements found to enter the isomorphous mixtures.

$\overset{I}{K}\overset{I}{Cl}$	$\overset{I}{K}\overset{I}{Cl}$	$\overset{I}{K}\overset{III}{Al}(\overset{VI}{S}\overset{II}{O}_4)_2 \cdot 12\,H_2O$	$\overset{I}{K}_2\overset{VI}{S}\overset{II}{O}_4$
K_2CrO_4	$KCr(SO_4)_2 \cdot 12\,H_2O$	$KCr(SO_4)_2 \cdot 12\,H_2O$	K_2CrO_4

PART II

THE BASE-FORMING ELEMENTS

CHAPTER X

ANTIMONY AND BISMUTH

ANTIMONY

103. Chemical Properties.—2. Add a few cubic centimeters of concentrated hydrochloric acid to some antimony trioxide, Sb_2O_3. The solution contains antimony trichloride. Write the equation for its formation.

3. Let a drop of the solution of antimony trichloride just prepared fall into a beaker of pure water. What is the white precipitate? Write the equation for its formation. Could you prove that this compound is formed by hydrolysis by testing the liquid above it with litmus?

4. Decant the liquid above the precipitate last formed, and add a few drops of concentrated hydrochloric acid to the residue. Write the equation which represents what takes place.

5. Pass hydrogen sulfide into some of either of the solutions of antimony trichloride which you have now prepared. Prepare some arsenic trichloride by the same method used for preparing antimony trichloride in (2) above, and pass hydrogen sulfide into this solution. Could you distinguish arsenic from antimony by this test? Could you separate these two elements from solutions of their compounds by this method? Try it.

6. Add five volumes of water to the solution of antimony trichloride which was treated with hydrogen sulfide in (5), and pass in more hydrogen sulfide. Write the reaction which takes place.

7. Digest the antimony trisulfide formed in the last experiment with ammonium sulfide. Write the reaction which takes place. Filter off any insoluble residue, acidify the filtrate with hydrochloric acid (why was the solution alkaline?), and write the reactions which ensue.

8. Treat a solution of antimony trichloride with " ammonia " in excess. The white precipitate is to be regarded as antimonious hydroxide in equilibrium with antimonious acid: $Sb(OH)_3 \rightleftarrows H_3SbO_3$. Treat this white precipitate with sodium hydroxide and write the reaction which takes place. Can you account for the last two reactions according to the rule: **Acids precipitate acids and dissolve bases; bases precipitate bases and dissolve acids.** What is the easiest way to remember that sodium antimonite is soluble in water? (Text, 73*c*, 1; Lab. Ex. P. 134.)

BISMUTH

107. Chemical Properties. — *c*. 1 to 8. Perform the same experiments with compounds of bismuth that you made with those of antimony. Devise a method of separating bismuth from antimony; bismuth from arsenic.

9. Make a solution of any soluble compound of bismuth alkaline with sodium hydroxide and then add a solution of stannous chloride, $SnCl_2$. The black precipitate is metallic bismuth, reduced from its compound by the stannous tin ($\overset{II}{Sn}$) which is itself oxidized to stannic tin, $\overset{IV}{Sn}$.

CHAPTER XI

TIN AND LEAD

TIN

112. Chemical Properties.—*c.* 1. Heat a small piece of tin with about 5 cubic centimeters of hydrochloric acid. After a few minutes add 10 cubic centimeters of water. Use this solution for the following reactions.

Dilute a portion of your stannous chloride solution with two or three volumes of water and neutralize this portion with ammonium hydroxide. Stannous hydroxide is precipitated. Write the reaction. Filter off or decant the supernatant liquid and add a solution of sodium hydroxide to the residue. The resulting solution contains sodium stannite. Write the reaction for its formation. **Never treat any material with any concentrated acid or alkali while on the filter paper,** as it will react with the cellulose (203*f*) of which the paper is composed.

Treat a small portion of your stannous chloride solution with hydrogen sulfide. The black precipitate is stannous sulfide, SnS. Is it soluble in ammonium sulfide? in light yellow ammonium sulfide (made by warming ammonium sulfide with a little sulfur)? Add hydrochloric acid in excess to the last solution obtained and compare the resulting precipitate with stannic sulfide, SnS_2 (below). Write the reactions involved, regarding light yellow ammonium sulfide as $(NH_4)_2S_2$. Polysulfides containing large amounts of sulfur are called dark yellow ammonium sulfide.

They probably contain the compound $(NH_4)_2S_5$. Prepare some dark yellow ammonium sulfide, and treat some of each of your yellow ammonium sulfide solutions with hydrochloric acid in excess. The precipitate thus formed is free sulfur. Can you write the reactions for its formation? Which polysulfide gives the larger precipitate? Can you separate the stannic sulfide reprecipitated from your solution of ammonium sulfostannate from the sulfur simultaneously thrown down? Try hydrochloric acid.

Add a solution of mercurous nitrate, $HgNO_3$, to part of your stannous chloride solution. The black precipitate is metallic mercury, the tin having been simultaneously oxidized to stannic tin. By boiling the liquid the mercury will gather into visible globules. Stannous chloride reduces mercuric compounds also, first to the mercurous stage ($HgCl\downarrow$, white), then to free mercury. Try it with a solution of mercuric chloride, $HgCl_2$. Write the reactions involved.

Treat the remainder of your stannous chloride solution with bromine-water until the color of the bromine just fails to disappear. The solution now contains stannic chloride and stannic bromide:

$$2\,SnCl_2 + 2\,Br_2 \rightarrow SnCl_4 + SnBr_4$$

Write all reactions performed with this solution as though either the chloride or the bromide alone were present. Perform the same experiments as those described for stannous chloride. If hydrogen sulfide does not give a precipitate with your stannic chloride solution, note how many volumes of water must be added in order that stannic sulfide may be precipitated from it. Compare this

experiment with the precipitation of antimony sulfide, especially with regard to the relative concentrations of hydrochloric acid in which the two sulfides will precipitate. These two metals are separated from solutions of their compounds by means of this difference.

LEAD

113. Occurrence. — Examine some galena. What kind of cleavage does it have? Powder a little of it for the next experiment.

114. Metallurgy. — Heat some powdered galena mixed with powdered aluminium in a test tube. Notice the combustion which takes place:

$$3\,PbS + 2\,Al \rightarrow Al_2S_3 + 3\,Pb$$

Treat the resulting mass, when cold, with water:

$$Al_2S_3 + 6\,HOH \rightarrow 2\,Al(OH)_3 + 3\,H_2S\uparrow$$

Examine the residue for lead (malleable). On the large scale iron takes the place of the aluminium.

Mix some litharge with some powdered charcoal and heat the mixture on a stick of charcoal with the blowpipe. Did you recover any lead? Write the reaction for its formation.

Mix some lead sulfate with charcoal and heat the mixture as in the last experiment. Did you recover any lead? Repeat the experiment, adding a little sodium carbonate to the mixture before applying heat. Did you recover any lead? The sodium carbonate here acts as a flux, showing, however, a different property of fluxes in general than that heretofore (Text, 23*c*; 80*b*, 4) pointed out; that is, that basic fluxes often facilitate the reduction of metals from their

compounds by releasing them from combination with active acid radicals. In this case the lead sulfate exchanges its strong sulfate radical for the weak carbonate radical, the double decomposition going to completion owing to the instability of lead carbonate at high temperatures. The reactions which take place may be represented as follows:

$$PbSO_4 + Na_2CO_3 \rightarrow (PbCO_3) + Na_2SO_4$$
$$(PbCO_3) + PbO \rightarrow CO_2\uparrow$$
$$PbO + C \rightarrow Pb + CO\uparrow$$

116. Chemical Properties.—*b*. 1. Treat some litharge with pure water and test the resulting solution with litmus.

See if yellow litharge (massicot) is soluble in nitric acid. See if it is soluble in concentrated caustic soda. If it does not all dissolve, decant the supernatant liquid and pass hydrogen sulfide into it. If any of the lead oxide dissolved, black lead sulfide will be precipitated. What sort of chemistry has lead oxide? Write the reactions involved in these experiments. Evaporate the lead nitrate solution nearly to dryness at a gentle heat, take up with water, and use the resulting solution for the following reactions.

4. To a solution of lead nitrate (or any other soluble salt of lead) add hydrochloric acid. Lead chloride will be precipitated. Determine the approximate magnitude of its temperature coefficient of solubility. Treat the cold filtrate from the lead chloride precipitate with hydrogen sulfide. What is the relative solubility of lead chloride and lead sulfide in cold water?

Treat a solution of lead nitrate with hydrogen sulfide until a small portion of the liquid, when filtered, gives no further coloration with hydrogen sulfide. Note the difficulty of adding hydrogen sulfide in excess.

Filter or decant the supernatant liquid from the last experiment and boil the lead sulfide with nitric acid (1 : 1). The sulfide will be oxidized to sulfate. Compare the properties of the lead sulfate thus formed (especially its solubility in acids and in ammonium acetate) with those of some lead sulfate precipitated by the addition of dilute sulfuric acid or any soluble sulfate to a solution of lead nitrate.

Treat a solution of lead nitrate with a solution of potassium chromate. The precipitate is chrome yellow. Write the reaction for its formation. Decant the supernatant liquid and treat the residue with limewater. The product is chrome red, $PbCrO_4 \cdot PbO$. Write the equation for its formation.

Sodium carbonate precipitates from solutions of lead salts the basic carbonate used commercially as the most important of all pigments, under the name of "white lead," $2\,PbCO_3 \cdot Pb(OH)_2$. Write the equation for its formation. Can you write its structural formula?

Lead nitrate plus potassium iodide in solution precipitates lead iodide. Write the equation for its formation, and investigate its temperature coefficient of solubility. Give the test tube containing the solution obtained by heating a rotatory motion while the solution is cooling.

What five acid radicals could you identify by use of a soluble lead salt?

CHAPTER XII

IONIZATION

118. Abnormal Freezing-point Lowerings.—*b.* From the following data calculate the molecular freezing-point lowerings at the given concentrations:

Substance	Grams of anhydrous substance dissolved *in 100 grams water*	Observed *freezing-point*
Calcium chloride	0.1111	− 0.0513°
	0.5580	− 0.2437°
	1.117	− 0.4823°
	5.635	− 2.605°
	10.5	− 5°
	27.0	−20°
	38.5	−40°
	42.5	−55°

119. Method of Calculating the Degree of Dissociation. — From the data obtained in the last exercise calculate the apparent degree of dissociation of calcium chloride at each concentration given.

120. Variation of the Degree of Dissociation with the Concentration.—Plot the values obtained in the last exercise, and connect them by a smooth curve. Extrapolate this curve to zero concentration, and compare the value at tenth-molal concentration with that given in the table in 134*g*, Text.

118. *a.* Determine approximately the freezing-point of a molal solution of common salt by the method described under 97*a*.

CHAPTER XIII

ALUMINIUM

121. Occurrence; *and* **124*b*,** 2. **Double Salts.** — Stir about 30 cc. of sulfuric acid (1 : 1) into about 20 grams of clay contained in an evaporating dish. Cover the dish with a watch glass and gently boil the mixture until the sulfuric acid fumes. Allow the mixture to cool, then cautiously add about 40 cc. of water, stir well, heat to boiling, let the residue settle, and then decant the warm supernatant liquid through a filter. The residue is mainly quartz and feldspars, mixed with silicic acids formed by the decomposition of the kaolinite of the clay by the action of the sulfuric acid. The filtrate contains aluminium sulfate in nearly pure condition. Add one-half volume of a hot saturated solution of potassium sulfate to the solution of aluminium sulfate just prepared; evaporate the mixture to one-half its volume and set aside till next time. Then compare the properties of the crystals which will have formed with those of pure alum, as indicated below.

124. Chemical Properties. — *b*. 4 and 7. Prepare a solution of alum of moderate concentration and use this solution for making the following tests. Write all reactions as though the solution contained aluminium sulfate only:

$$2\,(KAl(SO_4)_2 \cdot 12\,H_2O) \rightleftarrows K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O$$

The potassium sulfate present does not materially influence the behavior of the aluminium sulfate in the tests usually made.

Add a slight excess of ammonia to part of the alum solution. Test for the excess of ammonia by its odor. Boil the mixture until the odor of ammonia is no longer offensive when the hot solution is removed from the flame. Pour part of the mixture at once on to a filter paper and notice the rate at which it filters. Let the precipitate settle in the remaining portion, and then decant the supernatant liquid through another filter, and compare the rate of filtration with that previously observed.

Treat part of the aluminium hydroxide just prepared with a solution of sodium hydroxide, either on the filter paper or in a separate test tube. Does it dissolve? What does the solution now contain?

Treat part of the solution of sodium aluminate just prepared with carbon dioxide; treat another portion with ammonium chloride, solid or in solution, and warm the mixture; treat another portion with hydrochloric acid, finally adding this reagent in excess. Write all reactions. The precipitate obtained in the first two portions is artificial bauxite, $H_4Al_2O_5$. Filter it out from the supernatant liquid and compare the rate of filtration with the two rates previously observed. Which of the three methods of filtering tested in this way would be likely to give the better results in washing the aluminium hydroxide free from soluble salts?

Add a large excess of concentrated ammonium hydroxide to part of your alum solution; filter without boiling; then boil the filtrate. Explain the results.

Add a solution of sodium hydroxide to part of your alum

solution, finally adding the reagent in excess. Repeat this experiment with a solution made from your impure alum crystals obtained from clay, and explain the difference in the behavior of the two solutions. The brownish red residue obtained in the last case is ferric hydroxide, $Fe(OH)_3$. Why did iron crystallize out with the alum? Finally add ammonium chloride or some other ammonium salt to both solutions (previously filtered if not clear), and boil. Can you devise a method of separating iron from aluminium in solutions of their salts?

Test the following reactions and balance the equations:

$Al_2(SO_4)_3 + (NH_4)_2CO_3 \rightarrow Al(OH)_3\downarrow + \ldots ?$

$Al_2(SO_4)_3 + (NH_4)_2S \rightarrow Al(OH)_3 \ldots ?$ (Cf. Lab. Exp. 114.)

CHAPTER XIV

ZINC, CADMIUM, AND MERCURY

127. Metallurgy. — Heat some powdered cinnabar in an **open** (hard) glass tube, inclined at an angle of about 20°. If there are any drafts in the room, set the tube so that the wind will blow up the tube. What gas is given off (odor)? Is there any evidence of the liberation of metallic mercury? (Compare Exp. 21*b*.)

129. Chemical Properties.—Dissolve some **zinc chloride** in pure water and test the solution with litmus. What does the test indicate?

Add a solution of sodium hydroxide to some of your zinc chloride solution, finally adding a considerable excess. Write the reactions which take place.

Carefully add hydrochloric acid to the solution just prepared, finally adding a considerable excess, and write the reactions which take place. Could you repeat these two experiments by starting with the solution you ended with?

Add some ammonium chloride (solid or solution) to a portion of your zinc chloride solution, and then add to this solution, and at the same time to another portion of your zinc chloride solution, a small amount of ammonium hydroxide. Is there any difference in the behavior of the two mixtures? Add, now, a considerable excess of ammonia to each of the last two tests. How would you separate zinc from aluminium in solutions of their salts? Try your method, using three solutions whose contents are

unknown to you, but one of which contains a zinc salt, another a salt of aluminium, and the third some salt of both zinc and aluminium.

Pass hydrogen sulfide into a solution of zinc chloride to which a few drops of hydrochloric acid have been added. Now make the solution alkaline with ammonia, and compare the result with that obtained by adding a solution of ammonium sulfide to a zinc chloride solution. What is the color of the precipitate? What acids is it soluble in? Is it soluble in excess of ammonium sulfide? in excess of yellow ammonium sulfide? Why not?

d. Perform the same experiments with a solution of some **cadmium** salt that you performed with zinc chloride, and devise two or more ways by which these two metals could be separated from solutions of their salts. Try one or both of your methods, using the same plan as that recommended for testing your method of separating zinc and aluminium.

e. Perform the same experiments with a solution of mercurous nitrate and a solution of mercuric chloride, and note all possible means of separating each of these two kinds of mercury from each other and from cadmium and zinc. Balance the following reactions:

$$HgNO_3 + H_2S \rightarrow HgS\downarrow + Hg\downarrow +$$
$$HgNO_3 + HCl \rightarrow$$
$$HgNO_3 + NaOH \rightarrow HgO\downarrow + Hg\downarrow +$$
$$HgCl + NH_4OH \rightarrow NH_2Hg\cdot Cl\downarrow + Hg\downarrow +$$

The precipitate formed in this last reaction is called "black precipitate." Compare this reaction with the following, and explain why the former precipitate is black:

$$HgCl_2 + NH_4OH \rightarrow NH_2Hg\cdot Cl\downarrow +$$

Compare the solubilities of mercuric and cadmium sulfides in nitric acid of different concentrations, and determine the maximum strength of nitric acid with which mercuric sulfide can be boiled without dissolving sufficiently to give a coloration when the filtrate is diluted and treated with hydrogen sulfide. Concentrated nitric acid at the boiling temperature changes mercuric sulfide into the compound $Hg(NO_3)_2 \cdot 2HgS$, which is white, and may be regarded as a basic salt in which oxygen has been replaced by sulfur (Text, 43*c*, 5). The same salt is formed when hydrogen sulfide is first led into a solution of mercuric nitrate, and similarly with the chloride. Prolonged boiling with nitric acid changes this sulfo-basic nitrate into soluble mercuric nitrate, by oxidation of the sulfur.

Test a small amount of mercury with nitric acid of several different concentrations, shake the mixtures for some time, and then determine, either by means of stannous chloride (see tin) or by means of ammonium hydroxide, the kind of mercury which each solution contains. Can you explain the results? Shake some mercuric nitrate solution with metallic mercury and then determine what kind of mercury remains in solution.

CHAPTER XV

ELECTROCHEMISTRY

130 to **135***c*. If an electrical difference of potential and the necessary appliances are available, repeat such of the lecture experiments as time will permit.

134*h*. 3. Confirm Hess's law of the thermal neutrality of salt solutions, if satisfactory results were not obtained in 44.

h. 4. *Common-Ion Effect.*—Prepare a concentrated solution of soap, sodium stearate, $Na \cdot C_{17}H_{35} \cdot CO_2$. To a portion of the soap solution add a few drops of a saturated solution of sodium chloride. To another portion add a similar amount of potassium chloride. Explain the difference in the behavior of these two reagents as an illustration of the common ion effect. Write the equilibrium equations involved.

Prepare a saturated solution of sodium acetate and add acetic acid till it is neutral to methyl orange (orange color). Prepare a dilute solution of acetic acid, which is strong enough, however, to react distinctly acidic toward methyl orange. Now add some of the saturated solution of sodium acetate to the dilute acetic acid solution, divide it into two portions, and test one portion with litmus and the other with methyl orange. Explain the results observed as an illustration of the common-ion effect. Write the equilibrium equations involved. Try the same experiment with other indicators, such as congo red and phenol-

phthalein, and determine from the results observed which indicator is the most sensitive to acids.

Prepare a solution of ferric chloride. Test it with litmus. Boil it. Is any change noticeable? Add some of your saturated solution of sodium acetate to the ferric chloride solution and boil again. Assuming that the precipitate thus formed is ferric hydroxide, $Fe(OH)_3$, can you write the equations which led to its formation? The deep red color of the solution before it is boiled is sometimes used as a test for acetates.

Confirm in a general way the order of displacement of the metals indicated by the electromotive series. Write the reactions involved.

CHAPTER XVI

COPPER, SILVER, AND GOLD

139. Chemical Properties.—*b. Copper.*—1. Dissolve some blue vitriol in water, test the solution with litmus and make the following further tests with it, balancing the first two equations.

$$CuSO_4 + H_2S \rightarrow CuS\downarrow +$$
$$CuSO_4 + NaOH \rightarrow$$

Boil this mixture. The black substance is cupric oxide.

$$CuSO_4 + NH_4OH \text{ in excess} \rightarrow$$

Treat the solution just formed with potassium cyanide (**poison!**) in excess. Then treat this solution with hydrogen sulfide (make the same experiment with a salt of cadmium).

2. Mix some cadmium and copper salts and see if you can separate the cadmium from the copper.

3. Write the reaction for the hydrolysis of copper sulfate.

c. Silver. — 1. Dissolve some **lunar caustic** in water and test the solution with litmus. This solution is used to cauterize wounds and to destroy "proud" flesh. The moon, luna, was the alchemical sign for silver. Make the following tests, and balance all the equations:

$$AgNO_3 + H_2S \rightarrow Ag_2S\downarrow +$$
$$AgNO_3 + NaOH \rightarrow Ag_2O\downarrow +$$
$$AgNO_3 + KI \rightarrow AgI\downarrow +$$
$$AgNO_3 + HCl \rightarrow$$

Test part of this precipitate with the following reagents:

$NH_4OH \rightarrow$ Acidify the solution thus produced with nitric acid $\rightarrow$?

$KCN \rightarrow$

$Na_2S_2O_3 \rightarrow$

2. See if you can tell whether silver chloride, bromide, or iodide is the most sensitive to light.

d. Gold. — Test a dilute solution of chlorauric acid, $HAuCl_4$, with litmus. This solution will also act on the flesh. See what common reagents in the laboratory will reduce it, trying especially the compounds of the metals in their lower stages of oxidation and solutions of organic substances. The gold will come down in its red or blue colloidal form, or its massive, crystalline form (*e.g.*, when heated with oxalic acid: this is the form of gold used by dentists for filling teeth).

CHAPTER XVII

IRON, COBALT, AND NICKEL

IRON

142. Chemical Properties. — *b and d.* 1. Dissolve some **copperas** in freshly boiled water, add a drop of dilute sulfuric acid, and test the solution with potassium ferrocyanide and potassium ferricyanide to determine whether it contains ferrous or ferric iron. Test the solution to which no sulfuric acid has been added for the sulfate radical. What is the formula of copperas?

2. Dissolve some of the compound having the formula $FeCl_3 \cdot x H_2O$ in water and determine whether it contains ferrous or ferric iron.

3. Test the two solutions just prepared, when much diluted, with potassium or ammonium thiocyanate, $KCNS$ or NH_4CNS. Does this furnish a means of distinguishing ferrous from ferric iron?

4. Dissolve some of Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$, in water freshly boiled in a flask and cooled under running water. Add a drop of sulfuric acid and test this solution by the thiocyanate method for ferric iron. Let the mixture thus tested stand in a beaker for a few minutes and explain what happens.

5. Place a nail in a dilute solution of sulfuric or hydrochloric acid and test the mixture for ferric iron while hydrogen is still being given off. Write the reactions which

take place. Does the thiocyanate test for ferric iron seem very delicate? Try it with solutions of ferric chloride of varying concentrations.

6. Determine which ones of the common oxidizing agents (including nitric acid, hydrogen peroxide, and potassium permanganate) will oxidize ferrous salts to the ferric condition.

7. Using the solutions you have already prepared, make the following experiments, writing all reactions in so far as they represent double decompositions:

$$FeSO_4 + NH_4OH \rightarrow (Fe(OH)_2)\downarrow +$$
$$(Fe(OH)_2) + \text{air} \rightarrow Fe(OH)_3$$
$$FeSO_4 + (NH_4)_2 S \rightarrow FeS\downarrow +$$
$$FeS + H_2SO_4 \rightarrow$$
$$FeSO_4 + H_2S \rightarrow$$
$$FeCl_3 + NH_4OH \rightarrow Fe(OH)_3\downarrow +$$
$$FeCl_3 + NaOH \rightarrow$$
$$Fe(OH)_3 + NaOH \rightarrow$$
$$Fe(OH)_3 \text{ (mixed with a little water)} + Na_2O_2 \rightarrow$$
$$FeCl_3 + Na_2CO_3 \rightarrow Fe(OH)_3 +$$
$$FeCl_3 + (NH_4)_2S \rightarrow FeS\downarrow + S +$$
$$FeCl_3 + H_2S \rightarrow$$

8. Does ferrous iron oxidize the more readily in the presence of alkalies or in the presence of acids?

9. Are iron salts hydrolyzed in water solution? Which seems to be the more highly hydrolyzed: ferric chloride, Mohr's salt, or copperas (test with litmus)?

e. Mix some ferric salt and a salt of aluminium in solution and see if you can separate them.

c. Prepare some **blue-print paper**, using both ferric chloride and ferric ammonium citrate for this pur-

pose, and determine which is the better for blue-printing.

COBALT AND NICKEL

147. Chemical Properties. — *b.* Dissolve some cobaltous chloride, $CoCl_2 \cdot 6H_2O$, in water and make the following tests:

$$CoCl_2 + NaOH \rightarrow \text{basic salt}$$
$$CoCl_2 + NaOH_{ex} \rightarrow Co(OH)_2\downarrow +$$
$$Co(OH)_2 + \text{air} \rightarrow Co(OH)_3$$
$$CoCl_2 + H_2S \rightarrow$$
$$CoCl_2 + (NH_4)_2S \rightarrow CoS\downarrow +$$
$$CoS + HCl \rightarrow$$

c. $CoCl_2 + KNO_2$ (concentrated) $+ H \cdot CH_3CO_2 \rightarrow K_3 \cdot Co(NO_2)_6\downarrow$

$CoCl_2 + NaNO_2 + H \cdot CH_3CO_2 + KCl$ (small amount) $\rightarrow K_2Na \cdot Co(NO_2)_6\downarrow$

d. Make the same tests with a solution of nickel chloride, $NiCl_2$, that you made with cobaltous chloride.

e. Examine some cobaltous and nickel sulfides and mixtures of the two and see if you can detect cobalt by means of the borax bead.

CHAPTER XVIII

CHROMIUM AND MANGANESE

155*b*. *Chemical Properties of Chromium.* — 2. Mix some powdered sodium carbonate, potassium nitrate, and chromite and heat them to fusion in a test tube. The alkali fluxes the glass, but this does not interfere with the formation of a chromate (yellow color). Extract the melt with water, and test for chromates by lead nitrate (see below).

3. Pass hydrogen sulfide into some of the solution last prepared, previously acidified with sulfuric acid, and filter it if it is not clear. Try to balance the following reaction and test for as many of the resulting products as you can:

$$H_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow S + Cr_2(SO_4)_2 + H_2O$$

Cautiously add concentrated sulfuric acid drop at a time to a saturated solution of sodium dichromate, $Na_2Cr_2O_7$. The bright red needles which form are chromic anhydride. Write the reaction for their formation. Pour off the liquid, drain the crystals off on a porous plate, and wash them with a little concentrated nitric acid. Finally dry them at a temperature below 200°. Dissolve part of the crystals in water and test the solution with litmus. Let a few drops of warm alcohol fall on another portion of the crystals. The chromic acids and soluble permanganates oxidize the flesh.

4. Make the following tests and balance the equations:

$$Cr_2(SO_4)_3 + NH_4OH \rightarrow Cr(OH)_3 \downarrow +$$
$$Cr_2(SO_4)_3 + NaOH \rightarrow Cr(OH)_3 +$$
$$Cr(OH)_3 + NaOH \rightleftarrows Na_3CrO_3 + 3\,H_2O$$

This equilibrium reaction proceeds in the forward direction when the hydroxide is first formed from cold solution, but in the backward direction when the solution of chromite is boiled; after which the chromium hydroxide is not soluble in dilute solutions of alkalies. Compare aluminium hydroxide (freshly prepared, and air-dried), and cobalt and nickel sulfides. The reprecipitated chromium hydroxide may differ from the normal hydroxide as bauxite differs from aluminium hydroxide.

$$Cr_2(SO_4)_3 + (NH_4)_2S \rightarrow Cr(OH)_3 +$$
$$Cr_2(SO_4)_3 + H_2S \rightarrow$$
$$Cr(OH)_3 + \text{water} + Na_2O_2 \rightarrow Na_2CrO_4 +$$
$$Na_2CrO_4 + NH_4OH \rightarrow$$
$$Na_2CrO_4 + Pb(NO_3)_2 \rightarrow PbCrO_4 \downarrow +$$
$$PbCrO_4 + H \cdot CH_3CO_2 \rightarrow$$

c. Chemical Properties of Manganese. — 1. Treat a solution of manganous chloride, $MnCl_2$, with sodium hydroxide and observe the change of color as the resulting mixture stands in the air. Stirring facilitates the change. Explain.

2. Treat some pyrolusite with concentrated hydrochloric acid (compare chlorine), and write the reaction which takes place. Add one volume of water, filter, and test the filtrate for manganous chloride by the tests given below.

3. Fuse some powdered pyrolusite and sodium peroxide in a test tube, and extract the melt with a little water. Decant the green solution into a test tube, fill the test tube

with water, and note the gradual change of color beginning at the top of the solution. Explain. Add a concentrated solution of potassium or sodium hydroxide to the solution last prepared and note the change of color. Explain.

4. Make the following tests and balance the equations:

$$MnCl_2 + NH_4OH \rightarrow Mn(OH)_2\downarrow \text{ (partial)}$$
$$MnCl_2 + NH_4Cl + NH_4OH \rightarrow$$
$$MnCl_2 + (NH_4)_2S \rightarrow \text{“}MnS\text{”} \text{ (indefinite composition)}$$
$$\text{“}MnS\text{”} + HCl \rightarrow$$
$$\text{“}MnS\text{”} + H \cdot CH_3CO_2 \rightarrow$$
$$MnCl_2 + H_2S \rightarrow$$

Mix some zinc and manganous salts in solution and see if you can separate them.

3 (concluded). Dissolve enough potassium permanganate (which crystallizes in the anhydrous condition as $KMnO_4$) in distilled water to make a tenth-normal solution. Digest in a covered porcelain dish a weighed amount (about a gram) of a finely powdered iron ore with concentrated hydrochloric acid (10 cc.) until the decomposition seems complete. Cautiously add 10 cc. of sulfuric acid (1 : 1) and heat until white fumes appear or the mixture solidifies. Allow to cool, add 20. cc. of pure water, filter off the silica, and wash five times with hot water, letting the water drain dry each time before adding the next portion. Warm the solution with some granulated or mossy zinc until it becomes colorless (all of the ferric salts having been changed to ferrous salts, which are nearly colorless), filter out the excess of zinc by means of glass wool, and at once *titrate* the filtrate with your tenth-normal solution of potassium permanganate, adding the permanganate drop at a time from a **burette.** When one drop of the permanganate

solution turns the other solution permanently pink, all of the ferrous iron has been reoxidized to ferric iron. From the amount of the tenth-normal solution and the amount of the ore used calculate its content of iron as though it were present in the metallic state, remembering that a liter of this **standard** solution will oxidize one-tenth gram-atomic weight of iron from the ferrous to the ferric stage. Limonite ores running less than 45 per cent "metallic" iron are of doubtful commercial value.

Determine the strength of a commercial solution of hydrogen peroxide by titrating a known volume of it with your tenth-normal permanganate solution. The titration should take place in the presence of an excess of sulfuric acid. The permanganic acid then interacts (slowly at first) with the hydrogen peroxide according to the following equation:

$$2\,HMnO_4 + 5\,H_2O_2 + 2\,H_2SO_4 \rightarrow 5\,O_2\uparrow + 8\,H_2O + 2\,MnSO_4$$

It is thought that each of these strong oxidizers is in equilibrium with part of its oxygen either in the nascent state or something similar thereto and that atoms of this active oxygen from each of these compounds unite to form the stabler substance, O_2, which escapes as a gas, so that **these two powerful oxidizers reduce each other.** One liter of the tenth-normal permanganate solution will reduce one twentieth molecular weight of hydrogen peroxide to water, since the change from H_2O_2 to H_2O represents the loss of one atom of oxygen or **two oxidizing equivalents.**

Prepare a tenth-normal solution of oxalic acid, $H_2 \cdot C_2O_4 \cdot 2\,H_2O$, and titrate it with your potassium permanganate solution in the presence of an excess of sulfuric acid and at a temperature of about 60° (the temperature

the hand can barely withstand). The reaction which takes place is as follows:

$$5\,H_2 \cdot C_2O_4 + 2\,KMnO_4 + 4\,H_2SO_4 \rightarrow 10\,CO_2 \uparrow + 8\,H_2O + 2\,MnSO_4 + 2\,KHSO_4$$

Preserve this solution of oxalic acid for future use.

CHAPTER XIX

SOME RARER ELEMENTS

156 to **162**. Systematic laboratory work with the rarer elements is given only in advanced courses in chemistry.

CHAPTER XX

THE ALKALINE EARTH METALS

MAGNESIUM

166. Chemical Properties. — *b.* 1. Review Exps. 3 and 25*c*.

2. Shake an excess of magnesia with a solution of hydrochloric acid until the solution becomes neutral to litmus, filter off the excess of magnesia, and use the solution of magnesium chloride thus obtained for the following tests.

3. Evaporate part of your solution of magnesium chloride to dryness in a test tube and test the escaping gases for acidity. Explain.

4. Mix a saturated solution of magnesium chloride (made from the crystallized salt, $MgCl_2 \cdot 6\,H_2O$) with powdered magnesia, recently ignited. Explain. A basic salt is formed, which is used as a cement.

c. Make the following tests and balance the equations:

$$MgCl_2 + NaOH \rightarrow Mg(OH)_2\downarrow +$$
$$MgCl_2 + NH_4OH \rightarrow Mg(OH)_2 \text{ (partial)}$$
$$MgCl_2 + NH_4Cl + NH_4OH \rightarrow (\textit{magnesium mixture})$$
$$\text{Magnesium mixture} + \text{any soluble orthophosphate} \rightarrow MgNH_4PO_4\downarrow +$$

Decant the supernatant liquid from the last precipitate, filter and wash it, and heat some of it in a test tube. Test the escaping gases for alkalinity and explain your observations.

CALCIUM

170. Chemical Properties. — *c.* 1. Heat some hydrochloric acid with an excess of powdered limestone, chalk (not crayon — see below), or marble, until the solution becomes neutral to litmus. Write the reaction. Filter and test the filtrate for calcium (see below) and ferric iron.

2. (*a.*) Treat some powdered limestone with pure water and test the resulting mixture with litmus. Would you class limestone with the alkalies or the earths?

(*b.*) Heat in a test tube or crucible some of the powdered material used for the last experiment. Test the escaping gases for carbon dioxide (Exp. 2*b*).

3. (*a.*) After the mass has cooled nearly to the room temperature, add some pure water to the product of the last experiment and test the mixture with litmus. Would you now conclude that limestone is an earth, an alkali, or an alkaline earth?

(*b.*) Slack a fairly large piece of lime and shake the resulting slacked lime in a flask with about 500 cc. of pure water, maintaining the temperature of the mixture at about 20°. Filter the resulting solution (limewater) into a bottle, keeping the bottle stoppered when not in use.

(*c.*) Expose some clear limewater to the air for half an hour or longer and explain the result.

(*d.*) Shake a solution of sodium carbonate, Na_2CO_3, with some of the residue from the last filtration (**milk of lime**), filter, and evaporate the resulting solution to dryness. What is the residue? Write the reaction for its formation.

(*e.*) Cover the bottom of a beaker with a layer of milk of lime and set aside till next time. Then carefully observe the product obtained, and prove whether it contains slacked

lime (litmus), or calcium carbonate (hydrochloric acid), or both.

(*f*.) Repeat the last experiment, mixing about four volumes of **sea sand** and enough water with the slacked lime to make a paste—**mortar.** Compare the resulting product with that obtained in the previous experiment. What determines the strength of mortar? (Gently crush some of the mortar that has set and examine the grains of sand. The grains of sea sand were originally rounded due to friction produced by the waves.)

b. The solution of calcium hydroxide prepared from slacked lime, if saturated at 20°, is 0.044 normal. Determine its normality by titration with your tenth-normal oxalic acid solution, using phenolphthaleïn as indicator. Then determine, by titration with limewater, the normality of acetic acid in vinegar, and of hydrochloric acid (1 : 100). Preserve the last solution as a standard acid solution.

d. 1. Shake some plaster of Paris with an excess of pure water, filter, and test the filtrate for the sulfate radical.

2. Mix some plaster of Paris to a paste with water and fill a test tube with the mixture. Note the time required for it to set. Leave it till the next time, then break off the test tube, let it dry for another week, and then try to use it as a blackboard crayon.

e. 1. Cover the bottom of a beaker with a layer of cement and then cover the cement with water. Determine approximately the time required for the cement to take its initial set by noting how much time elapses before a stirring rod under its own weight fails to penetrate the cement.

2. Repeat the last experiment, using concentrated

hydrochloric acid instead of the water. If much gas is evolved, the cement is of poor grade. Explain.

STRONTIUM AND BARIUM

174. Chemical Properties. — *b.* 1. Test a saturated solution of barium hydroxide with litmus.

2. Test a solution of barium chloride with litmus.

3. Why cannot the following hydrolyses take place in cold water solution?

$$MgCl_2 + 2HOH \rightarrow Mg(OH)_2 + 2HCl$$
$$CaCl_2 + 2HOH \rightarrow Ca(OH)_2 + 2HCl$$
$$SrCl_2 + 2HOH \rightarrow Sr(OH)_2 + 2HCl$$
$$BaCl_2 + 2HOH \rightarrow Ba(OH)_2 + 2HCl$$

c. 1. Make the following tests and balance the equations:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow +$$
$$SrCl_2 + Na_2CO_3 \rightarrow$$
$$BaCl_2 + Na_2CO_3 \rightarrow$$

2. Decant the supernatant liquids from the precipitates made in the last experiment, add a few drops of concentrated hydrochloric acid, and test the resulting solutions by the **spectroscope**. Observe the different spectra until you can reproduce them from memory, especially their relative positions with respect to the sodium line (lines).

3. Mix the chlorides of calcium, strontium, and barium by twos, and finally all three together, and see if you can detect the spectra of the individual metals in these mixtures.

4. Test your original solution of calcium chloride made from limestone, chalk, or marble for calcium by the spectroscope.

5. $CaCl_2 + (NH_4)_2C_2O_4 \rightarrow ?$ 6. $BaCl_2 + H_2SO_4 \rightarrow ?$

CHAPTER XXI

THE ALKALI METALS

176. Historical. — *b.* 1. Leach some wood (or coal) ashes with a small amount (100 cc.) of hot water, filter, and test the filtrate with litmus. Test it also for carbonates and for potassium (see below).

2. Repeat Experiment 170*c*, 3, (*d*) as far as the filtration, using, however, one half of your solution leached from ashes instead of the pure sodium carbonate of that experiment.

3. Add a few cubic centimeters of the solution prepared in *b*, 1 and *b*, 2 to a small amount of a solution of alum and explain the results.

180. Chemical Properties. — *e.* Confirm any of the hydrolyses given in this section in the Text with which you may not be familiar, adding the same salts of ammonium to the list.

g. Prepare some cooking soda by Solvay's process, subjecting the solution of salt and ammonia to an atmosphere of carbon dioxide in a closed flask. Wash the resulting product two or three times with a little water. Dissolve some of the bicarbonate in a little water and taste the solution and test it with litmus. Boil the solution and repeat the tests. Explain. Try this solution before and after boiling on an aqueous solution of iodine. If a large amount of cooking soda were used in making biscuit and little or no cream of tartar or sour milk (76*c*, 2) were used along with it, in what form would part of the soda probably be

present in the biscuit? Would the biscuit be especially wholesome?

Mix in solution some salt of magnesium with some salt of sodium and some salt of potassium and see if you can detect the presence of all three of these metals in the mixture (see Text).

182. **Ammonium.** — *a and c.* Repeat the last experiment, adding to the mixture, however, some salt of ammonium.

TO ACCOMPANY CHAPTERS XXII TO XXVII INCLUSIVE — QUALITATIVE ANALYSIS

Analyze two or three unknown solutions according to the **scheme of analysis**, opposite. If any difficulties arise, consult the work given under the individual metals in the Text. If still unable to proceed, consult the instructor. The following table of **general solubilities** may also be found helpful:

	Nitrates, Acetates, Chlorates	Chlorides	Sulfates	Hydroxides	Carbonates, Sulfides, Silicates, Phosphates and Soaps
Soluble	All	All others	All others	NaOH KOH $Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$	Na salts K salts NH_4 salts
Insoluble	None	AgCl HgCl $PbCl_2$?	$PbSO_4$ $CaSO_4$? $SrSO_4$ $BaSO_4$	All others	All others

After satisfactory results have been obtained with the unknown solutions, analyze two or three naturally occur-

ring solids, paying particular attention to the Preliminary Examination (*infra*), which is usually more than sufficient to enable the trained analyst to identify most naturally occurring solids.

PRELIMINARY EXAMINATION OF AN UNKNOWN SOLID

1. If the original material has a metallic luster and is malleable, it is a **free metal.** Hence no acid radical is present. In case the original material looks earthy (that is, dull and not well crystallized), it is probable that it is an oxide or clay (**a silicate**). In case the material is not a metal and is not a silicate and no acid radical can be detected (see below), it is assumed to be an **oxide** (since tests for the oxygen of most oxides are not readily made). In case the material is not a metal, an oxide, or a silicate, it is some **salt** easily decomposable by acids, or it is an **organic** compound (chars or gives an empyreumatic odor when heated or burned in a porcelain dish — not further treated of in this course).

2. The following tests often serve for the identification of the material, especially if it is of natural occurrence.

a. Moisten part of the material with pure water and test with litmus.

(1) If the **litmus turns red,** an acid salt (like $KHSO_4$) or a salt formed by the interaction of an active acid with an inactive base is present (hydrolysis).

(2) If the **litmus turns blue,** the original substance is an oxide of some of the metals of the alkalies or of the alkaline earths, or of lead or silver; or it is a salt formed by the interaction of one of these metals with an inactive acid (hydrolysis).

b. Heat a little of the material over the Bunsen flame in a porcelain dish. If it all disappears, it is carbon, sulfur, iodine, mercury or a compound of mercury, arsenic or a compound of arsenic, or an ammonium salt (or organic matter). If a residue is left, note its color and other obvious characteristics and compare them with those of substances with which you are familiar, especially oxides. Cool and moisten with pure water. Test with litmus. If the original material is neutral to litmus and the residue is alkaline, the material is an alkaline earth (probably limestone). In that case treat the original material for carbonates (see below), and test the solution thus formed for calcium by the spectroscope.

c. Solubility. — The tests already made in moistening the material with water should have indicated whether it is appreciably soluble in water. If it is, grind up a fair-sized piece and dissolve it in pure water, using heat to facilitate solution if necessary. From the rate at which the material dissolves, judge as nearly as possible what salts might be present and what ones are probably not present (consult the table of solubilities). If a slight residue remains, of no particular characteristics, filter it off and discard it. If the residue is markedly different from the original material taken as a whole, analyze it separately. If the residue is considerable in amount, do not filter it off, but acidify the whole solution with hydrochloric acid (unless a free metal was found to be present, in which case nitric acid is usually used as the solvent; arsenic, antimony, tin, gold, and platinum are dissolved in **aqua regia**). If under these conditions the residue seems to dissolve partially but not completely, decant the supernatant liquid, add a few drops of the concentrated acid to the residue, and warm. Mix this

solution with that decanted, and proceed to test the resulting solution systematically for the metals, after having tested the original material for ammonium and the acid radicals (see below). Call all material not dissolved by the treatment just described silica and silicates unless instructed how to proceed farther.

3. The **acid radicals** frequently serve for the identification of substances, especially when taken into consideration with the other indications of the preliminary examination. The commonest acid radicals are identified as follows:

a. All *carbonates* effervesce when treated with concentrated hydrochloric acid.

b. Chloride Radical. — Acidify the aqueous solution with nitric acid and add a solution of silver nitrate. The formation of a white precipitate, which turns dark on standing, proves the presence of chlorides.

c. Sulfate Radical. — Acidify the aqueous solution with hydrochloric acid, filter if necessary and add a solution of barium chloride. The formation of a white precipitate, insoluble in hydrochloric acid, proves the presence of sulfates.

d. Orthophosphate Radical. — Boil a little of the material with nitric acid (1 : 1). Dilute with two volumes of water. Add a solution of ammonium molybdate acidified with nitric acid, and warm. The formation of a yellow precipitate proves the presence of phosphates, unless arsenic is present. In that case, repeat the test with a portion of the filtrate from which the arsenic has been removed in the systematic examination for the metals.

e. Nitrate Radical. — Make the aqueous solution alkaline with sodium carbonate and boil. Filter. Acidify the solution with sulfuric acid and cool in running water.

Add one volume of concentrated ferrous sulfate solution and shake. Carefully pour 1 cc. of concentrated sulfuric acid down the side of the test tube, shaking the test tube as little as possible, so that the concentrated acid will not mix with the solution but form a distinct layer beneath it. If a brown or red ring appears between the two layers thus formed, nitrates are present.

f. Sulfide Radical. — If the material is sulfur or a sulfide, it will burn, evolving sulfur dioxide (odor). Most sulfides will generate hydrogen sulfide (odor or paper dipped in a solution of a lead salt) when treated with hydrochloric acid, and will throw out free sulfur (floats) when treated with nitric acid (1 : 1).

4. By reason of the use of ammonium salts as group precipitants of the metals, the **ammonium radical** must be tested for in the original material; and furthermore, by reason of the prevalence of ammonium salts and ammonia in the atmosphere of the laboratory, this test should be made **among the first**. Heat the material with a concentrated solution of sodium hydroxide, and test the escaping gases for ammonia.

5. Unite the metallic and non-metallic radicals found into the form of the substances shown to be present, or into the form of the commonest substances containing them.

PART IV

APPLIED CHEMISTRY

CHAPTER XXVIII

THE ATMOSPHERE

216. Respiration and Ventilation.—*a.* **Blow** through some limewater and explain the result.

b. Place 20 cc. of a saturated solution of magnesium hydroxide in a 50-cc. graduated cylinder, add a few drops of phenolphthalein solution, close the cylinder with a two-holed rubber stopper, passing a glass tube, drawn to a fine point at the lower end, through one of the openings, leaving the other one open. Force various different samples of air through the glass tube by means of a rubber bulb, noting in each case how many compressions of the bulb are necessary to decolorize the solution. The total acidity of the different samples of air varies approximately inversely as the amount of air necessary to decolorize the solution. The only acid ordinarily present in living rooms is carbonic acid. Estimate the amount of carbonic acid in each sample of air tested by comparison with pure outdoor air, assumed to contain 0.03 per cent CO_2.

CHAPTER XXIX

NATURAL WATERS

219. Potable Waters.—*a. Solid Contents.*—A pseudo-quantitative analysis of the salt content of waters may readily be made by carrying out the ordinary scheme of qualitative analysis, and noting the approximate bulk of the precipitates obtained with the different reagents. This method is especially useful in estimating, roughly, which of two waters is the more highly charged with any given ingredient. The total solids may be obtained by evaporating off the water.

b. Contamination. — 1. The presence of **nitrites** in a surface water usually indicates bacterial activity, and renders the water open to suspicion, even if it does not absolutely condemn it. Such a water should not be used without being boiled or Pasteurized unless shown to be potable by further examination. The test for nitrites is easily made, as follows:

(1) Dissolve one gram of sulfanilic acid in 30 cc. of a warm solution of acetic acid (1 : 1), using pure (glacial) acetic acid in making this solution. Dilute to 300 cc. and keep in a bottle.

(2) Dissolve 0.2 gram of α-naphthylamine in 45 cc. of a warm solution of acetic acid (1 : 2), and dilute to 340 cc. Keep in a closed bottle.

(3) Mix 20 cc. of the water to be tested with 1 cc. of each of the solutions just prepared and warm gently

(70°). If nitrites are present to the extent of one part in 1,000,000,000, a pink coloration will develop within one minute.

2. *Organic Matter.* — Approximately the total content of organic matter contained in a water may be estimated by noting the amount of permanganic acid which it will reduce. Pseudo-quantitative determinations of this value will often enable one to decide which of two waters is the more suitable for drinking or other purposes. The test may be made as follows: Dilute your tenth-normal solution of potassium permanganate with one volume of sulfuric acid (1 : 3). Put 50 cc. of the water in a flask and add 1 or 2 cc. of the permanganic acid solution thus prepared. Bring the contents of the flask to boiling and carefully add more permanganic acid solution until it no longer becomes decolorized on boiling one minute. The relative amount of total reducers in the different specimens of water varies approximately as the amount of the permanganic acid solution used to produce a permanent color. It should be remembered, however, that many such reducing substances are harmless, especially non-nitrogenous organic matter derived from leaf mold; moreover, part of the reducing substances may be inorganic, such as sulfides (sulfur waters).

3. *Ammonia.* — Test several samples of water for ammonia by Nessler's reagent (Text, 129*h*). Any water which gives more than a faint yellow coloration with this reagent is open to suspicion as a drinking water.

c. Turbidity. — Determine the concentration of a solution of alum or of aluminium sulfate necessary to precipitate the turbidity from various colloidal suspensions, including turbid water (shake some water with dirt and

decant), by adding to 20 cc. of each of the different liquids contained in test tubes a certain number of drops of a hundredth-normal solution of the aluminium salt, beginning with five drops and increasing the number by one drop for each test until twenty drops have been added. Add the salt solution from a burette and note the amount used in each case. Let the tests stand until the next time, then calculate the coagulative concentration of the aluminium compound used from that test which causes the clarification of the solution with the least addition of the aluminium compound. Test the clear liquid thus obtained for aluminium.

The coagulative concentration of various other salts, as well as acids and alkalies, may be determined in the same way. A colloidal suspension of arsenious sulfide suitable for such work may readily be prepared by treating a solution of arsenious acid with a solution of hydrogen sulfide. Write the reaction. Why does not the arsenious sulfide precipitate out as in ordinary analytical work? The solution of arsenious acid is made by boiling white arsenic with pure water.

220. Boiler Waters. — *a. Total Solids and Alkalinity.* — For estimation of solid contents see 219*a*. All natural waters except those from mines and peat bogs react alkaline. The relative alkalinity of two waters can readily be determined by titrating them with any acid solution, using methyl orange as the indicator. The absolute amount of total alkalinity can readily be determined by titrating with your standard hydrochloric acid solution and calculating the alkalinity as calcium carbonate, according to the reaction:

$$Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

When carbonates of the alkali metals are absent, this value corresponds to the **temporary hardness** (see below).

b and c. Hardness and Scale Formation. — 1. *Temporary Hardness.* — Boil 100 cc. or more of the water in a beaker until about half of it has evaporated. Then transfer the liquid to a large test tube and let it stand until all the turbidity settles out. Note the bulk of the precipitate obtained with various waters, or filter it out on a weighed porcelain Gooch crucible and heat it to about 500° and weigh, regarding the precipitate as calcium carbonate. Compare the temporary hardness thus obtained with that obtained in 220*a*.

2. *Permanent Hardness.* — Evaporate the clear filtrate to dryness on the sand bath, lifting the evaporating dish from the sand occasionally just before the last of the water has evaporated off to avoid " spitting." Treat the residue with 10 cc. of distilled water and note the relative bulk of insoluble material thus obtained, or filter it off on a Gooch crucible and weigh.

3. *Scale Formation.* — The sum of the temporary and permanent hardness thus obtained equals, approximately, the scale-forming ingredients of the water under examination. The total scale-forming ingredients of the water may be found in the first instance by applying the method given in 2 to the original water.

5. Add to 100 cc. of the water as much limewater as corresponds to the temporary hardness. Filter and determine the hardness of the filtrate. This should equal the permanent hardness already determined. To one-half of the last filtrate, not used for determining the hardness, add as much sodium carbonate as is equivalent to the

permanent hardness. Filter and determine the hardness of the filtrate, as indicated above, or by means of a soap solution (see Text).

CHAPTER XXX

ROCKS

221 to 224. Examine a collection of classified rocks until you can identify most or all of them without looking at the labels.

Classify various fragments of rocks which will be handed to you and determine their relative stability when treated with hydrochloric acid of different concentrations (for example, 1 : 1 and 1 : 10). What conclusions can you draw with regard to the cementing material in the different rocks examined?

CHAPTER XXXI

THE SOIL

226*b*. Treat a number of powdered silicates with concentrated hydrochloric acid and classify them as to whether they are decomposed by this reagent. Those which are so decomposed are, on the whole, more soluble in water and dilute salt solutions than those which are not so decomposed.

227*a*. Classify all the soils of your neighborhood with regard to their origin. **Residual** soils should show gradual variations from soil to the solid rock from which they were derived. They are not common in valleys. **Alluvial** soils are nicely stratified, the size of all the particles in any given stratum being nearly the same. **Glacial** soils are unstratified.

b. The following pseudo-quantitative method of analyzing soils will usually furnish a sufficient basis for comparing two or more soils as to their principal ingredients:

1. *Limestone.* — Leach about 10 grams of the soil with hydrochloric acid (1 : 10). Filter and wash. Test the filtrate for calcium.

2. *Humus.* — Leach the residue from the last experiment with ammonium hydroxide (1 : 10). Filter and wash. Evaporate the filtrate to dryness on the water bath. The residue is humus plus some clay.

3. *Clay.* — Treat the residue from the ammonium hydroxide extraction with sulfuric acid (1 : 1), as in Exp. 121. Dilute and filter and wash. Test the filtrate for aluminium, noting in each test the relative volume or bulk of the precipitate (measures the percentage of clay).

4. *Sand and Feldspars.* — Treat the residue from the sulfuric acid extraction with 50 cc. of water, add 1 gram of sodium carbonate, and warm over boiling water for one minute, then add one half gram of caustic soda and continue to warm until the liquid clears. Filter and wash. The residue is sand and feldspars, the relative proportions of which can usually be determined by microscopic examination, the grains of feldspar being opaque, those of sand transparent.

When necessary, both of these ingredients may be decomposed by treatment with hydrofluoric acid in a platinum vessel. Subsequent precipitation of the aluminium of the feldspars by ammonia measures the percentage of feldspars present.

229. **Ceramics.** — *a. Plasticity of Clays.* — The relative plasticity of clays may be approximately determined by kneading about 20 grams of each specimen into a dough with water, added a little ($\frac{1}{2}$ cc.) at a time until the mixture reaches its greatest firmness, as determined by the touch, and then noting how far the same iron bar will sink into each sample of mixed clay. For this test the mixture should be filled into an evaporating dish and smoothed off on top.

b. Air Shrinkage. — Fashion some of these mixtures into the form of brick, using molds, if available; measure their length and set them aside till next time. Then measure their length. The ratio of the loss of length to the original length measures their air shrinkage.

c. Heat these brick in a furnace and note: (1) whether they melt; (2) whether a glass forms on the outside; (3) the amount of fire shrinkage; (4) the change in color; (5) their relative soundness (that is, whether any cracks have developed); and (6) whether any discolorations have appeared.

CHAPTER XXXII

THE FERROUS METALS

231*a. To Detect Cold Shortness in Steel.* — Dissolve about 0.2 gram of the metal in 5 cc. of concentrated nitric acid. Add excess of a nitric acid solution of ammonium molybdate and warm. Either make the different solutions tested up to the same volume and observe their relative turbidities, or let the precipitates settle and observe their apparent volumes. This method may be made pseudo-quantitative by comparing the metals with a steel of known phosphorus content. More than 0.08 per cent phosphorus is objectionable in steels.

b. To Distinguish Wrought Iron from Mild Steel. — Dissolve about one gram of the metal in nitric acid (1 : 15); filter and wash. Treat the residue with hot caustic soda, specific gravity 1.1. The residue is slag and iron oxides.

232. Distinguishing Steel from Cast Iron. — Dissolve 0.2 gram of the metal in about 6 cc. of nitric acid (1 : 1), placing the test tube in cold water until after the action moderates. Then heat in boiling water until all action ceases. Dilute with one volume of distilled water and filter. Save the filtrate for Exp. 233. Wash the residue with hot caustic soda, specific gravity 1.1. The residue is graphite. By weighing the residue, the experiment may be made more nearly quantitative. Or, it may be weighed and ignited, the loss in weight representing the graphite (absent in steels).

233. **Combined Carbon.** — Fill each of the test tubes containing the filtrates from the previous experiment nearly full of distilled water. The test tubes used for this purpose should have approximately the same dimensions. Shake up the mixture and observe the relative depth of color of the different solutions by looking downward into them when placed half an inch above a white paper. By comparing the results with those of a steel of known content of combined carbon, the results approach a quantitative character.

234. **The Condition of Cast Iron.** — Determine by the methods given in Exps. 232 and 233 the relative amounts of graphite and combined carbon in some filings of white cast iron and in the same material after it has been heated half an hour in a closed crucible over the Bunsen flame and then allowed to cool in the crucible.

235. **Case-hardening.** — Determine the relative ease with which a file will scratch an ordinary wire nail (low-carbon steel) and another nail of the same kind after it has been heated for a few minutes in molten potassium cyanide.

CHAPTER XXXIII

FUELS AND OILS

237. Proximate Composition of Coals. — Quickly powder a sample of coal and place it in a closed bottle. Weigh 1.5 grams of the powdered sample into a weighed and cooled porcelain crucible. Cover the crucible and let it stay one hour in an oven previously heated to 105° and kept at about that temperature. At the end of that time, take the crucible out and let it cool, and weigh it again. The loss in weight is **water.** Then heat this same crucible and its contents for a few minutes (till no further change is apparent) over the Bunsen flame, heating it slowly at first if the specimen is lignite. Or, to save time, a fresh specimen may be heated in another crucible. From either of these determinations the **volatile hydrocarbons** may be calculated. Finally heat the crucible used for determining the volatile hydrocarbons without its cover over the Bunsen flame till there is no further apparent change in its contents. The loss is **"fixed" carbon.** The residue is **ash.**

242. To Distinguish Hydrocarbon, Drying, Nondrying, and Semidrying Oils. — *a. Fluorescence.* — If the oil looks turbid, warm it before making the test. Petroleum oils are plainly fluorescent to the naked eye when viewed in reflected sunlight.

b. Maumené's Test. — Weigh 50 grams of the oil into a small beaker and place the small beaker in a slightly larger one. The space between the two beakers may be partially filled with cotton, especially around the top. Let 10 cc. of concentrated sulfuric acid, having about the

same temperature as the oil, drop into the oil, with constant stirring (with the thermometer). Note the highest temperature attained. The rise in temperature is the Maumené number.

c. Saponification. — Place about 5 grams of the oil in a beaker, add 30 cc. of water and about 2 grams of solid caustic potash. Heat just below boiling until no further change is apparent. Cool in running water. The saponifiable fats which an oil contains will be completely saponified by this process and the soap produced will form a layer on top of the water. Or the soap may be precipitated out from the hot solution by adding common salt (Exp. 134*h*, 4). The percentage of mineral oil mixed with the fatty oils may readily be determined approximately by this experiment. If the soap formed by the saponification of the fatty oil is dissolved in hot water, the mineral oil rises to the top of the liquid. In order to measure its volume accurately, the mixture should be transferred to a separatory funnel, the bulk of the soap solution run out, and the remaining soap solution together with the mineral oil run into a graduated cylinder of small bore.

d. Make the special test for linseed oil given in the Text.

243. Determine the **relative viscosity** of two or more samples of oil by the method described in the Text.

244. **Acidity.** — Shake 5 grams of the oil with 50 cc. of alcohol (1 : 1), and test the alcoholic extract with litmus. If, however, 95 per cent alcohol is used and the mixture is boiled for five minutes in a flask connected with a **return condenser**, and the amount of acid in the alcoholic extract is titrated with standard alkali, the experiment becomes quantitative. A caustic alkali should be used, with phenolphthalein as the indicator.